FABRICATION AND CHARACTERIZATION
OF SILICON CARBIDE NANOCLUSTERS

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To my Family
“All things are difficult before they are easy”

Thomas Fuller
DECLARATION

This dissertation is the result of my own work and includes nothing, which is the outcome of work done in collaboration except where specifically indicated in the text. It has not been previously submitted, in part or whole, to any university of institution for any degree, diploma, or other qualification.

Signed:________________________________________________________

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SUMMARY

Silicon carbide nanoparticles in the range of 1-10 nm are in the center of interest because of the possible applicability in quantum optics, bioimaging, medical diagnostics, and therapy thanks to the bioinert nature of such luminescent nanoparticles. Semiconductor nanoparticles below 10 nm show size dependent physical and chemical properties but this phenomenon has not been demonstrated accurately in a silicon carbide colloid system yet, because of the lack of synthesis method that allows monodisperse silicon carbide nanoparticle preparation with simple surface termination. In my work, I improved the existing stain etching synthesis method to prepare SiC NPs in the size range of 1-3 nm in large quantity and developed a simple surface modification method to simplify the surface chemistry of such particles. The narrower size distribution together with the engineered surface allowed me to unravel the physics behind the photoluminescence of SiC nanoparticles. By using optical characterization in steady-state and time resolved manner together with infrared spectroscopy I described the solvent, size and pH dependent emission of such particles with proving that the luminescence is originated from the delocalized surface states when SiC is smaller than 4 nm.

Despite the biocompatibility of SiC, nanoparticles usually emit in the blue upon UV excitation and both characteristic should be changed in order to realize an in vivo fluorescence probe based on SiC NPs. The complexity of SiC sometimes can be turned into the positive way. Point defect in SiC, like a missing C or Si atom can generate color centers that can be paramagnetic. We speculate that these defects have size independent emission, and the realization of such color centers in molecular size SiC NPs can open the door for a new era of nanoscale sensing and imaging. I just took the very first steps presented in my dissertation, to achieve this goal.
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1 Introduction

Bioimaging and Nanostructures. Two words and two worlds describe my research during my Ph.D. The investigation with my supervisor, Adam Gali, began at 2011 and we started to work on a new type of fluorophores, based on silicon carbide (SiC) nanoparticles for fluorescent bioimaging from the very bottom. The motivation was to develop a fluorescent probe that is not just bright but has very good biocompatibility; therefore, it can be used for in vivo bioimaging, medical diagnostic, and even for therapy beyond the limitation of current alternatives.

Bioimaging is a term that covers the broad area of acquiring, processing, and visualizing structural and functional images of living objects. Image modalities used in bioimaging is a broad field including: X-ray, computer tomography (CT), magnetic resonance imaging (MRI), positron emission tomography (PET), magnetoencephalography (MEG), and so on\(^1\). We are focusing in this dissertation on medical imaging, and fluorescence imaging that used to create images of the human body, anatomical areas, tissues and cells, down to the molecular level; for clinical purposes, seeking to reveal, diagnose, or examine diseases; medical science, including the study of normal anatomy and physiology\(^2\).

Fluorescence imaging has become one of the most important key tools for molecular biology and in vivo studies, by following cellular processes, quantifying ion or metabolite levels, and measuring interactions of molecules live where they happen; aimed at delineating cancerous tissues, and anatomic structures for accurate diagnosis and surgical treatment\(^2-4\). For in vivo imaging a fluorophore, or a fluorescent label or dye, i.e. a material is needed that is able to emit light; and has to fulfill numerous criteria, for ex-
ample, low toxicity, and good clearance but accurate retention time. Specialized in vitro imaging needs special fluorophores. For example blinking fluorophores with long dark state is needed for localization based superresolution microscopy, but these probes are not ideal for conventional fluorescence microscopy. Therefore, clinical research and new visualization techniques have an immediate quest for new types of fluorophores for special purposes and the development of the conventional organic dyes. In order to satisfy these demands, colloid semiconductor nanoparticles, i.e., quantum dots, and metal coordinated compounds are studied by many research groups, with the promise to overcome the existing limitations.

Indeed, one of the most promising labels for in vitro and in vivo imaging is a quantum dot. Quantum dots are solid state materials at the nanoscale. Nanostructures are taking the lead in many research areas because of the high diversity of the properties that can be engineered via size, shape, surface, and composition. Here I have to define the size range of particles I am working with. Nanoscience, colloid science covers a relatively broad range from 1-100 nm or even to 1000 nm. Nanomaterials used in the medical research are often in the range of 50-200 nm. In my dissertation, I will speak mostly about particles under 5 nm. This is the dimension where silicon carbide has interesting optical properties, and we believe, this is the range of size where nanoparticles interaction with living matter could be useful for even clinical application. By this claim, I also define that we are working at the very bottom of the colloidal range, where borders between molecules and colloids are blurred; and where the numbers of elements or molecules in the nanoparticles become countable, that adds a new variable to an inherently complex system, where the surface could be of prime importance. Even though, many research groups study materials that have at least one dimension below the microscale, they call “nano”, but in colloid science, the actual size is of high importance. When material is prepared few nanometers small, the surface atoms play a major role in determining the catalytic, electronic, and even optical properties of nanomaterials. As the radius of a particle decreases, the ratio of its surface area to volume rapidly increases where larger number of atoms resides on the surface. This is the upper limit, where we start to speak about nano. At the lower limit, where bulky materials become molecules or even atoms by reducing the size, beyond the surface, the number of building blocks (atoms, ions, or molecules) becomes relevant too. This is the reason why we believe that silicon carbide (SiC), a material with indirect band gap with negligible photon emission efficiency in the visible wavelengths can be still applied as a fluorophore for
biology. In fact, SiC at the nanoscale is luminescent and it simultaneously preserves its biocompatibility. Furthermore, the strength of the Si-C bond does not change with size giving significant stability to the nanoparticle form of SiC. In addition, the most recent research on color centers in diamond and silicon carbide implies that multimodal probes might be prepared from diamond, or SiC nanoparticles hosting paramagnetic color centers that can be simultaneously employed in different techniques and applications. The color centers are often simple native point defects in the host material. For example, a missing Si atom in the SiC matrix introduces such electron states, that it will emit infrared light and it has a high spin ground state. These paramagnetic color centers can exhibit spin-selective fluorescence that can be employed to prepare ultrasensitive magneto-optical sensors at the nanoscale. These special color centers may act as building blocks of quantum information technology too.

_Aour mission is to develop methods to prepare molecular size SiC nanoparticles with engineered surface, crystal structure, and defect type with adjusted concentration._

A few nanometer quantum emitters with impressive stability and biocompatibility could change our world in many fields from biological research through medical therapy to information technology.

In my dissertation, I present results toward realization of this ultimate goal. First, I would like to introduce our motivation further with a chapter about the history, current states, and unsolved issues in bioimaging and fluorophores, then I present the properties of silicon carbide; and I show what the state-of-the-art in the field was when I started to work on these issues in 2011. In the following chapters, I present my own research beginning with a chapter about research objectives and approach following with an overview of applied methods, and results.. I divided my work into three main parts: i) synthesis of small SiC nanoparticles, ii) optical properties of SiC nanoparticles and iii) synthesis of SiC ceramic as a precursor for nanoparticle synthesis. At the end of my dissertation, I give a short outlook and overview of the ongoing research we are doing.

### 1.1 Motivation

**Introduction to bioimaging – importance of the probes**

In 1882 Paul Ehrlich used uranin, the sodium salt of fluorescein to track aqueous humor secretion in the rabbit eye (or other words he followed how the transparent fluid that fill
the anterior and the posterior chambers in the eye leaves from the ciliary epithelium cells which generate such fluid) taking the very first in vivo use of fluorescence. Shortly later, at 1887 Karl Noach published a book listing more than 600 fluorescent compounds. The first fluorescent microscope was built by Otto Heimstaedt, and Heinrich Lehmann at 1911 and 1913 separately; and at 1914 Stanislav Von Prowazek used this instrument to study dye binding to living cells. Then the field developed rapidly. Why fluorescent imaging becomes the ruling procedure in life sciences?

“Believing in seeing”

Most of the book and review that try to summarize the field start with this sentence. I think the most important feature of luminescent techniques is the high sensitivity of photon detection. The sensitivity of the human eye to light is below 0.003 cd/m² in the case of scotopic vision) that makes fluorescence a very salutary method in surgery. With instrumental measurement, we have the ability to detect even a single photon. Only few techniques are available that have comparable sensitivity.

Fluorescence imaging is often connected to microscopy. Indeed, microscopes are great tools in imaging used to observe and describe cell, tissue, or a whole organism enabling scientists to better grasp the often-misunderstood relationship between microscopic and macroscopic behavior. The inherent specificity and sensitivity of luminescence; the high temporal, spatial, and in some cases, three-dimensional resolution; and the enhancement of contrast resulting from the detection of an absolute rather than relative signal (unlabeled features do not emit) rose luminescence techniques as standard techniques in biology. Additionally, the variation of well-described spectroscopic techniques provides different types of information, and the commercial availability of fluorescent probes increases the range of possible applications, such as the development of biosensors for basic and clinical research. Recent advancements in optics, light sources, digital imaging systems, data acquisition methods and image enhancement, analysis, and display methods have further broadened the applications in which fluorescence microscopy can be applied successfully. Another development has been the establishment of multiphoton microscopy as a three-dimensional imaging method that allows researchers to study biomedical specimens from single cells to whole animals with submicron resolution. An example for the wide use of fluorescence imaging is demonstrated in Figure 1-1.
Despite many of the above techniques can be used as so-called non-labeled imaging where the emission from an organism or a biomolecule is detected instead of a foreign chemical injected into the system, in many cases fluorescent probes are essential tools for imaging.
Fluorophores are great tools because they can be modified in different ways, or be conjugated to various molecules to give them a certain function; or allow them to bind to specific organelles, or proteins. Through chemical modifications, a single fluorophore can be produced in a number of variant forms, each with a different specificity (Figure 1-2). For specific targeting, a fluorophore with active site and a special molecule, for example an antibody is needed. These two combined and the composed molecule exhibits high selectivity to the fluorophore. Even though it sounds simple, the dreadful properties of the first generation fluorophores frightened researchers to use labeling frequently; and the discovery of green fluorescent protein was needed for developing the new era of fluorophores that lighted up the world.

Figure 1-2. An example of different application possibilities is using fluorophore in biology. Labelled cell structure components such as actin (A) and tubulin (B) and salt forms for whole-cell staining (C). The picture was taken from thermofisher.com.

**Fluorescence Proteins**

Indeed, after the discovery of dyes and fluorescence microscopy the next boost in the field was the discovery of green fluorescence protein (GFP) in *Aequorea victoria* jellyfish by Milton Cormier and Osamu Shimomura at 1964; and the encoding of the GFP sequence by Douglas Prasher that led later the demonstration that GFP can be produced in organisms other than *Aequorea victoria* by Roger Y. Tsien, Osamu Shimomura, and Martin Chalfie. This was the first reported successful gene transfer. This work was honoured by Nobel Prize in chemistry in 2008. The key feature of fluorescent proteins is their ability to self-generate the intrinsic chromophore from three amino acids at positions 65–67 (numbering is given according to *Aequorea victoria* GFP), and this does not
involve cofactors or enzymatic components. Since the discovery of GFP, many GFP-like proteins have been cloned and engineered for live-cell imaging applications providing the rainbow of fluorescence proteins; including fluorescent probes utilizing Förster resonance energy transfer (FRET) mechanism\textsuperscript{19}. Fluorescent proteins and their engineered variants can be used for routine monitoring of gene activation, as well as the selective labelling and analysis of single proteins, cellular organelles, and even whole cells. Creation of a genetic in-frame fusion of a fluorescent protein to a protein of interest enables localization of that protein to specific tissues, cells, or subcellular compart-
ments. It means that the fluorophore is generated inside cell band to the protein or other molecule to interest (Figure 1-3)

Even though fluorescent proteins revolutionized the field of biology, they have several disadvantages. They may lose its fluorescence during tissue fixation or subsequent processing; and GFP expression can vary considerably even among similar cell types in a single animal. There are conflicting results on whether GFP is toxic to cells. Aggregation of fluorescent proteins can lead to cellular toxicity. In addition, fluorescent proteins for an extended time may generate free radicals that are toxic to cells. The attachment of a fluorescent protein to a protein of interest often has effects on the function, structure, and localization of a protein19.

**Organic Dyes**

Beside fluorescence proteins, the high variation of fluorescence organic molecules have been developed and being developed even nowadays. Fluorescent dyes have several benefits over fluorescent proteins. It is easier to synthesize by using conventional organic chemistry instead of gene manipulation. Organic dyes are usually much smaller than proteins, and it makes possible, for instance, to measure Ca concentration next to the pore of an ion channel20. Fluorescent dyes can be synthetized with variety of functional groups allowing special targeting.

The optical properties of organic dyes depend on the electronic transitions involved; and can be tuned by elaborate design strategies20. The emission of organic dyes typically originates either from an optical transition delocalized over the whole chromophore (resonant dyes) or from intramolecular charge transfer transitions20. Resonant dyes usually have narrow absorption and emission bands that often mirror each other, with a small Stokes-shift (Figure 1-4). Dyes with intramolecular charge transfer such as coumarin, have well separated, broader, and structureless absorption and emission bands in polar solvents; and a large solvent sensitive Stokes shift (Figure 1-5). Their molar absorption coefficients, and their fluorescence quantum yield, are generally smaller than those of dyes with a resonant emission21.

Essentially, fluorescent probes are available as conjugated antibodies, which are labelled (or ‘tagged’) with fluorophores. The two most commonly employed fluorophores are FITC (fluorescein isothiocyanate) and TRITC (tetramethyl rhodamine isothiocyanate).
Introduction

One of the most important problems with fluorescent dyes is photobleaching. Photobleaching is the photochemical alteration of a fluorophore, which turns it dark\textsuperscript{22}. This is caused by reactions between the fluorophore and surrounding. Practically it means that dyes lose their most favorable property because of the excitation\textsuperscript{22,23}.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure1-4.png}
\caption{Typical absorption and emission spectra of a resonant dye (schematic representation). This type of dye is usually characterized by small Stokes-shift.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{Figure1-5.png}
\caption{Absorption and emission spectra of coumarin. Coumarin is an intramolecular charge transfer dye with large Stoke-shift and solvent sensitivity.}
\end{figure}

Many dyes also suffer from poor thermal stability in aqueous media. Most of the reactive oxygen species generated in a living object also can attack numerous dyes.
Even though, many organic dyes, such as the Alexa™ dyes have been designed that display enhanced photostability in comparison to first-generation fluorophores such as fluorescein (see Figure 1-6), limited dye photostability can still hamper microscopic applications requiring high excitation light intensities in the UV-visible light region or requiring long-term imaging.24

Colloidal size semiconductor particles, quantum dots can overcome this limitation.

Quantum Dots
Quantum dots (QD) are often defined as semiconductor nanoparticles made from 100-1000 atoms of group II and VI elements (e.g. CdSe and CdTe) or group III and V elements (e.g. InP and InAs)6. These crystalline particles are in the range of 2 to 10 nanometers in diameter; and were discovered in the 1980’s by Louis Brus, who was working at the AT&T Bell Laboratories25. He discovered that the properties of such particles related to their physical characteristics: as the size of a particle decreases, the energy of emitted light increases. It looks like that the particle has quantized properties under a certain size, where the diameter is in the same magnitude as the Broglie wavelength of the electron wave function and below the exciton Bohr radius. Indeed, physical size smaller than the exciton Bohr radius results in a 3-dimensional quantum confinement of charge carriers within the QD and limits the number of possible energy states that an electron can exhibit, thus giving nanoparticles novel properties not achievable in bulk materials6. The new functionality of quantum dots belongs to the tunable physical properties simply by the variation of size and shape counter to the properties of bulk crystalline solids, which are ordinarily not referred to their size. Below 10 nm, in the
case of CdS, for example, the band gap can be tuned between 2.5 eV and 4 eV by decreasing the size of spherical shaped CdS nanocrystals\textsuperscript{26}. Figure 1-7 demonstrates such effect.

![Figure 1-7. Quantum Confinement: Smaller the size of a QD shorter the emitted wavelength is. © image is from Sigma Aldrich](image)

Quantum confinement affects other properties too. Taking CdS again, the melting temperature varies from 1600 °C down to 400 °C\textsuperscript{27}. The pressure required to induce transformation from a four-coordinate phase to a six-coordinate phase increases from 2 to 9 GPa, even as the number of nucleation events for the transition becomes one\textsuperscript{28}. This enormous range of fundamental properties is all realized in a material of a single chemical composition. The variation is achieved by reducing only the size of the crystal.

I mention here that not only colloid semiconductors are called quantum dots. Generally speaking, there are two families of quantum dots: colloidal quantum dots we are discussing here, and epitaxial quantum dots that are defined by electrostatic gates on substrates. It is also possible to make a quantum dot by trapping a single molecule or nanoparticle between two electrodes\textsuperscript{29}. We only focus on colloid QDs made from nanocrystals in the context.
Despite the recognized possibility in QDs, these types of materials have never been as famous as carbon related counterparts like nanotubes and graphene. Certainly, the lack of stability and the difficult synthesis processes did not favor any research. A major milestone was achieved by Bawendi and coworkers: they were able to synthesize highly uniform colloidal CdSe QDs by developing a high-temperature organometallic procedure in 1993\(^{30}\) (equation 1-2).

\[
\begin{align*}
& \text{CdSe} + \text{Cd} \rightarrow \text{CdSe} + \text{Cd}\text{OH} + \text{O}_2
\end{align*}
\]

(1)

\[
\begin{align*}
& \text{HO}[\text{Cd} \text{Cd} \text{Cd}]_{\text{n}} \text{OH} + \text{SeP} \rightarrow \text{CdSeCd}_{\text{n}} \text{SeCd}
\end{align*}
\]

(2)

In the year of 1997, Dabbousi and co-workers reported the synthesis of core/shell structure that solved the photostability problem and resulted in a 50% of quantum yield\(^{31}\). This landmark achievement initiated a new era in QD research. The first water soluble QDs that could be applied for labeling were reported one year later\(^{32}\).

In comparison with organic dyes, the absorption of QDs gradually increases toward shorter wavelengths and they have narrow emission band allowing free selection of the excitation wavelength and multicolor probing\(^{24}\). QDs have longer fluorescence lifetimes\(^{33}\) allowing temporal discrimination and lifetime imaging\(^{2}\). Furthermore, the relatively small size of QDs comparable to that of large biomolecules (e.g. antibodies) makes possible to engineer biologically functional materials.

The advantage and the drawback of QDs in bioimaging application is the huge variety of such systems. The inorganic nanoparticle core provides a rigid foundation for the development of QD probes\(^{6}\). Manipulation of the core chemical composition, size, and structure controls the photo-physical properties of the probe\(^{34}\). However, bare nanoparticles usually cannot interact with biological systems and do not possess any biological functionality. Careful design of coating materials that can protect the QD core from the environment is needed for biocompatible probes with controllable physicochemical properties. Further decoration of QDs with biomolecules is also necessary to dress
them with biofunctionality, in order to probe interaction with biological systems. Therefore, preparation of QD-based probes and nanodevices represents a multi-step process. Each step is guided by individual design principles, in order to control optical, physical, and chemical properties of the final probe.

The original organometallic synthesis route for QD core produces QDs with low quantum yield. Even the TOPO-coated (TOPO – trioctylphosphine oxide) QDs are unstable with respect to photooxidation, resulting in degradation of nanocrystals and toxicity due to leakage of free Cd or other toxic ions. Both issues arise from the relatively large number of atoms exposed on the surface of nanoparticles. Surface atoms lack neighbor atoms with which to form chemical bonds and thus possess unoccupied electron orbitals (dangling bonds or surface trap sites). These orbitals can trap charge carriers and prevent or delay electron-hole recombination reducing quantum yield. In order to prevent these undesirable characteristics, surface should be protected with inorganic capping layers. The most used technique is applying inorganic shells (e.g. CdS and ZnS) that passivate the highly photoactive core. Careful choice of core and shell materials as well as optimization of the shell thickness are necessary to minimize the lattice strain between the core and shell and maximize the QD photo-physical properties. Figure 1-8 represents the most used core/shell structures.

![Figure 1-8 Different core/shell structures. The band gap of the shell can be higher or lower than the band gap of the core. CB: conduction band, VB valence band, the plots represent the corresponding wave functions](image)

Although thin shells (1–2 monolayers) often produce the highest fluorescence yields, thicker shells (4–6 monolayers) provide more core protection from photooxidation and degradation. Thicker shell can also significantly reduce QD blinking (intermittence in the luminescence).

In any relevant application environment-particle interaction, hydrophilicity and surface chemistry should be well controlled. Organic phase synthesis produces hydrophobic
QDs soluble only in nonpolar organic solvents. However, in order to be useful for biological applications QDs must be made water-soluble. This is the most challenging part of the synthesis. Several different approaches have been developed to produce water-soluble QDs satisfying these criteria. One approach involves replacing hydrophobic surface groups with hydrophilic ones by means of ligand exchange. This is usually accomplished by substituting of the native TOPO coating with bifunctional ligands, which consist of surface-anchoring groups (e.g. thiol), and hydrophilic terminating groups (e.g. carboxyl, hydroxyl or amine). Mercaptoacetic (MAA)\textsuperscript{32} or zwitterionic molecules, such as cysteine\textsuperscript{42} is often used to produce carboxyl terminated hydrophilic surface. Amine and carboxylic acid groups provide binding sites for cross-linking to proteins, peptides, and nucleic acids. These procedure offer simple method for realizing nanoparticles with small hydrodynamic diameter, but often compromises the fluorescence efficiency, photochemical stability, and shelf life of the probes, as ligands tend to detach from the QD surface leaving behind surface trap sites and causing nanoparticle aggregation\textsuperscript{43}.

Another ligand-exchange approach involves formation of polymerized silanol shells on the QD surface making (1–5 nm thick) silica/siloxane shell and rendering particles soluble in intermediate polar solvents (e.g. methanol or dimethyl sulfoxide)\textsuperscript{44}. Further reaction with bifunctional methoxy compounds renders QDs soluble in aqueous buffers. Polymerized siloxane coated nanoparticles are highly stable against aggregation. However, residual sylanol groups on the QD surface can lead to precipitation and gel formation at neutral pH\textsuperscript{6}.

An alternative approach to water-solubilization is to retain the native TOPO coating and encapsulate it with amphiphilic molecules such as polymers and phospholipids. The hydrophobic portion of the amphiphilic molecule intercalates within surface ligands while the hydrophilic portion (e.g. charged groups, PEG, etc.) faces outwards, interacting with the aqueous solvent and rendering the particle water-soluble\textsuperscript{45}. This method produces exceptionally stable water-soluble QDs with preserved optical properties, but steric stabilization results in a dramatic increase of the nanoparticle hydrodynamic size (up to 30 nm)\textsuperscript{45,46}. Size increase might be detrimental for quantitative biomarker detection in a crowded biological environment and hamper intracellular penetration of the QD probes.

An overview of the different encapsulation techniques is shown in Figure 1-9.
Indeed, preparation of QD-based probes and nanodevices represents a multi-step process. Every step has a huge effect on the physical and chemical properties that is very challenging and provides beauty for chemists in this field. In general, the size of QDs should be small after coating, the surface should be biocompatible, reactive groups should be available for conjugation of biomolecules and targeting ligands, and QDs should show negligible non-specific interactions with the biological environment. Unfortunately, such a method that satisfies all the design criteria imposed by increasing demands of biomedical research is still missing. Even though, my overview is based on the results obtained before 2011, this statement is still valid as I write my dissertation.

Not surprisingly, several other systems are intensively studied to overcome the limitation of QDs with the hope that all the good properties can be “transferred” from the existing QDs. Some examples can be found in a review paper from 2011\(^{47}\). The most in-
interesting examples are dye doped silica nanoparticles, upconverting nanomaterials, nanodiamonds, silicon nanoparticles, carbon based nanomaterials and silicon carbide.

1.2 Properties and recent applications of silicon carbide

The applications of quantum dots in biology rose rapidly but limitations in these applications were also discovered that accelerated the research for seeking other possibilities. Silicon carbide (SiC) is a remarkable material that can be employed in a variety of industries. I will show that nanosized SiC is a potential candidate to overcome the limitations of traditional quantum dots.

Properties of Silicon Carbide

Silicon carbide can be used as an abrasive material for machining industry (also called carborundum); and as a wide band gap semiconductor for high power, high temperature electronic devices\textsuperscript{48,49}. SiC is the third known hardest material beside diamond and boron nitride. This property led to applications in machining and grinding tools as a high performance ceramic\textsuperscript{49}. Thanks to the semiconductor type electronic band structure and doping capabilities of SiC, SiC can be used in high power electronic devices as well\textsuperscript{50}.

SiC is built up from covalent bonding of Si and C atoms in biatomic layers. These form tetrahedrally oriented structure of Si–C, with a very short bond length (202 pm) and, hence, a very high bond strength (381 kJ/mol) which give extremely high chemical and mechanical stability to SiC\textsuperscript{51}. SiC can be formed in amorphous, polycrystalline, and monocristalline solid forms\textsuperscript{51}. An important characteristic of SiC is that the bilayers of Si and C can be stacked one upon the other in different crystal orientations that called polytypism\textsuperscript{52}. The ability of compound and element to occur in more than one crystal structure is called polymorphism. Polytypism is a one-dimensional variant of this phenomenon. SiC can form zinc blende structure that is called cubic SiC with face centered cubic (fcc) lattice. Along the (111) lattice direction one can find Si–C bilayers where the stacking sequences follow a fcc type closed pack structure and the periodicity can be described by three cubic (k) bilayers along that direction. Thus, cubic (C) SiC is called 3C-SiC in Ramsdell notation. It is also possible to form hexagonal closed pack (hcp) structure from the tetrahedrons that lead to hexagonal (h) stacking sequence. The well-known crystal structure is the wurtzite lattice, which is a hexagonal (H) lattice, and two h bilayers provide the periodicity of that lattice, called 2H. Different combination of stacking sequences of cubic and hexagonal bilayers can form different crystal struc-
Introduction

tures. To date, more than 250 polytypes is known for SiC. The most common polytypes 4H and 6H with \(hkk\) and \(hk_1k_2hk_1k_2\) stacking sequences along the \(c\)-axis, respectively (Figure 1-10).

![Common polytypes of SiC represented by using ball and stick model. yellow balls: C, blue balls: Si. Bilayers are labelled with h (hexagonal), and k\(_n\) (cubic). The lines guide the eyes on the layer orientation. 3C-SiC has a zinc blende type structure.](image)

The bandgaps of 3C, 6H and 4H polytypes are 2.4 eV, 3.0 eV, and 3.3 eV, respectively. This is a large variance despite the fact that the chemical Si-C bonds are the same in all of these polytypes. While this is an interesting phenomenon on its own merit, the various forms of SiC actually can be used in numerous applications. The dominant crystal of choice is 4H-SiC for power electronic devices because it exhibits the largest bandgap (3.2 eV), while 6H-SiC is ideally suited for solid-state lighting (LEDs), as its lattice constant is close to that of GaN family of alloys used in advanced LEDs that have enabled DVD and blue ray technology.

**Synthesis of SiC powder**

Numerous methods have been developed for SiC synthesis. The method for SiC production depends on the desired material structure (powder, ceramic, single crystal etc.). The most widely used conventional approach for powder synthesis is known as the Acheson process. Here, SiO\(_2\) reduction by carbon at about 2500 °C leads to the formation of SiC under the general reaction (3)

\[
\text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO}
\]
Both, the SiO\textsubscript{2} and the C source can be varied. For example, they can be premixed in a sol-gel process.

Another large-scale production method is the reaction between Si and C (4). This reaction has a moderate enthalpy changes (-73 kJ/mol)\textsuperscript{57}.

\[
\text{Si} + \text{C} \rightarrow \text{SiC} \quad (4)
\]

The reaction is often characterized as combustion synthesis (CS), or self-propagating high temperature synthesis (SHS), but this is the general reaction in the case of reactive infiltration too, when porous carbon body is immersed into the molten Si\textsuperscript{58}.

In a conventional SHS scheme, a reactive mixture of solid powders is ignited at one side of the green body (a form of bonded powder of the desired composition before it has been sintered or fired), and a high-temperature combustion wave front propagates through the system, that converts the precursors to the desired product. This is also called combustion wave propagation. Combustion synthesis can be also ignited by uniform heating of the whole body (volume combustion synthesis). This mode of synthesis is more appropriate for weakly exothermic reactions that require preheating prior to ignition\textsuperscript{59}, like the reaction of Si and C. Combustion synthesis is known for short (seconds) reaction time; energy efficiency, as the chemical energy of the internal system is primarily used for the production of the material; simple technological equipment; an ability to produce high purity products with a high production rate.

*We used volume combustion synthesis to produce SiC powders by heating the Si and C mixtures up in an induction furnace.*

It was demonstrated that a uniform preheating of the stoichiometric Si + C mixture in a flow of argon gas leads to the self-ignition of the heterogeneous media at temperature about 1300 °C with formation of 3C-SiC powders, which has a morphology similar to that of initial carbon\textsuperscript{60}; and the use of chemical additives as an activation agent to Si + C mixture, e.g., polytetrafluoroethylene (PTFE), allows gas-phase reaction routes that leads to SiC powder with high porosity\textsuperscript{61}. PTFE decompose at 300 °C while highly reactive radicals are formed. These radicals react with Si in an exothermic reaction (5).

\[
\text{Si} + -\left(\text{C}_2\text{F}_4\right)_n \rightarrow \text{SiF}_4 + \text{C} \quad (5)
\]
It is also reported that PTFE content can increase vacancy concentration in SiC$^{62}$.

**Biological Application of SiC**

In biological applications, the degree of success of a material depends on its biocompatibility, and on its capacity of directly interfacing cells and tissues. The biocompatibility and hemocompatibility$^{63}$ of SiC with living tissue and safely contacting blood has been largely reported by the biomedical research community$^{63,64}$. SiC has been used in virtually every part of the human body from a durable coating for bone prosthetics$^{65}$ and in dental applications$^{66}$, to coatings for brain machine interface (BMI) devices$^{67}$, myocardial heart probes$^{68}$, and nonfouling coatings for coronary heart stents$^{69}$. In all of these instances, SiC materials were in amorphous, crystalline, or thin-film (monocrystalline or polycrystalline) form.

1.3 Luminescent silicon carbide nanostructures

Even though SiC has enthralling biocompatibility, it has negligible luminescence because of the indirect nature of its electronic band structures that gives poor optical characteristic to bulk SiC$^{51}$. This may change at the nanoscale. Indeed the effect of size restriction on indirect gap semiconductors may be two-fold. First, the shift of the band edge toward higher energy as crystal size decreases is expected$^{70}$. Second, the shape of the bands and the selection rules governing the transitions between bands might also be affected$^{71}$ because the confinement of the wavefunctions in small crystals causes a breakdown in selection rules, and the ordinarily forbidden band edge transition of the indirect gap material becomes "less forbidden"$^{70}$. And it has been also hypothesized that mixing of surface state wave functions into those of the bulk will cause the behavior of an indirect gap material some direct band gap-like characteristic$^{72}$ (this was demonstrated on Si nanocrystals in 2013$^{73}$). It means that even indirect semiconductors could emit light with appropriate efficiency when their size is substantially reduced.

**History of Synthesis**

Intense visible luminescence from SiC structures without any relevant luminescence impurities was reported by Matsumoto and co-workers in a conference paper presented by the Materials Research Society in 1993$^{74}$. In this work, the group created porous SiC by anodic etching that had been a known process to form porous Si$^{75}$. The porous SiC layer made from 6H-SiC emitted light at around 500 nm, below the energy bandgap of
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6H-SiC (around 433 nm), and the luminescence was five hundred times stronger than that of the free electron to acceptor recombination in the bulk crystal. (The bulk emission maximum was at around 600 nm, which should be originated to donor and/or acceptor impurities, for example, Al – N donor-acceptor pairs – DAP). The origin of the luminescence is still in the center of intense research. Many authors attributed the reported luminescence to the quantum confinement effect, however, the emission from porous SiC is usually above the band gap, and polytype independent that led to the conclusion that the emission must be originated from the surface states instead of quantum confinement. Indeed, even though the group of Prof. Choyke measured the particle sizes in the porous layer and they found many “particles” with size below 3 nm and emission peaks below the band gap of 6H-SiC, they concluded that even the UV emission could be due to the surface states.

The properties of porous SiC are important not just because of their room temperature luminescence in these nanostructures, but these nanostructures can be converted to colloid particles. Recently, this has become the main method to produce colloid SiC nanoparticles below 10 nm. Alternatively, SiC nanoparticles below 10 nm can be synthesized by CVD method also, but in most cases, these products suffer from impurities, broad distribution of crystal structure, and composition variations with weak or negligible luminescence at room temperature. Silicon carbide nanoparticles are also produced in solid matrixes like Si or SiO₂. Nowadays, this technology is very useful for physical characterization but not relevant for colloid SiC production. Even though, I would like to mention this alternative here because currently, the conventional technology for Si nanoparticle production is the synthesis in SiO₂ matrix from HSQ (hydrogen silsesquioxane) derivatives and I believe that this might be an alternative synthesis route for SiC too.

SiC nanoparticles made from porous SiC was reported in a Physical Review Letters paper in 2005. It is a bit surprising that more than ten years research was needed to achieve colloid SiC nanoparticles from SiC while the method was known from Si research, where Si particles had been synthetized just a year after the discovery of the red luminescence of porous Si. By inspecting the research articles, one can realize the challenge. In the case of Si, after a single-step electrochemical etching a highly porous layer is formed and this layer can be broken down that finally form colloidal nanoparticles. In the case of porous SiC research, one can find a quite huge variation in the properties of the porous layer formed by the same method. Most of the time, the thickness of the
resultant pore skeleton, the thickness of SiC walls, are more than 20 nm. Wu and his colleagues invented a multiple etching process that led to the production of SiC nanoparticles below 10 nm at the end of the synthesis. This article is a milestone in colloid SiC research. Not just because an efficient synthesis route was reported in it, but numerous statements have been claimed in this Letter that were accepted through years without any reproduction. One of the main claims in this paper was that the observed blue-green luminescence of SiC nanoparticles was caused by quantum confinement of SiC nanoparticles, which will be revised in this dissertation.

Even though, electrochemical etching and subsequent ultrasonication can produce SiC nanoparticles below 10 nm, this method is very inefficient and expensive because of the need of high quality epitaxial SiC layer and electrochemical chamber made of polytetrafluoroethylene (PTFE). For comparison Figure 1-11 represents the photoemission of porous 3C-SiC and NPs made from 3C-SiC.

The next step in the evolution of SiC nanoparticle synthesis was the electroless wet etching route reported by the same Chinese team who previously developed the electrochemical etching process. Again, a porous layer is formed by wet chemical etching but the process is stain etching. Stain etching is an electrochemical reaction takes place in a redox electrolyte without applying bias. In the case of stain etching one can use cheap SiC powders instead of SiC wafers and the porous layer is formed by immersion of such powders into hot HF:HNO₃ mixture. This process is also a copy from Si research where Si nanoparticles made from Si wafers contacted with HF:HNO₃ solution in a short period of time. The main difference between the two materials is that SiC is much more stable against mineral acids than Si is; therefore, hot solution is required to promote the process. Indeed, SiC is known for its chemical resistivity and SiC can even

![Luminescence of porous SiC](image)

Figure 1-11. Luminescence spectra of porous 3C-SiC (a.), and 3C-SiC NPs (b.). Figures are reconstructed based on refs. 85 and 84, respectively.
stand against hot HF:HNO₃ solution. If we are seeking an etchant for SiC then only molten salt mixtures are usually suggested in the literature, in order to etch SiC. The only well functioning aqueous etchant for SiC is boiling phosphorous acid that can attack SiC but during the etching, a protective oxide layer (SiO₂) is formed and the etching rate is very low. SiC etching in HF:HNO₃ mixture, however, have been reported from the 60’s. The main problems with these reports that most of the time, the quality of samples are questionable. In 2006, Campaz et al. reported that hot HF:HNO₃ solution can selectively etch 3C-SiC leaving patterned 6H-SiC structures from a whiskers built up from 3C-SiC/6H-SiC bilayers. This result is very interesting because clearly demonstrates that hot HF:HNO₃ mixture is polytype selective, which is quite surprising because of the same chemical structure of different polytypes. Campaz et al. employed HF:HNO₃ solution and ultrasonication but they studied only the residual whiskers. Actually in this year, the luminescence of stain etched SiC was also observed, however, the authors did not characterize their samples from structural point of view.

We also use stain-etching method to form SiC nanoparticles.

The mechanism of porous etching

In the process of SiC NPs synthesis, pore formation is the key chemistry that is worthwhile to discuss a little further. I have to mention here that despite anodic porous etching onto Si and Ge was already shown by Uhlir at Bell Labs in 1956, the exact mechanism behind porous etching is still under discussion between researchers.

Wet etching of semiconductors is a material dissolution that can proceed by chemical, electroless, photochemical, anodic or cathodic etching. The main differences between chemical and electrochemical etching is that chemical etching is not potential dependent, while electroless, photochemical, anodic and cathodic dissolutions are potential dependent; and are therefore referred to electrochemical processes. Pore formation is reported only in the case of electrochemical etching. In these cases, free charge carriers are required. Electrons are involved in cathodic decomposition while holes are supplied by an oxidizing agent in the case of electroless dissolution. Carriers are generated by absorption of photons in the photochemical processes while an external circuit is used during anodic etching.

In the case of anodic dissolution, one should place the material into a beaker, in order to transform it into its porous form, add a counter electrode, and connect both electrodes to a current source in order to anodize strongly the semiconductor surface (Figure 1-12).
The semiconductor – electrolyte junction that is established when the semiconductor is immersed in the solution plays an important role since the charge distribution at the interface controls the etching phenomena. According to the Gerischer’s model, which applies the Schottky’s theory combined with the Marcus theory, close to the surface a depletion region or space charge layer is formed that is either in accumulation or depletion of majority carriers. When depletion conditions are established, an energetic barrier is formed, called the Schottky-barrier. The Schottky-barrier and the semiconductor – electrolyte interface behaves like a diode. Depending on the type of doping and the applied potential (Figure 1-12), the junction is either conducting or rectifying: anodic etching occurs, onto p-type materials in the dark (forward bias - conduction) while illumination is necessary for an n-type semiconductor (reverse bias - rectification).

Pore formation begins with pore initiation. Unfortunately, the origin of nucleation is often unknown. Many studies treat pore initiation as a random phenomenon where
localized dissolution occurs at surface inhomogeneities inducing an enhancement of the current flow at the interface. In regions of locally high current density, preferential attack occurs and pores can nucleate at surface defects, like intrinsic point defects and impurities, or hydrogen related defects. The nucleation can also take place at roughened surfaces.

While there are only a few models that try to describe pore nucleation, there are many competitive models for the description of pore growth. These concepts are mainly about porous Si, however, most of the descriptions are attempted to apply to other systems. Indeed, pore propagation was tried to describe either with a “chemical” approaches or “physical” approaches. In chemical models, an autocatalytic effect or competitive reactions play the key role. Unagami\(^{99}\) proposed that localized dissolution of p-type silicon was due to the divalent (direct Si dissolution) and the tetravalent reactions (formation and dissolution of SiO\(_2\)) of silicon with HF, without the disproportionation reaction. The dissolution of the walls is hindered by a layer of silicic acid. Kooij\(^{100}\) suggested a model assuming that the chemical oxidation of an Si(II) intermediate to an Si(IV) product is catalyzed by a mobile Si(I) dissolution intermediate. Based on chemical kinetics, Soares et al. proposed that SiF could also play a catalytic role in the localized dissolution process\(^ {101} \). During the etching, surface is covered by passive Si-H and activated Si-F bonds. Parkhutik et al. suggested the concept of the virtual passive layer\(^ {102} \): two competitive processes take place simultaneously during the pore growth: the formation of a passive oxide layer at the bottom of each pore and the electrochemical dissolution of the oxide. The parameter determining the morphology of the porous films is the rate of electric-field enhanced dissolution of the electrode material at pore tips. Depending on its value, pores with different morphologies may be formed.

The main problem of chemical models is that they cannot describe precisely the pore formation mechanism, and developing new pore structures with these models cannot be accounted. On the other hand, \textit{in situ} characterizations usually cannot confirm such models. Oxide formation, for example, is detected in systems that do not contain HF.

The physical theories consider the semiconducting properties of the electrode to explain the pore formation. It is therefore easy to extrapolate such models to other semiconductors. However, these models do not explain the surface chemistry during the dissolution. In physical models, dissolution of silicon involves the transfer of several charges, and the first rate-limiting step is to supply holes to the surface\(^ {103} \). All these models con-
sider the space charge layer configuration or the electric field at the interface. In the model of Beale et al., due to the low resistivity of the electrolyte relative to the fully depleted porous Si, the current flows preferentially to the electrolyte$^{104}$. The material dissolution is therefore confined in the pore apex. The mechanism by which current flows across the Schottky-barrier is dependent on the doping level (Figure 1-13).

Figure 1-13 The role of space charge layer. SCR represents the space charge layer, Si(N) and Si(P) are n doped and p doped Si, respectively. $I_{\text{diff}}$ represents diffusion current while $I_{\text{cond}}$ is for conduction current. $h\nu$ is for photon illumination. If SCR occupies the whole pore wall then etching is possible only at the pore apex.

Searson et al. also proposed a mechanism based on the modifications of the space charge region or layer (SCL) in the porous region$^{98}$. By solving the three-dimensional Poisson’s equation for a semispherical pore tip, the SCL is found to be thinner at the pore apex; therefore, the electric field is enhanced. Hole supply and charge transfer through the interface are therefore favored at the surface located in the pore tip while the pore sides are passivated. The pore wall thickness is controlled by wall-SCL. The ratio between the applied and the electropolishing currents drives the pore diameter and the porosity. Understanding of these mechanisms has enabled the growth of well-defined and well-controlled macropore structures.

The pore formation mechanism in the SiC etching is believed to be similar to that of Si. This issue is not well studied as most of the articles pay attention to the optical properties or the different pore morphologies. Indeed, porous etching of SiC result many different pore morphologies that depend on the applied voltage, surface (surface recon-
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structions, C face or Si face, etc.) and the quality of the sample. It is important to mention in this context that single crystalline SiC wafers are not perfect. The main problem with SiC wafers is the different density of micron scale dislocations like voids and pipes. These imperfections can vary the final pore morphology as well\textsuperscript{105}. Konstantinov tried to describe pore formation in SiC porous etching process using existing phenomenon and in this work. They suggest Fermi-level pinning to describe wall thickness variations\textsuperscript{106}. While Fermi-level pinning, which is a situation, where the band bending in a semiconductor contacting a metal or electrolyte is essentially independent of the metal/electrolyte, can explain the wall thickness variations in thick pore wall systems, one should note that porous SiC with several nanometer thick walls is also produced where quantum confinement could play an important role. The pore formation is described by the following reaction\textsuperscript{107},

\[
SiC + 8OH^- + \gamma h^+ \rightarrow SiO_2 + CO_2 + 4H_2O + (8 - \gamma)e^-
\]  
(6)

Where \( \gamma \in \mathbb{N}, \gamma < 8 \) and \( h^+ \) represents hole. Even though, the knowledge about pore formation during SiC etching is scarce, it is still more studied than the pore formation in stain etching. Electroless etching is still an electrochemical reaction, or a redox reaction without an external bias. Because bonding states correspond to the valence band of the semiconductors, it is necessary to supply holes to the semiconductor surface in order to achieve electrochemical etching. In the case of stain etching, holes are created by reducing an oxidizing agent via the valence band of the semiconductor. The oxidant extracts electrons from the solid, or in the other words, it injects holes into the valence band. The electron acceptor levels of the redox couple must have an energy distribution that overlaps with the valence band of the semiconductor (see Figure 1-12). The dissolution process takes place because hole injection leads to bond breaking that follows new bond formation between the semiconductor surface and the electrolyte. In the case of silicon, porous stain etching in HF/HNO\textsubscript{3} has been extensively studied\textsuperscript{108-110}. The overall chemical reaction is very simple. However, in reality, Si dissolution and pore formation are very difficult and multi-step processes, where nitrogen goes through all of the possible oxidation states, and the actual reaction mechanism depends on the composition and temperature of the acid mixture.

Stain etching mechanism of silicon carbide is even less known. Campaz proposed the following reactions\textsuperscript{91}:  

\[  \]
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\[
\begin{align*}
SiC + 2HNO_3 + H_2O &\rightarrow 2HNO_2 + 4OH^- + SiC^{4+} \quad (8) \\
SiC^{4+} + 4OH^- &\rightarrow SiO_2 + CO_2 + 2H_2 \quad (9) \\
SiO_2 + 6HF &\rightarrow H_2SiF_6 + 2H_2O \quad (10)
\end{align*}
\]

The overall chemical reaction is

\[
SiC + 2HNO_3 + 6HF \rightarrow H_2SiF_6 + 2HNO_2 + CO_2 + 2H_2 \quad (11)
\]

The SiC\(^{4+}\) means that four holes must be injected to the valence band to promote dissolution of SiC. In this reaction, neither the temperature dependency (the reaction takes place only over 80 °C) nor the very polytype dependency is explained. The redox potential of HNO\(_3\) (0.8 V vs SHE – standard hydrogen electrode) should not be appropriate for SiC etching because the valence band maximum of SiC in an electrolyte at acidic conditions is about 1.5 V vs SHE for all polytypes\(^{48}\). That means that the conventional stain etching model where hole injection into the valence band is the key step cannot explain the reported polytype selectivity. Actually, my recent work is to study the etching mechanism and polytype selectivity of such chemical process but this work is not the part of this dissertation. However, I will discuss this reaction based on my observations.

Size distribution of colloidal SiC nanoparticles

The size distribution of the SiC particles was varied in the studies reported before the year 2011, but in general, broad size distribution was found in most of the cases. Particle diameter was varied between 1-6 nm and the main particle size was between 3 nanometers and 5 nanometers. In 2011, Fan et al. reported closed packed SiC nanoparticles with average diameter of 2.3 nm\(^{111}\). Figure 1-14 shows the reported size distribution in 2005\(^{85}\) and 2011\(^{112}\) for colloid solutions.

However, we also characterized samples taken from other groups in the beginning of the research, and we found a large portion of larger particles that was not mentioned in these reports. Indeed, top-down method usually results in broad size distribution and further separation is needed for proper sample preparation. In a book about silicon carbide biotechnology, Prof. Saddow mentioned that particles produced and/or characterized in his laboratory contained many unbroken porous structures\(^{113}\).
Optical properties

SiC nanoparticles have broad emission spectra in the range of 350-550 nm that was attributed to their broad size distribution and the quantum confinement effect. However, SiC nanoparticles in aqueous solution have peak maxima at about 450-470 nm that do not vary with SiC polytypes. The solution usually can be excited up to 500 nm and the highest emission intensity can be obtained when excitation between 320-370 nm is applied. 3C-SiC nanoparticles prepared by electrochemical etching exhibit smooth spectral lines without substructures, with a typical wavelength width at half maximum of about 120 nm. As the excitation wavelength increases from 250 to 500 nm, the...
emission wavelength continuously shifted from 450 to 540 nm (Figure 1-15a). This was attributed to the quantum confinement effect. The suspension contains 3C-SiC particles of different sizes and smaller particles have larger band gaps as expected from quantum confinement. As the excitation wavelength increases, carriers in smaller particles cannot be excited because the excitation energy becomes smaller than that of their band gaps leading to a continuous redshift in the photoluminescence. Indeed, the emission wavelength at 540 nm is close to the band gap of bulk 3C-SiC that is around 560 nm (2.3 eV). This excitation dependent spectral shift was reported most of the articles published before 2011 regardless of the SiC polytypes. Despite the fact that this spectral shift was associated with the quantum confinement effect, this effect was not directly proven by correlation measurements of fragmented SiC nanoparticles vs. photoluminescence signals. The fact that even 6H-SiC nanoparticles show spectral shift in the same energy region while the band gap of such polytype much larger (3 eV which is about 410 nm in wavelength) than that of 3C-SiC weakens the quantum confinement theory and demonstrates that other factors than size determine the optical properties of SiC nanoparticles. Indeed, the same group that had reported the experimental evidence of quantum confinement reported later such spectra where the spectral shift was not observed for SiC nanoparticles with the same size distribution but prepared by a different synthesis method (see Figure 1-15b).

Surface chemistry

Silicon carbide is a covalent material therefore the surface should reconstruct after the etching. The study of bulk SiC in HF solution reveals that the surface is covered with
hydroxyl and sylanol groups (C-OH and Si-OH) instead of hydrogen\textsuperscript{116}. Infrared spectroscopic and X-ray photoelectron spectroscopic studies revealed that the surface of SiC nanoparticles is very rich in different moieties\textsuperscript{117,118}. FTIR studies revealed the presence of carboxyl groups and oxygen bridges (C-O-C, Si-O-Si, C-O-Si) which is not surprising because of the strong oxidant used in stain etching but authors did not report any differences on the surface groups as a function of synthesis routes (Figure 1-16).

**Environment sensitivity.**

Environment sensitivity is a very important issue because it defines the applicability of the system (for example, pH or polarity dependent emission can be employed for pH nanosensors), and can help reveal the origin of luminescence as well. The emission of SiC nanoparticles show moderate to strong environment sensitivity. Solvent effect was studied by Fan et al. and they did not find solvent effect for 3C-SiC particles with an average size of 4 nm. They concluded that the emission is originated from band to band recombination\textsuperscript{119}. Zakharko et al. also studied the solvent effect on 3C-SiC colloids and they reported hypsochromic shift in the emission\textsuperscript{119}. They explained such a shift with band tail screening effect: a highly polar liquid surrounding the nanoparticles induces a global increase in the effective dielectric constant of the nanoparticle environment. The increased effective dielectric constant of the medium (solvent+nanoparticles) leads to ionization energy decrease in the donor- and acceptor like energy states inside the band gap. This result is interesting from different point of views. First, the difference in the environment sensitivity led to a different conclusion on the optical properties than that by Fan group. While negligible solvent effect can lead to the conclusion that SiC nanoparticles exhibit band edge luminescence, solvatochromism and band tail screening effect can be described only with surface states. Indeed, Zakharko studied the surface termination of the synthetized particles by (FTIR), and temperature programmed desorption mass spectroscopy (TPD-MS); and fingerprint of carboxyl, Si-OH, Si-CH\textsubscript{3}, and even Si-F groups was reported. Because Fan and co-workers did not explicitly study the surface groups of their SiC nanoparticles, their SiC nanoparticles might or might not have different surface termination than those of Zakharko and co-workers. Assuming similar surface terminations (which may be expected because of the same synthesis methods and earlier reports by the group), the only reported differences between these two batches of samples are their size distribution. Zakharko and co-workers reported broader size distribution up to 10 nm vs. 6 nm of Fan and co-workers, which is a bit
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surprising because the properties of larger particles should be closer to that of bulk counterpart, therefore less solvent effect should have been detected. This example represents well the diversity of reports about SiC nanoparticles in the early stages. Beside no-shift and hypsochromic shift, bathochromic shift also can be found in the literature\textsuperscript{112,115}. In Figure 1-17 I plotted the different solvent effect based on the three different reported shifts. At the top, I represent the results of no solvent effect. SiC NPs were dispersed in water (W) ethanol (E), and toluene (T). The luminescence of SiC NPs is shown in water, ethanol, and dichloromethane. The red shift with decreasing the dielectric constant of the solvent was explained by band tail screening effect. At the bottom, an opposite shift can be seen and that was explained by different surface termination: authors claimed that Si-H bonds form on the surface in ethanol while these bonds are oxidized in water, and Si-OH bonds form\textsuperscript{112}.

Beside solvent sensitivity, pH dependency is also studied\textsuperscript{115}. At acidic condition, a “green band” appears as a shoulder at around 510 nm that disappears at very low pH value (pH 1) and at alkaline conditions. The “blue band” at 450 nm starts to shift to longer wavelengths when pH value is increased. It seems that there are at least two different pH sensitive relaxation routes. This may occur because of the numerous dissociative groups on the surface of SiC nanoparticles (carboxyl, C-OH, Si-OH etc.) and dissociation can vary the optical properties. Wu and co-workers attributed the solvent and pH dependence to the reaction of Si surface (on SiC) and water molecule, however, the suggested Si-H bond in their model is not too stable in aqueous conditions and should be slowly oxidized even in ethanol (because of the hygroscopic nature of ethanol), and this explanation goes against the results they reported a few years later\textsuperscript{117} where they reconstructed the Si surface with Si-O-Si bonds in ethanol.

The UV-VIS absorption spectra of SiC nanoparticles usually show featureless monotonous increasing from the absorption edge (around 500 nm) toward shorter wavelengths that correspond to the absorption characteristic of indirect semiconductors. However, Fan and co-workers tried to explain the small shoulders in the absorption spectra by studying SiC nanoparticles in different solvents\textsuperscript{120}. They assumed that the size distribution of SiC nanoparticles in heptane, dichloromethane, and water differs that is manifested in the absorption spectra. They concluded that the nanocrystals with a mean size of 4 nm retain the indirect-gap nature whereas the particles about 1 nm in size display discrete and sharp absorption features. Despite they highlight the existence of polar surface groups such as carboxyl groups that make SiC nanoparticle stable in polar solvent
Figure 1-17. Demonstration of different solvent effect reported in literatures. See more details in th tex..
they did not mention in the explanation of the absorption characteristic that surface moieties with double bonds (mainly C=O) also have absorption in the UV regime because of the allowed $\pi \rightarrow \pi^*$ and the forbidden $n \rightarrow \pi^*$ transitions. Indeed, they reported later that surface termination varies in different solvents\(^{116}\). Furthermore, scattering effect is always an issue in the case of colloid solutions and even though, the particles were small and the solution is transparent in the visible range, scattering always affect the absorption spectra of nanoparticles. On the other hand, theoretical calculations from Gali’s group predicted that the luminescence is surface related\(^{121}\) that was a driving force in the design of our experiments.

1.4 Research objectives

From previous chapters, one can conclude that SiC has unique properties making SiC NPs a promising candidate for biological and optical application. However, the properties of SiC NPs under 10 nm were largely unknown in-depth; and there many inconsistencies can be found in the literatures that should be addressed. For in-vivo application, the blue-green emission should be shifted to red, that might be achieved by introducing appropriate point defects. Before that, the nature of the optical properties should be clarified and a synthesis method with large-scale potential is necessary. Based on these needs I setup the following scientific goals and the direction of research:

1. The synthesis of SiC NPs should be improved to produce smaller nanoparticles with higher yield.
2. The physics behind the luminescence should be revealed by answering the following questions
   - Are there any size dependent optical properties below 10 nm?
   - How surface moieties affect the optical properties of SiC NPs?
3. Going beyond the present limitation and prepare SiC particles with red emitters
2 MATERIALS AND METHODS

For the synthesis and characterization, I employed several different methods and equipment. The theoretical background for synthesis methods can be found in the preceding chapter, while the parameters and conditions of the methods or equipment applied in the experiments will be presented in the Results chapter. Here, I give a short overview about the background of the employed techniques and equipment. I also introduce abbreviations of these methods that are commonly used in the literature.

For the characterization of SiC ceramic powders and SiC nanomaterials, I used numerous methods. I give a brief overview about those, however, more details can be found in the referred books and articles. I usually give the references in the beginning of the description.

2.1 SiC powder synthesis

SiC synthesis was carried out in an induction furnace. The induction furnace is basically a coil of copper wire\textsuperscript{122,123}. A powerful alternating current flows through the wire and the coil creates a rapidly reversing magnetic field that penetrates to the conducting material placed inside the coil. The high voltage electrical source from the coil induces a low voltage, high current in a conductor material. The magnetic field induces circular electric currents inside the conductor and heats it by Joule heating or magnetic hysteresis. An advantage of induction heating is that the heat is generated within the furnace's charge itself rather than heat transfer. In the beginning of my research, we worked with green body made of Si powder and graphite powder. Thanks to the conductivity of graphite, the sample could be heated up directly (volume combustion synthesis). Later,
I made some development on the synthesis of SiC powder where I used activated charcoal (see results and discussion). Charcoal is a resistive material; therefore, a redesigned furnace was needed. With my help, István Balogh designed a new furnace for the experiments and I designed a new sample holder. In the new setup, precursors were loaded into a conductive graphite crucible. The generator heats directly the graphite crucible and the heat is transferred to the sample by radiation and conduction. Samples inside the crucible are heated up to 1000 °C at 4 mins and at 5 mins 1300 °C is reached. We measured the temperature evolution by annealing of alloys with known melting points. After the reaction, the system cools down naturally. It takes 20 mins to cool down to 400 °C. At this point, the crucible was removed. The crucible and sample temperatures were measured with pyrometer after the crucible was removed.

Photograph of the operating furnace is shown in Figure 2-1. Figure 2-2 is the schematic representation of the furnace. Figure 2-3 shows the three parts of the crucible. The induction generator operates at 400 kHz and the current is varied between 0.8 A and 1.5 A. The graphite crucible is 40 mm wide and 70 mm high, the wall thickness is 5
mm, the extender is also 70 mm high (Figure 2-3).

For SiC synthesis we used Si wafer, Si powder (99%, 325 Mesh, Sigma) graphite pow-
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der (analytical grade, Reanal), and activated charcoal (Norit CA1, Sigma). In some cases, we also added PTFE to the mixture that propagates the reaction between Si and C. Because of the low decomposition temperature of PTFE (about 300 °C), a high amount of gas generated during the annealing. We designed the crucible in a way to keep most of the gases and powders inside the crucible. We used an extender to increase the volume of the crucible and it was closed with a lid. Lid contains a pinhole to avoid high pressure.

2.2 Stain etching of SiC

I applied stain etching method described in Chapter 1 for the synthesis of SiC NPs. For development of the described procedure, I run the experiments in different conditions. These experiments will be demonstrated in the Results chapter. Stain etching was performed in a 200 ml PFA (perfluoroalkoxy alkane polymer) round flask by using hydrofluoric acid and nitric acid when open system was employed. The flask was connected to a 1500 mm long PTFE tube. 300 mm parts of the tube were cooled by water.

For hydrothermal route, I used acid digestion bombs with 23 ml capacity for synthesis development experiments and another vessel with 250 ml capacity for bulk synthesis (Figure 2-4). The applied materials were hydrofluoric acid (HF) of 45%, analytical grade from VWR and nitric acid (HNO₃) of 65%, analytical grade from VWR, Sigma, or Reanal.

Figure 2-4. Berghof DAB 3 acid digestion bomb: 250 ml PTFE insert, 250°C max operating temperature, 200 bar max pressure. © berghof.com
2.3 Infrared absorption measurements

Infrared absorption spectroscopy (I refer it as FTIR) was used to study the surface properties of SiC NPs. Because SiC contains Si and C atoms and surface reconstruction should give different type of Si and C bonds on the surface. These bonds should yield signals in the infrared. The simplest reconstruction gives hydrogen terminated particles with C-H and Si-H bonds. The applied synthesis method, however, results in oxygen terminated surface with different types of carbon-oxygen and silicon-oxygen bonds (see Chapter 1 and Figure 2-5). These surface groups or functional groups are infra-active, and because of the small size of the nanoparticles, surface atoms are overrepresented making infrared spectroscopy a sensitive tool to study the surface properties. For instance, a SiC NP with 2.18 nm of diameter consists of 633 Si and C atoms as total and 321 atoms from them are at the surface, i.e., the surface to volume ratio is close to 1:1.

![Infrared absorption spectrum of SiC NPs measured on ZnSe ATR crystal. As can be seen I use absorbance spectra instead of transmittance in all FTIR plots.](image)

I applied group frequency analysis on the recorded infrared spectra in order to follow changes on the surface during surface modification reactions. Theoretical background of infrared absorption measurements can be found in many well written books and articles\textsuperscript{124-127}. Briefly, infrared spectroscopy is an absorption method in the wavelength
region of 1 to 100 µm. The energy of infrared light is often not sufficient to induce transitions between electronic states. Instead, infrared radiation excites vibrational and rotational motions of atoms in molecules. In the studied nanoparticles, the surface groups did not rotate, thus I concentrate on the vibrations in the context. The interaction of the radiation with molecules can be described in terms of a resonance condition where the specific oscillating radiation frequency matches the natural frequency of a particular normal mode of vibration. The intensity of the absorption at this resonance condition for an individual molecule is proportional to the change in the dipole moment caused by the vibration. Therefore the vibrational bands are characterized by their frequency, intensity (polar character or polarizability), and band shape (environment of bonds). The frequencies of these molecular vibrations depend on the masses of the atoms, their geometric arrangement, and the strength of their chemical bonds. The spectra provide information on molecular structure, dynamics, and environment. Two different approaches may be applied for the interpretation of FTIR spectra:

- Group theory analysis for the vibration modes of a given molecule that can reveal the allowed or weakly allowed FTIR transitions.
- Database analysis based on empirical characteristic frequencies of chemical functional groups that were already identified in previous studies.

Certain functional groups show characteristic vibrations in which only the atoms in that particular group are displaced. Since these vibrations are mechanically independent from the rest of the molecule, these group vibrations will have a characteristic frequency, which remains relatively unchanged regardless of how this group is built in. Group frequency analysis is used to reveal the presence and absence of various functional groups on the surface of SiC NPs. Further study at presented stage of research would be difficult because

- While the presence or absence of surface functional groups can be predicted from the infrared spectra, we actually measure the multitude of particles with slightly different surface terminations and size distributions of nanoparticles. These broaden the peaks and make it difficult to exactly identify the surface groups or monitor the environment sensitivity (solvent, effect of neighbor groups, particle size, etc.).
- Most of the recorded peaks lie in the region of 700-1800 cm\(^{-1}\). Most of the characteristic organic vibrations appear here that makes it difficult to unambigu-
ouisly identify the functional groups (for example, distinguish Si-O-Si, Si-O-C or C-O-C groups)

- SiC NPs consists of crystalline SiC core that is a small piece of solid. The collective motion of atoms in perfect solid results in phonons (vibration waves) that might be detected for SiC NPs by FTIR method. A detailed description on the infrared absorption of solids can be found in ref.\(^{427}\). For the cubic SiC crystal the transversal optical phonon mode is at around 800 cm\(^{-1}\) that can be detected by FTIR. Our SiC NPs may contain defects and their size is comparable with the wavelength of the IR active phonons. As a consequence, the reduced size and imperfections in SiC NPs relax the selection rules of the perfect solid that can result in forbidden modes and overtones in the FTIR spectrum. Indeed, the intensity of the IR transition associated with the typical transversal optical phonon mode of crystalline SiC is suppressed while the IR intensity of overtone modes could enhance beside the peaks associated with surface groups in the FTIR spectrum. In this context, FTIR was used to monitor the surface modification upon different treatment of SiC NPs.

Infrared measurements were carried out on drop-drying SiC nanoparticles (NPs) solutions at the surface of a ZnSe multiple internal reflection crystal and measured in attenuated total internal reflection (ATR) mode\(^{128-131}\). An ATR accessory operates by measuring the changes that occur in an internally reflected IR beam when the beam come contact with the sample. An infrared beam is directed onto a crystal with a high refractive index at a certain angle, where total reflection happens. This internal reflectance creates an evanescent wave that extends beyond the surface of the crystal into the sample (figure 2-6). In the regions of the spectrum where sample has absorbance, the evanescent wave will be attenuated. The detector records the attenuated beam as an interferogram, which can then be used to generate an infrared spectrum. This technique generally described as a surface sensitive infrared measurement because evanescent wave penetrates only hundreds of nm or a few micrometers to bulk material. However, we used that to measure nanoparticles with 1-4 nm of diameter. That means, in our situation evanescence wave penetrates through a bunch of nanoparticles and ATR spectra shall be equal to conventional infrared absorption spectra (figure 2-6). Indeed, Zsolt Szekrényes and I developed this technique by measuring SiC NPs in KBr pellet, drop drying on Si wafer, and ATR crystal and we saw no differences between the final spec-
tra recorded in these various conditions. SiC NPs in aqueous solution can be hardly measured in KBr pellet, thus I rather carried out ATR measurements on our samples.

![Figure 2-6. Schematic representation of an ATR crystal (orange) and the total reflection of the infrared light (red). In the case of total reflection, a small part of the light goes through the crystal (evanescence wave – black at the top) and can penetrate to the sample (green). In the energy region, where the sample can absorb infrared light, the light is attenuated.](image)

**Measurement**

I used Bruker Tensor 37 with 4 cm⁻¹ resolution and DTGS (deuterated triglycerine sulfate) detector. Spectra were recorded in the 700–4000 cm⁻¹ range due to the multiple internal reflections; the multiphonon modes of ZnSe crystal absorb IR light below 700 cm⁻¹. The baseline was corrected by an adjusted polynomial function.

**2.4 UV-VIS and Photoluminescence Measurements**

Luminescence is the spontaneous emission of optical photons from an excited electronic state to the ground state. Photoluminescence process starts with absorption of photons and continues with subsequent emission of light. Absorption processes separates an electron and a hole that build up a state with short lifetime that relaxes back to the ground state. This can proceed in either radiatively or non-radiatively. Radiative decay is called luminescence.

The probability of a molecule changing its state by absorption or emission of a photon depends on the nature of the wavefunctions of the initial and final states. The probability of a transition occurring is described by the optical dipole transition strength. As a first approximation, the optical dipole transition strength is governed by selection rules at a given symmetry of the molecule or solid that determines whether a transition is allowed or forbidden. In the classical theory of light absorption, matter consists of an array of charges that can be set into motion by the oscillating electromagnetic field of the light. The electric dipole oscillators set in motion by the light field have specific natural characteristics. When the frequency of the radiation is near the oscillator frequency, absorption occurs, and the intensity of the radiation decreases on passing through the
substance. The intensity of the interaction is known as the oscillator strength, and it can be thought of as characterizing the number of electrons per molecule that oscillate with the characteristic frequency.

The quantum mechanical description is based on time-dependent perturbation theory\textsuperscript{127,134}. Transition from one state to another occurs when the radiation field connects the two states. In quantum mechanics, the connection is described by the transition dipole moment, $\mu_{GE}$ (12)

$$\mu_{GE} = \int \psi_G \mu \psi_E d\theta$$

where $\psi_G$ and $\psi_E$ refers to the wavefunction of the ground and excited state, respectively, and $\mu$ is the quantum mechanical operator of the electrical dipole moment. If the transition dipole moment is nonzero then absorption occurs.

For relatively large fluorophores containing more than 30 atoms, such as the organic dye molecules or quantum dots\textsuperscript{135} many normal vibrations of differing frequencies are coupled to the electronic transition. This results in a quasicontinuum of states superimposed on every electronic level. Vibrational levels and wavefunctions are those of quantum harmonic oscillators. At room temperature the molecule generally starts from the $\nu=0$ vibrational level of the ground electronic state as the vibrational energy will normally be $1000$–$3000$ cm$^{-1}$, many times the thermal energy $kT$ ($k$ is the Boltzmann-factor, $T$ is the temperature), which is about $200$ cm$^{-1}$ at room temperature. Upon absorption of a photon of the necessary energy, the molecule makes a vertical transition to the excited electronic state. The occurrence of vertical transitions on the potential energy curve is explained by the Franck–Condon principle within the Born–Oppenheimer approximation that describes electronic motions as if the nuclei were fixed in place viewed from the perspective of the nuclear coordinates. The quantum mechanical formulation of this principle is that the intensity of a vibrational transition is proportional to the square of the overlap integral between the vibrational wavefunctions of the two states that are involved in the transitions. This overlap integral will define the shape of absorption and the width of the absorption peak. If the optical excitation leads to a large change in the position of the atoms (large electron-vibration coupling), then the resulted absorption peak associated with a single electronic transition can be very broad even at cryogenic temperatures.
Dependent on their fluorescence quantum yield the electron can decay to the electronic ground state via photon emission from the electronic excited state. The Franck–Condon principles are applied equally to absorption and to fluorescence. Kasha’s rule states that emission will occur from the lowest lying electronic excited state. The applicability of the Franck–Condon principle in both absorption and emission, along with Kasha’s rule, leads to the mirror symmetry of the absorption and the fluorescence spectrum of typical organic dye molecules, as the energy gaps between electronic excited states are sufficiently large to selectively excite only the lowest electronic excited state. Owing to the loss of vibrational excitation energy during the excitation/emission cycle, fluorescence emission induced by one-photon absorption always occurs at lower energy, that is, spectrally red-shifted (Stokes shift). This phenomenon is not valid for semiconductors with optical transitions between continuous bands. Optical absorption and emission characteristics of semiconductor materials are affected by the state of electrons and holes whose distribution is governed by Fermi-Dirac statistics. Therefore, the absorption and emission characteristics of semiconductors differ in an essential way from that of molecular (Boltzmann) systems. In general, the absorption coefficient of semiconductors depends on photon energy. Higher the photon energy, higher the absorption coefficient is, however, excitons with higher energy than the band gap quickly relax to the band edges (in the case of pure semiconductors). The manifestation of such phenomena is that organic dyes usually can be excited only in a short region of wavelength, while

![Figure 2-7. Schematic representation of absorption and emission spectra of luminescence dye, and semiconductor quantum dot.](image-url)
the absorption intensity of semiconductors continuously increases after a certain energy
threshold. Similar feature can be detected for semiconductor quantum dots (see QD ab-
sorption in Figure 2-7) where the crystalline core produces quasi-continuous bands sim-
ilar to solids.

In my studies, steady state emission spectra were recorded on SiC NPs solution using
Xe lamp as a continuous light source by varying the excitation wavelength between
300 nm and 500 nm. Even though, the absorption of SiC NPs also increases with the
energy of the absorbed light, our light source has very low intensity with wavelength
below 300 nm, therefore, excitation with wavelength below 300 nm is not shown in my
dissertation.

Beside steady state emission spectroscopy, I used time resolved emission spectrosc-
ropy\(^{132}\), a method that is based on luminescence lifetime measurements, for describing
the emission mechanism of SiC NPs. Time-resolved data often provide information
that is not available from the steady-state data.

Luminescence emission can be described as a random process, and lifetime is an aver-
age value of the time spent in the excited state. When a fluorophore is excited with an
infinitely sharp pulse of light, an initial population \((n_0)\) of fluorophores excited. The
excited-state population decays with a rate \(\Gamma + k_{nr}\) according to

\[
\frac{dn(t)}{dt} = (\Gamma + k_{nr})
\]  

(13)

where \(n(t)\) is the number of excited molecules at time \(t\) following excitation, \(\Gamma\) is the
emissive rate, and \(k_{nr}\) is the nonradiative decay rate. Because emission is a random
event, each excited fluorophore has the same probability of emitting in a given periods
of time. This results in an exponential decay of the excited state population,

\[
n(t) = n_0 e^{(-t/\tau)}
\]  

(14)

In a luminescence experiment we do not observe the number of excited molecules but
only the fluorescence intensity, which is proportional to \(n(t)\). Integration of eq. 13 with
the intensity substituted for the number of molecules yields the expression for a single
exponential decay:
\[ I(t) = I_0 e^{-\frac{t}{\tau}} \tag{15} \]

where \( I_0 \) is the intensity at the initial time. The lifetime \( \tau \) is the inverse of the total decay rate and

\[ \tau = (\Gamma + k_{nr})^{-1} \tag{16} \]

In general, the inverse of the lifetime is the sum of the rates, which depopulate the excited state. The fluorescence lifetime can be determined from the slope of a plot of \( \log I(t) \) vs. \( t \), but more commonly by fitting the data to decay models.

Two methods of measuring time-resolved fluorescence are in widespread use: the time-domain and frequency-domain methods. In time-domain method, the sample is excited with a short light pulse. The time dependent intensity is measured following the excitation pulse, and the decay time is calculated from the slope of a plot of \( \log I(t) \) versus \( t \), or from the time at which the intensity decreases to \( 1/e \) of the intensity at \( t = 0 \), the initial time. I should mention here, that the intensity decays are often measured through a polarizer oriented at 54.7° from the vertical \( z \)-axis. This condition is used to avoid the effects of rotational diffusion or anisotropy on the intensity decay. In my study, we did not apply angle oriented polarizer, however, we did apply magic angle oriented polarizers in simple lifetime measurements and we found that the polarizer has some effect to the measured lifetimes but the difference between the detected average lifetime with and without polarizer was about 3%. The size of the SiC NPs is in the range of small proteins that is much larger than most of the organic fluorophores, therefore, diffusion and rotation does not affect the short emission lifetime.

Another method to measure the decay time is the frequency domain method. In this case, the sample is excited with intensity-modulated light. The intensity of the light is varied at a high frequency, so its frequency is comparable to the reciprocal of decay time. When a sample is excited in this manner the emission is forced to respond at the same modulation frequency. The lifetime of the fluorophore causes the emission to be delayed in time relative to the excitation. This delay is measured as a phase shift, which can be used to calculate the decay time.
We used time domain method connected with time correlated single photon counting (TD-TCSPC) and I describe only this method further.

**Time correlated single photon measurement**

Instruments for time correlated single photon measurements use high repetition rate mode-locked picosecond or femtosecond light sources, and high-speed microchannel plate photomultiplier tubes. The principle of TCSPC is based on single photon counting. The system is adjusted to emit only one photon during excitation and measures the time between excitation and the observed incoming photon. The conditions of the experiments are adjusted so that less than one photon is detected per laser pulse (typically 1 photon/100 excitation pulses). The experiment starts with the excitation pulse that excites the samples and sends a signal to the electronics. This signal is passed through a constant function discriminator, which accurately measures the arrival time of the pulse. This signal is passed to a time-to-amplitude converter, which generates a voltage ramp where the voltage increases linearly with time on the nanosecond timescale. A second channel detects the pulse from the single photon. The arrival time of the signal is accurately determined using a constant function discriminator, which sends a signal to stop the voltage ramp. The time-to-amplitude converter now contains a voltage proportional to the time delay (Δt) between the excitation and emission signals. The voltage is converted to a digital value that is stored as a single event with the measured time delay. A histogram of the decay is measured by repeating this process numerous times with a pulsed-light source.

**Timer resolved emission spectroscopy**

Time resolved emission spectra (TRES) are ideally the measured emission spectrum of the system at a given time following a pulsed excitation\textsuperscript{132,137} that are recorded in a series of instant times within a certain period. This measurement technique is able to provide additional information about the nature of the emitters with respect to the steady-state spectra. SiC NPs in solution yield complicated PL spectra due to the following reasons: i) several processes compete in the excited state of the emitters (solvent relaxation, dissociation, conformational changes, etc.) and those are able to change the emission wavelength and/or decay time of SiC NPs; ii) multiple emitters in a solution could exhibit overlapping spectra. Both can result in change in the shape of the spectra over the time.
One example of using TRES is to unravel the number of individual fluorophores in the studied system. When TRES normalized to the same total area, spectral shift provides information about the system. The number of isoemissive points (where spectra cross each other) defines the number of emission centers in the studied system: \( N = \pi_{ie} + 1 \) where \( N \) is the number of fluorophores and \( \pi_{ie} \) is the number of isoemissive points; while a continuous shift reveals a relaxation process – or multiple emission points in the system.

**Decay associated spectra**

From the time resolved data, one can construct the decay associated spectra (DAS) as well with the following equation\textsuperscript{132,137}

\[
I(\lambda, t) = \sum_{i=1}^{N} \alpha_i(\lambda)e^{-\frac{t}{\tau_i}}
\]  

(17)

Where \( \lambda \) is the emission wavelength and \( \alpha_i \) is the decay associated spectra. DAS usually corresponds to the emission spectra of the individual components. This is only true for fluorophores with a single exponential decay. For example, in the case of time-dependent spectral relaxation, DAS can be positive or negative, and hence it does not correspond to the emission spectra of any particular component. However, this is the simplest kinetic scheme where every component decays independently resulting in decay associated spectra.

I will show that SiC NPs have multiexponential decay. Still, I applied DAS for global analysis of aqueous SiC NPs. It would be neat to test a more complicated scheme like a combination of the parallel and sequential model, and involve branching, back-reactions or multiple compartment excitation. In this case a so-called linear time-invariant compartmental model can be used, which allows much more flexibility in modeling data. However, the danger lies exactly in this flexibility. One very important aspect of using compartmental models is that different compartmental schemes can result in the same model output, rendering the system structurally unidentifiable, thus such models should be applied with great caution. Structural unidentifiability is caused by incomplete information on the system, which is exactly the case of colloid SiC NPs.

The parameters of the employed equipment are as follows:
Fabrication and characterization of silicon carbide nanoclusters

- UV-VIS spectrometer: Ocean Optics-QE65000 (wavelength range: from 200 to 950 nm)
- PL spectrometer: Horiba Jobin-Yvon Fluorolog-3 450 W Xe light source (exc.: 240nm - 850 nm); PMT detector: from 190 nm to 860 nm
- In both measurements, quartz quette with 1 cm path length was used.
- For time resolved measurement we used NanoLed LED laser source with 321 nm peak wavelength and 0.8 ns pulse width.

2.5 Electron microscopy

Electron microscopes work just like optical microscopes as a first approximation but they use a beam of accelerated electrons as a source of illumination\textsuperscript{138,139}. As the wavelength of an electron can be as short as 0.002 nm (200 keV acceleration), the resolution is greatly enhanced compared to that of conventional optical microscopes. Electron microscope techniques can yield information about the topography, morphology, composition and crystallographic information.

The basic steps involved in all electron microscopes are the following: A stream of electrons is formed in high vacuum by electron guns. This stream is accelerated towards the sample.

![Figure 2-8. Interactions between electron beam and sample. Interactions noted on the top side of the diagram are utilized in scanning electron microscopy (SEM) operation while those on the bottom side are recorded and analyzed in transmission electron microscopy (TEM) operation.](image)
specimen with a positive electrical potential while is confined and focused using apertures and magnetic lenses into a thin, focused, monochromatic beam. The sample is irradiated by the beam and interactions occur inside the irradiated sample affecting the electron beam. These interactions and effects are detected and transformed into an image. When an electron beam interacts with the atoms in a sample, individual incident electrons undergo either elastic or inelastic scattering. In the former, only the trajectory changes and the kinetic energy and velocity remain constant. In the latter, some incident electrons will actually collide with the sample and displace electrons from their electron shell. This specimen interaction makes electron microscopy a feasible analyzing tool. In figure 2-8 I noted the most common interactions between electrons and the material. The (inelastic) interactions noted on the top side of the diagram are utilized in scanning electron microscopy (SEM) operation while those on the bottom side are recorded and analyzed in transmission electron microscopy (TEM) operation.

I used SEM for visualizing SiC particles after synthesis and I used TEM or atomic force microscopy (AFM) images for analyzing size distribution of the prepared SiC NPs. For the analysis of small SiC nanoparticles, the most common methods for imaging in the TEM are bright-field, dark-field, and phase-contrast imaging. At large magnifications, phase-contrast imaging is commonly referred to as high-resolution electron microscopy (HR-EM or HR-TEM)\(^ {18(139)} \).

A drawback with decreasing the particle size of the crystal is that small nanoparticles tend to become less stable upon exposure to the electron beam. Instabilities may arise from particle motion, structural fluctuations, atom sputtering, coalescence, and particle destruction or decomposition. To test the stability of our samples, we recorded images of our samples by HR-TEM, and compared them as a function of physical, structural, and positional changes over time. We found that the smallest SiC NPs tend to destruct over 200 kV acceleration voltage, however, the highest applied acceleration energy (200 keV) is suitable for measurements.

For image analysis I used Gwyddion software. The advantage of software assisted methods is that each particle is scrutinized and measured, the signal-to-noise requirement is less stringent, and the analysis is straightforward. It is critical, however, that a consistent measurement method should be employed. Significant drawbacks of manual measurements include user biases and limited sampling statistics because only a few hundred particles can be measured within reasonable time.
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Beside statistics, discrepancy in the image size and the physical size of nanoparticles is another important factor. The discrepancy between the image size and physical size of a single particle can be described as

\[ X_i = X + \varepsilon \]  

(18)

where \( X_i \) is the measured size, \( X \) is the real physical, but unknown size and \( \varepsilon \) is the associated error. The contributions to \( \varepsilon \) include the pixel resolution, the determination of the particle-substrate boundary, the magnification calibration, and image distortions due to stage drift, improper focus conditions, delocalization due to spherical aberration, and various sources of astigmatism (objective lens, condenser lens, coma, etc.).

The size distribution is typically expressed by a Gaussian or log-normal function, characterized by the mean and the standard deviation. For small particles, the value of the mean and standard deviation are very sensitive to the choice of imaging and analysis conditions, and the results obtained by this analysis can result in a larger intrinsic variability in the particle sizes than the physical intrinsic variability. Two significant factors that contribute to uncertainty in both the mean and the standard deviation are the pixel resolution and the bias associated with the determination of the particle edge at coarse magnification. Image resolution should be considered with caution. I used images with 2024×2024 resolutions with a covered area of 47×47 nm. Therefore, the image pixel length is 0.023 nm. However, the best point-to-point resolution can be achieved with the used instrument is 0.17 nm. It means that at the measured diameter of a 5.00 nm particle the deviation is estimated to be about 5% while the 1.0 nm sized image of a nanoparticle this deviation might reach 25%. Since I prepare nanoparticles in this size range with the tendency of destruction of the smallest nanoparticles, reporting size distribution in common formats would be inaccurate. Therefore, I usually refer size distribution with the boundary of the measured population in the context. For accurate representation of the size distribution I applied standard protocols suggestions and I measured at least 300 particles for every sample (usually 500-600 particles). The SiC NPs usually show closely spherical shape with small deviations. I chose the longest diameter as the physical diameter of the SiC NPs.

Equipment: JEOL JEM-3010 HR-TEM with up to 300 kV acceleration.
2.6 Atomic force microscopy

AFM provides a 3D profile of the surface on a nanoscale, by measuring forces between a sharp probe and surface at very short distance\textsuperscript{141}. The probe is placed at the end of a cantilever, which can bend. The motion of the probe across the surface is controlled by the use of feedback loop and piezoelectronic scanners. The deflection of the probe is typically measured by a beam bounce method. A laser is bounced off the rear of the cantilever onto a position sensitive photodiode detector. The measured cantilever deflections are used to generate a map of the surface topography.

The radius of an AFM tip that approximated with a sphere, was R=20 nm in the measurements, much larger than particles I wanted to detect causing inappropriate recorded shape of the nanoparticle. Indeed, the tip size and its geometry lead to a broadening of the lateral dimensions of the nanoparticle imaged by AFM and their real diameter can be hardly measured accurately in the surface plane, but, in the case of spherical NPs, a reliable method for determining the size of NPs is to measure the height of the particles\textsuperscript{142}. A certain precautions must be taken in order to avoid the measurement error and minimize the uncertainties. First of all, nanoparticles have to be correctly dispersed and immobilized on a flat substrate. A minimal distance is required (mean NP size + tip size) between NPs to obtain a complete image on the individual NPs. Two points are then needed to measure precisely the height of a nano-object. The first data point corresponds to local maximum on the nanoparticle, the second one is the mean height of the surface topography. The height of the particle is calculated as the difference of both data. Furthermore, a second problem arises concerning the substrate roughness. In fact, a non-homogeneous roughness will introduce an error and the real height of the NP cannot be accurately determined. As a result, the substrate roughness is a key parameter.

For size distribution characterization by AFM I used silicon wafer with a roughness of about 0.5 nm. The samples were put to the surface by drop casting method: a drop of SiC NPs solution placed on the Si surface and then removed after a certain amount of time. Both the concentration of the solution and the activation time are optimized for each sample, in order to maximize the signal to noise ratio. Complete drying could lead to aggregation and causes artifacts while sorption from solution usually underestimates the particle sizes.

Equipment: Neaspec NeaSNOM AFM
3 RESULTS AND DISCUSSION

We began our research with a promising goal in the Wigner Research Centre for Physics that we will be able to prepare SiC nanoparticles with size below 5 nm by combining the theoretical knowledge in the group of Ádám Gali with further experimental developments that will exhibit red or infrared emission. This would significantly improve the current state of bioimaging application. When I joined to the Semiconductor Nanostructures Group, some of the conditions on the feasible preparation processes were set by the existing equipment and laboratorial facilities, and previous experiments:

1. It was already demonstrated that it is possible to synthesize micron size SiC crystals from its elements using induction furnace. We shall use this technique for the source of nanomaterials.
2. Because we do not expect that small nanoparticles with desired size can be directly produced in an induction furnace, I had to find or develop a suitable top-down method.
3. The top-down method should be based on wet chemistry or oxidation.

These conditions implicated stain etching for the choice of top-down method that was already employed by others to prepare SiC nanoparticles. We thought that the combination of rapid SiC synthesis and a simple etching method is a promising route for realization of a new type of fluorescent probes based on SiC because

1. The synthesis of SiC in an induction chamber is a rapid combustion synthesis where the material is far from the equilibrium condition, therefore, introduction
of defects with desired photoemission properties with high concentration is possible.

2. The properties of SiC is readily variable that could improve the quality of nano-crystals made from them.

3. The available high purity source materials guarantee the proper characterization.

3.1 Improvement in the synthesis of SiC nanoparticles

Based on the afore-mentioned facts, the first task for me was to develop a synthesis route for SiC nanoparticles and we quickly found that the reported protocol\textsuperscript{87} gives poor quality therefore an improvement is needed. The size distribution of the particles was very broad (1-15 nm). To make samples that contain particles with size below 5 nm only, I further developed both the stain etching process and the synthesis of SiC powder.

Development on SiC NPs synthesis

Briefly, stain etching made under the following condition: HNO$_3$:HF with a volume ratio of 1:3 at 100 °C for 1 h was used to etch SiC powder produced at our laboratory. After removing the acids and washing the samples, the SiC NPs were obtained by sonication of the porous SiC macro-crystals in water for 40 minutes to remove the porous layer and suspend the NPs. At first, the decanted liquid, that contains the colloidal SiC NPs, was obtained without any centrifugation or other separation technique\textsuperscript{143}.

In the original method the mixture of SiC powder, HF and HNO$_3$ was heated up in an open system like in a round flask made from fluorinated polymer. This method limits the maximum temperature that can be reached because of the boiling point of the mixture (which is about 110°C) based on the boiling point of hydrofluoric acid (108°C) and nitric acid (122°C). It is worthwhile to mention that despite careful construction of the reactor, the release of such toxic and corrosive vapors to the fume hood cannot be completely eliminated. Therefore, I transferred this reaction to a closed acid digestion system that can be heated up to 250 °C, and acids contact with the environment only at ambient temperature for a limited time\textsuperscript{144}.

To compare the efficiency of the open and closed reaction conditions I prepared samples with the same conditions except that one sample was produced at open condition and the other at closed condition. 2.0 g clean SiC powder and 10 ml HF:HNO$_3$=3:1 mixture was placed into a perfluoroalkoxy (PFA) flask (20 ml) with 5-mm aperture that
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was connected to a reflux column and heated in a 120 °C oil bath (open), or in a 23 ml Teflon-lined acid digestion vessel and annealed at 120 °C for 2 h. Then the acid was decanted after centrifugation and SiC was washed with distilled water five times and dried at 80 °C overnight. The product is porous SiC with thin porous layer. To produce SiC QDs, acid-treated samples were sonicated in 30 ml water for an hour and centrifuged at 4000 rpm for 1.5 h. The top 20 ml of the supernatant was removed and used for further characterization. The pellet was washed with water 10 times and dried at 80 °C.

To determine the superiority of the closed system I made several measurements on the SiC powder that still existed after treatments and on the colloid nanoparticle solution. The measurements were the follows:

1. Weight loss during the etching – determines the dissolution yield during the etching (anything that lost here was in the acidic solution and will not become nanoparticle)
2. Weight loss during ultrasonication – Theoretically determine the mass of the porous layer.
3. Total mass of SiC nanoparticles suspended in water – This is the yield, that is equal to the total dry matter content of the removed 20 ml colloid.
4. Size distribution – shows if there are differences in the pore structures between the two methods.
5. Photoluminescence intensity – indirect determination of the yield.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Open system</th>
<th>Closed system</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss during etching</td>
<td>0.100 g</td>
<td>0.101 g</td>
</tr>
<tr>
<td>Weight loss during sonication</td>
<td>4.1 mg</td>
<td>3.8 mg</td>
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<td>Total mass of NPs</td>
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<tr>
<td>Average size</td>
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<td>3.1 nm</td>
</tr>
<tr>
<td>PL Intensity (a.u.)</td>
<td>5×10⁴</td>
<td>1.5×10⁵</td>
</tr>
</tbody>
</table>
As can be seen in Table 3-1, the properties of the final nanoparticles improved. While I measured the same loss during the etching reaction, closed reaction produces more particles with smaller sizes (I used TEM images for size distribution analysis). While the total mass of the particles in solution increased by 1.75 times, the PL intensity is increased by 3 times. This can be explained with the differences in size distribution. Figure 3-1 shows the size distribution of such samples while Figure 3-2 shows photoluminescence emission at 340 nm excitation.

The wider temperature range available in the closed condition compared to that in open condition allowed us to optimize the reaction parameters in closed condition experiments. First, I studied the temperature dependence in the range of 80-200°C. 2 g of SiC powder was placed in a 23 ml PTFE acid digestion vessel and annealed for 2 hours in an oven. Samples annealed at 150°C or higher suffer exactly the same mass loss, and the masses of the produced nanoparticles are also the same. In order to study the effect of reaction time, I prepared samples that were digested for 24 hours. In that case, the
weight loss was only twice as I measured for 2h reaction time but the mass of the produced nanoparticles was the same. All of these facts implied to me that neither the temperature nor the reaction time affect greatly the product yield. The optimal temperature for annealing is 150°C and the reaction time is 2 hours.

Some speculations about the stain etching reaction
I already mentioned that the mechanism of Si dissolution and pore formation had been in the center of discussion between several qualified researchers for decades and SiC is even a more complex system. In our research, we are focusing on the optical properties of SiC NPs and surface modification reactions. The detailed study of pore formation mechanism is beyond our research. Nevertheless, I made observations during the experiments that may explain why the closed condition process is superior over the open condition process.

In a closed system, neither the acid vapors nor gas phase products can escape during the reaction while high pressure is formed inside the reactor. In the reaction, two gas phase products form, according to the reported chemical reaction, namely, carbon dioxide and hydrogen (Eq. 11):

![Figure 3-2. PL intensity differences of NPs made under open and closed conditions.](image-url)
Both components have very low solubility in acids even at high temperature and ambient pressure. Thus, they can induce bubble formation on the SiC surface. These bubbles mask the SiC surface and most likely staunch the formed pores. The higher pressure increases the solubility of gases and the diffusion of the bubbles away from the surface takes place more easily. The generation of relatively small pores during etching is possible in this way, which may lead to a narrower size distribution. Deeper understanding of wet etching of SiC with HF/HNO₃ may come from the studies of isotropic etching of silicon using the same mixture. The HF/HNO₃ etching system is one of the most widely used isotropic etchants for silicon, but reduction of nitrogen during the reaction shows very complex chemistry. Actually, nitrogen was found all of its oxidations states\textsuperscript{145}. Indeed stain etching can produces several different nitrous compounds, and some of them are gases and they can escape from the reaction mixture. However, in the closed system these products stay in the mixture and can react further. An example is nitric oxide (NO) which has low solubility in water\textsuperscript{146} and it is a free radical, which can participate in oxidation and reduction reaction as well\textsuperscript{147–150}. The evolution of dark brown gases that are always associated with the presence of NO₂ is clearly visible both in the open and closed systems. After the vessel is opened, a slow evolution of brown gas can be observed, and it takes several minutes to stop (closed condition). Additionally, when a scrubber was placed at the end of the condenser (open condition), instead of a constant bubbling, water was sucked inside the tube periodically as a sign of pressure drop. Pressure drop in the system can be due to a rapid cooling or due to a reaction between two molecules in the gas phase reducing the pressure. Because the reaction was immersed in a hot oil bath and such endotherm reaction is not likely to take place in the system, I speculate that nitric oxide is a main final product in the stain etching of SiC that reacts rapidly with oxygen to produce NO₂. Similar results were reported about stain etching of Si\textsuperscript{151} where the evolution of NO₂ was hinted as a final product of several reactions where NO is formed:

\begin{align}
HNO₃ + 2H^+ & \rightarrow HNO₂ + H₂O + 2h^+ \quad (18) \\
3HNO₂ & \rightarrow HNO₃ + 2NO + H₂O \quad (19) \\
NO + H^+ & \rightarrow e^- \rightarrow HNO \quad (20) \\
2HNO & \rightarrow H₂N₂O₂ \rightarrow N₂O + H₂O \quad (21)
\end{align}
Finally,

\[ 2NO + O_2 \rightarrow 2NO_2 \]  \hspace{1cm} (21)

To test my hypothesis that one of the main gas products is NO, I opened an acid digestion vessel after the reaction under nitrogen flow, NO\(_2\) was not detected. I conclude that a certain amount of NO is formed during the reaction which escapes slowly from the acid and reacts with oxygen in the air. This result does not provide clear understanding of pore formation during stain etching of SiC, but demonstrates that Eq. 11 should be revised.

**Development on the synthesis of SiC source**

Whereas closed reactor process significantly improved the quality of our SiC nanoparticles (NPs), it is a bit surprising that we were not able to make further improvement with temperature and time variations. As I mentioned in the introduction, pore formation and pore propagation is a very complex mechanism. When a certain wall thickness is reached, dissolution becomes very slow because of the quantum confinement that determines the band bending. With stain etching the thickness of the porous fraction usually goes through a maximum during in time because either further dissolution removes the top layer, like the case of Si, or the dissolution is stopped by the very limited diffusivity of reactants in the pore.

Because the thickness of the porous layer cannot be increased with longer reaction time, a possible way to produce more nanocrystals is the increase of the surface area of the source. Therefore, I modified the original SiC synthesis, in order to achieve higher porosity. Based on the literature reports (see Chapter 1 for synthesis of SiC powder ), I made the following changes:

1. I changed graphite powder to activated charcoal.
2. I added PTFE to the reaction mixture.
3. I shortened the annealing time.
4. I redesigned the furnace geometry and designed a graphite crucible for the new reaction.

SiC firstly was produced as follows: Silicon and graphite powders were mixed with a molar ratio of 1:1.2 in an alumina mortal and pressed into a pellet, then placed into an induction chamber and heated under argon to about 1300 °C where the reaction began.
Results and Discussion

In this case, heating is possible due to the conductivity of graphite. When Si and C reacted to make SiC, pellet lost its conductivity, therefore annealing stopped. The residual graphite was removed by annealing the sample at 800 °C for 10 h under air, and the residual Si was eliminated by using HF:HNO₃:H₂O=1:1:10. According to scanning electron microscope (SEM) measurements, micron size SiC grains formed with low porosity (Figure 3-3). It is easy to determine from the literature that the production of SiC particles can be improved. SiC produced with combustion synthesis usually conserve the morphology of the graphite source. Therefore, activated charcoal with high surface area was rather chosen as a carbon source. I realized that the mixture of charcoal and Si powder cannot be pressed into a pellet, or even if I was able to make green body with desirable stability, the resistivity of such samples obstructed the direct annealing in an induction furnace. István Balogh and myself redesigned the furnace for our new samples. In the new system, the mixture is annealed in a graphite crucible. I designed a crucible that consists of three parts: a conventional crucible with proper geometry except that one can screw another tube onto the top of the crucible to increase the lengths but keeping the loading and unloading easy. On the top of this system a lid with a small hole can be screwed. These systems give us confident security during the experiments (see Figure 2-3). Even though, the reaction between Si and C is barely exothermic, we wanted to avoid that any dust can go outside the crucible. It is very important when PTFE is added which is reported to propagate the reaction but also decompose over 300 °C.

I ran experiments with the mixture of Si and charcoal (2.5g) and 0.2 g PTFE powder with different annealing time, by holding the current at 1.1 A. I wanted to define only the reaction time needed to initiate the reaction. Longer reaction time makes too large crystals while shorter reaction time produce low quality SiC crystal. It is found that 8-minutes reaction time is needed to initiate the reaction and after 16 minutes the total mixture transformed to SiC. This result was obtained by measuring the weight before and after annealing in air, and before and after acidic treatment. 8 min reaction time gives 80 % yield with high surface area while 16 min gives crystals with low surface area. The differences in porosity between SiC made from graphite source (Figure 3-3) and SiC made from charcoal (Figure 3-4, Figure 3-5) can be seen on the following SEM and transmission electron microscope (TEM) images.
Fabrication and characterization of silicon carbide nanoclusters

Figure 3-3. SEM images of SiC particles made from Si and graphite powder

Figure 3-4 SEM image of SiC made from Si and activated charcoal

Figure 3-5. TEM image of SiC made from Si and activated charcoal
Comparing those samples made from graphite and made from charcoal and PTFE, higher porosity is evident. We did not make records about samples that were produced by 16 min annealing time. Those crystals can be seen with a naked eye. I studied whether these highly porous SiC crystals could improve the synthesis of SiC NPs. I prepared SiC nanoparticles in the closed system at 120 °C with 2 h reaction time. The weight loss after etching was 0.8 g, about 50%; the mass of synthesized nanoparticles was 65 mg when the starting material was the SiC powder with high surface area. This result represents about 20 times improvement over the samples achieved with SiC powders made from graphite source. That means the final solutions had 3.25 mg/ml concentration. In addition, we were able to reduce the size distribution of SiC NPs even further (compare Figure 3-1 with Figure 3-6).

![Figure 3-6. Size distribution of SiC NPs made from SiC with high surface area. Size distribution was measured by analyzing TEM images.](image)

**Claim of contribution**

In the experiments above, I

- synthesized the SiC NPs both in closed and open reactor. I optimized the synthesis process by running the described experiments;
• made the SiC powder source for the synthesis of SiC NPs and ran experiments for optimization;

• measured the size distribution by measuring the diameters of the NPs on several TEM images recorded by Zsolt Czigány (H.A.S. EK MFA);

• characterized the XRD diffractograms to identify if the product is 3C-SiC recorded by Lajos Károly Varga (H.A.S. Wigner RCP) and Gábor Bortel (H.A.S. Wigner RCP); XRD used to identify the purity and crystal structure of SiC powders such data was not showed here;

• characterized the Raman spectra recorded by Miklós Veres (H.A.S. Wigner RCP). Raman spectra were used also to identify the polytype of SiC powders and follow the cleaning process by tracking the elimination of Si and C peaks from the spectra.

• Measured and characterized the optical properties of the samples (UV-VIS, PL, FTIR)

István Balogh and I

• operated the induction furnace;

• designed the new furnace.

3.2 Synthesis of different surface terminated SiC NPs

We expected from theoretical calculations, made by our group, that surface termination influences the optical properties of SiC NPs. To study such effect I synthesized SiC NPs with different surface terminations. As-prepared SiC NPs of diameter between 1-4 nm are terminated with a variety of oxygen-containing species with high concentration of carboxyl groups. I label here such samples as ‘as-prepared’. For the preparation of -OH terminated SiC NPs as-prepared SiC NPs were reduced by NaBH₄ in aqueous solution (‘BH₄⁻ reduced’). Hydrogen terminated SiC NPs were fabricated by reducing as-prepared samples dispersed in HCl by dissolving Zn powder (‘Zn/H⁺ reduced’). The oxidized sample (‘reoxidized’) was created by 2-hour illumination of the hydrogenated SiC NP sample with 320 nm wavelength. Oxidation of Zn/H⁺ reduced SiC NPs was a little bit unexpected because of the known stability of SiC. The conversion degree was studied by FTIR and steady-state PL spectroscopy. FTIR spectra of samples with different surface termination are shown in Figure 3-7. As can be seen, borohydride re-
duces carboxyl groups under applied conditions: peak at ~1700 cm\(^{-1}\) correspond to the carboxylic group is disappeared. Whereas this reducing agent is known for its selectivity to carbonyls, in aqueous media, BH\(_4^-\) reacts with water to form hydrogen that can enhance the reduction capacity.

Figure 3-7. FTIR spectra of SiC NPs with different surface terminations

Zn/H\(^+\) reduced and reoxidized SiC NPs with size distribution of 5-30 nm are shown in Figure 3-8. This fraction of SiC NPs has the same surface properties as smaller (1-4 nm) NPs\(^{153}\) but can be purified from the reactant. The broad peak at 900-1200 cm\(^{-1}\) attributed to the asymmetric stretching and bending modes of Si-O-Si, C-O-C, Si-O-C and Si-OH bands is eliminated by the Zn/H\(^+\) reduction and is shifted to lower wavenumbers after reoxidation, confirming that the distribution and composition of these
groups at the SiC NP surface is different. Vibrations of C-O-C and Si-O-C bonds usually appear at higher wavenumbers than those of Si-O-Si bonds while oxygen deficiency in SiO₂ also shifts this type of vibration bands to lower wavenumbers. Reduction and reoxidation cause changes in the region of 3000-4000 cm⁻¹ too. The as-prepared sample shows a strong and broad peak at around 3300 cm⁻¹ because of the strongly hydrogen-bonded OH groups on the surface and hydrogen-bonded water molecules. Complete reduction removes the strong H-bonds, leaving only non-bonded OH groups behind (IR bands above 3600 cm⁻¹). In the reoxidized sample, the OH vibrational modes shift to lower wavenumbers and the OH band becomes broader, due to strongly H-bonded OH groups partially formed on the developed oxide. In conclusion, after the Zn/H⁺ reduction most of the carbon and oxygen groups were eliminated from the surface and reoxidation enriched the surface with Si – O bonds.

![Figure 3-8 FTIR spectra of as prepared, Zn/H⁺ reduced and reoxidized SiC NPs](image)

**Claim of contribution**

In these experiments I made all of the described experiments and measurements.

**3.3 Titrimetric investigation of surface groups**

The emission of SiC NPs shows pH dependency which was associated with surface changes, especially with dissociation of carboxyl groups followed by changes of intramolecular hydrogen bonds, or with the presence of Si-OH bonds on the surface, but from the results of quantum mechanical calculations carried out by Bálint Somogyi,
it was concluded that SiC NPs in aqueous solutions are not sensitive to the dissociation of carboxyl groups. With the help of my student, Áron Dániel Major, we measured the relative quantity and contribution to the luminescence of these groups. We performed potentiometric titration from pH 2 to pH 13 and monitored the PL signals. The titration was carried out as follows: 20 ml aqueous of SiC NPs solution was titrated against NaOH solution. pH was recorded with a pH electrode at every 0.1 ml addition of NaOH. Titration was thrice repeated with different concentrations. For measuring the whole range, pH was also adjusted to 2 with HCl and this solution was titrated with NaOH. The pKₐ values were determined by derivation and line fitting methods. We found three dissociation processes with pKₐ 4.2, 7.1, and 9.5. The pKₐ 4.2 is attributed to the dissociation of carboxyl groups and pKₐ 9.5 is due to the dissociation of hydroxyl groups. pKₐ 7.1 could be the dissociation of sylanol groups. These three major dissociative groups usually occur on the surface of SiC NPs.

Gravimetric analysis, with known size distribution can give an adequate approximation of NPs concentration in solution. Titration on the other hand gives the concentrations of surface groups with acid-base characteristic which can be used for further surface modifications. Combining these two results, now we are able to calculate the approximate number of groups on an average size of SiC NPs. We found that about 100 carboxyl groups reside on 2.5 nm as prepared nanoparticles.

**Claim of contribution**

In these experiments I made all of the described experiments and measurements, however, a student, Áron Dániel Major, also synthesized SiC NPs with different surface termination and ran titrimetric measurements and calculations under my supervision. The reported results based on his work too, that was aimed to reach higher accuracy. Dániel wrote two BSc works entitled “Szilícium-karbid nanoklaszterek pKₐ értékének meghatározása” and “Szilícium-karbid nanoklaszterek redukciójának vizsgálata” and a TDK work entitled “Szilícium-karbid nanoklaszterek felületének hatása az optikai tulajdonságokra”.

**3.4 Size and surface dependent optical properties**

As an indirect-bandgap semiconductor, bulk SiC has weak luminescence, however, porous SiC\(^7\), small nanocrystals\(^157\) and nanowires\(^158\) show bright photoluminescence. Even though the applicability of SiC NPs in biological environment\(^159,160\) and therapy\(^161\)
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was demonstrated, understanding the physics behind the luminescence is still in the centre of intense research. In porous SiC bright luminescence was reported, similar to that in porous Si, but the origin of this luminescence is still unclear. This holds for SiC NPs too. I carried out several different optical measurements on SiC NPs with different sizes and different surface terminations to unravel the connection between surface moieties and optical properties.

Study of Size Dependent Optical Properties

The luminescence of porous SiC is often associated with the quantum confinement effect\textsuperscript{76}, however, the relatively large crystallite size and the polytype independent luminescence implied that the luminescence was related to surface defects\textsuperscript{77}. Experimental results\textsuperscript{152,156} and theoretical calculations showed that the luminescence of SiC NPs is strongly influenced by the surface groups\textsuperscript{162}. Indeed SiC NPs solution containing 2-nm nanoparticles shows luminescence with emission at 450 nm (2.75 eV), nearly independent of excitation wavelength, while calculation showed that hydrogen terminated NPs with this size should emit in the deep UV\textsuperscript{163,164}. Wu and co-workers stated experimental evidence of quantum confinement in SiC NPs\textsuperscript{85} based on the excitation dependent luminescence properties of such NPs solution. This dependence is a necessary but not sufficient condition to unambiguously prove the quantum confinement effect. There are several reports about excitation dependent luminescence properties of carbon dots\textsuperscript{165,166} and graphene oxide solutions\textsuperscript{167} where this property is explained by different surface groups and the distribution of these groups\textsuperscript{168}. Guo \textit{et al.} reported that SiC NPs prepared in ethanol solution possessed low excitation dependent emission in the case of fresh samples but aged samples showed strong excitation dependence\textsuperscript{169}. Their size measurements suggested that SiC NPs aggregated quickly in ethanol solution and they associated the changes in the luminescence properties with the change in size distribution of SiC NPs\textsuperscript{169}. These contradicting results shed doubt on the simple quantum confinement model and the varying conclusions might come from the different size distribution of the colloid SiC particles. I developed an effective size separation method which allows preparing a SiC NPs solution containing only 1-4 nm particles. With the separation of small individual SiC NPs from larger or aggregated NPs the measurement on size dependent optical properties became possible.

To study the size dependent optical properties of SiC NPs, I prepared nanoparticles with broad size distribution. I have found that repeated etching damage the SiC crystals that
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cause larger fractions in the final colloid solution. The recorded PL spectra of as-prepared SiC NPs are shown in Figure 3-9. As can be seen the peak maximum at ~450 nm shifts only 8 nm upon changing the excitation wavelength between 310-370 nm

![PL spectra of SiC NPs](image)

Figure 3-9. Photoluminescence spectra of SiC NPs in water at different excitation wavelengths.

(marked with a vertical dashed line) but shows a severe reduction in the measured intensity upon excitation with wavelengths longer than 320 nm. We can observe another more intense red shift upon excitation with wavelengths of 370-450 nm (marked by the slant dashed line). This shift was previously associated with the quantum confinement effect\(^8\).

A sample with broad size distribution was centrifuged through a 30 kDa Pall\(^\text{TM}\) macrosep filter. 30 kDa filters contain pores with about 3 nm theoretical sizes. The remaining solution (sample II) was washed 10 times to remove most of the small particles. As shown in Figure 3-10, that filtrate (sample I) exhibits a similar peak maximum as the as-prepared sample but the long-wavelength shoulder is missing and there is almost no sign of changing the emission with excitation wavelength.
Figure 3-11 shows the size and atomic structure of sample II observed by high resolution transmission electron microscopy (HRTEM) and atomic force microscopy (AFM), whereas Figure 3-11(e) plots the corresponding PL spectra. The PL spectra of sample II show excitation independent emission with peak maximum at 530 nm (2.39 eV). The shape and intensity of the luminescence band are very different from those of sample I. Despite the wide size distribution, no shift occurs in the emission maximum upon changing the excitation wavelength. The 530 nm (2.39 eV) PL signal is in good agreement with the band gap of 3C-SiC (2.35 eV). The Bohr radius of 3C-SiC is about 2.7 nm and calculations implied that 4-nm 3C-SiC NPs have an almost bulk like absorption band. Based on these arguments I attribute the 530-nm peak to the band edge luminescence of larger particles. While SiC has an indirect band gap, consequently weak luminescence at room temperature, exciton recombination can be enhanced by the relaxation of selection rules due to the relatively small size of the particles and dielectric confinement. Several additional peaks appear in the PL spectra of sample II at about 408 nm (3.02 eV), 460 nm (2.67 eV) and 492 nm (2.52 eV). The first peak may correlate with the band edge luminescence of 6H polytype inclusions whilst the other two may originate from their stacking faults. 6H inclusion in 3C-SiC may be considered as an “ordered” sequence of stacking faults that can be described as 3-3 zig-zag lines consisting of 6 Si-C bilayers along the c-axis. Stacking faults within the 6H inclusions
embedded in 3C-SiC result in irregular stacking sequences. A demonstration such irregular stacking sequences in a larger SiC nanoparticle observed by HRTEM can be seen in Figure 3-11 (a-c). Even though the SiC is cubic 3C powder confirmed by X-ray diffraction measurements before and after etching it, polytype inclusions are common defects in SiC and may appear at low concentrations in the 3C-SiC powder. Since the applied etching method works mainly on the cubic 3C-SiC\textsuperscript{91}, the hexagonal polytypes...
remain mostly intact. Therefore, selective etching of 3C-SiC enhances the concentration of polytype inclusions in our system. While I connect the presence of polytype inclusions to the description above, it should be noted that phase transformation was claimed during preparation of SiC NPs by laser ablation\textsuperscript{172} and also by an etching process similar to ours\textsuperscript{169}.

6H inclusions in 3C-SiC enhance the luminescence of 3C-SiC\textsuperscript{173} which further explains the detectable band edge luminescence of 3C-SiC at room temperature. Figure 3-12 shows the photoluminescence excitation (PLE) spectra of sample I and sample II. Sample I has maximum emission efficiency at 320 nm excitation while the PLE spectrum of sample II corresponds to the PLE of bulk 3C-SiC\textsuperscript{174}. These observations further strengthen such conclusion that the properties of large particles are close to those of bulk 3C-SiC.

![Figure 3-12. PLE spectra of SiC NPs with different size distribution](image)

Large particles may either form because of the repeated etching of SiC powder reducing the size of the starting materials or may come from the aggregation of smaller particles. To unravel the role of either of these mechanisms in the change of the luminescence...
band I dried a droplet of sample on Si surface consisting of only molecular-sized nanoparticles and measured the PL during drying. Figure 3-13 shows how the PL changed during water evaporation. First, SiC NPs are surrounded with strongly adsorbed water molecules\textsuperscript{152}, thus the PL of this sample is almost identical to the PL of SiC NPs in solution. As the hydration shell around the SiC nanoparticles is removed, the emission maximum shifts to lower wavelengths typical of the PL signal of sample II. It can be concluded from the change in the PL bands that water evaporation is a two-step process: first the disappearance of the excess water, leaving the hydrated nanoparticles intact, followed by the disruption of the hydration shells and the subsequent forming of aggregates which leads to the PL bands characteristic of sample II. We confirmed the process with FTIR measurements too\textsuperscript{151}.

Aggregated or closely packed NPs usually have different optical properties from those of the individual particles\textsuperscript{175,176}. The wavefunctions in two closely lying SiC NPs may

Figure 3-13. PL spectra of SiC NPs solution containing small particles during drying on Si surface
overlap building up crystalline bands\textsuperscript{175,177} that can lead to bulk-like optical properties. This effect is known in similar nanoparticle systems\textsuperscript{175–177}.

I did not find any sign of size dependent optical properties in the 3C-SiC colloid systems; however, the size distribution was relatively broad in both parts of the separated samples. SiC NPs made by electroless wet chemical etching contain a large number of oxidized surface groups because of the applied strong acids. I propose here that SiC NPs could be rather described as $\text{Si}_x\text{C}_y\text{O}_z\text{(H)}$ systems. In the case of molecular-sized SiC NPs surface related luminescence is dominant\textsuperscript{167,178}. The surface related luminescence originates from localized states that have weak NP size dependency.\textsuperscript{11} However, various oxygen-containing surface groups may contribute to the PL spectrum depending on the surface environment possessing considerable Stokes shifts that result in a relatively broad PL signal at room temperature. As the particles become larger, the surface to volume ratio becomes small and the oxygen content becomes negligible. These results confirm the conclusion of theoretical calculations stating\textsuperscript{163,178} that the core recombination becomes dominant for nanoparticles with size of 4 nm and above while surface related luminescence dominates in smaller SiC nanoparticles.

**Study of Surface Dependent Optical Properties**

The broad luminescence from molecular size SiC NPs may play an important role in the context of magneto-optical color centers in nanocrystalline SiC.\textsuperscript{179,11} It has been proposed that molecular-sized SiC NPs embedding paramagnetic color centers may be ultimate fluorescent biomarkers that might be used even for quantum metrology going beyond the traditional dyes.\textsuperscript{180} However, molecular-sized SiC NPs themselves possess complex emission properties and fluorescence of color centers introduced in these SiC NPs might be compromised by the surface groups responsible for the emission of SiC NPs, which is a subject of studies in the near future.

The surface modification of this complex system with a core of crystalline SiC drastically affects its optical properties, as shown by our previous theoretical calculations. Experimental results established that the optical properties of SiC NPs are also influenced by the environment and by intramolecular interactions\textsuperscript{119,120,143,152,156}. However, the relatively broad size distribution and the possible distribution of surface terminators made it difficult to unambiguously prove the connection between surface termination and optical properties.
For these measurements I used SiC NPs with different surface termination presented in Chapter 3.2.

**Steady state photoluminescence study of different surface terminated SiC NPs**

The effect of the reduction processes described previously was monitored by steady state PL measurements too. Figure 3-14 shows the PL spectra of the samples at 320 nm excitation. There is a clear blue shift with increasing reduction degree with emission maxima at 450, 435 and 380 nm for as-prepared, BH$_4^-$ reduced and Zn/H$^+$ reduced samples, respectively. While the as-prepared and OH terminated (BH$_4^-$ reduced) samples show no changes in the emission spectra at the surveillance time, the emission of Zn/H$^+$ sample shows significant time evolution by shifting the peak maximum from around 380 nm to 410 nm during the reoxidation process of 2 hours.

![Figure 3-14](image)

**pH dependent optical properties**

By tracking the titration with PL, we found that the peak at 450 nm shifts to 435 nm at around pH 9, which does not match the measured inflexion points. In the case of back titration of the basic samples, the emission maximum shifts back to 450 nm at about pH 4 that implies a hysteresis loop in the PL by changing the pH value. As a consequence, the emission shift during titration cannot be associated with simple dissociation of a given surface group. It could be due to quenching effect of alkali ions, which form complexes with dissociated carboxyl groups at high concentration. To clarify this, I increased the ionic strength with addition of NaCl at pH 7 where carboxyl groups are dissociated but the PL remains unchanged. Indeed, the PL is shifted to 435 nm after
this treatment proving that the blue shift is not associated only with the dissociation of surface groups. According to calculations, carboxyl groups shift the highest occupied molecular orbital (HOMO) level associated with surface C-OH groups. When a non-hydrogen cation interacts with carboxyl groups this energy shift decreases and the HOMO level becomes similar to that of OH terminated SiC NPs. The titration curve with marked color changes is depicted in Figure 3-15.

Figure 3-15. Titration curve of SiC NPs in the 2-13 pH range. Color changes below the titration curve represent the color changes of the solution when pH was changed from 2 to 13. Color changes above the curve represent the color changes of the solution when pH was changed from 13 to 2.

These results imply that either substitution of carboxyl groups by hydroxyl groups or quenching them by alkenes causes about the same blue shift in PL. Different solvatochromic shifts were also reported demonstrating the surface sensitivity of the obtained PL, but much larger size distribution of SiC particles was applied in those studies that can seriously alter the spectrum with respect to molecular-sized SiC NPs.

**Wavelength dependent time-resolved emission spectroscopy studies**

Even though, steady state luminescence measurements demonstrate that the emission of SiC NPs is highly influenced by surface termination; such results do not unravel the physics behind the emission mechanism. To reveal the nature of the luminescence of small SiC NPs I applied the combination of advanced time resolved spectroscopic techniques together with infrared absorption measurements and steady-state photoluminescence spectroscopy on surface engineered colloid molecular-sized SiC NPs. Particularly, decay associated spectroscopy (DAS) and time-resolved area normalized emission spectroscopy (TRANES) methods were used, that have been so far applied only to few other systems. Time resolved emission spectra were recorded at the University of
Pécs by János Erostyák and Zoltán Tibor Jánosi. We applied time resolved emission spectroscopy (TRES) going beyond the conventional time-correlated single photon counting\textsuperscript{184–187} that represents a collection of measurements using two independent variables: wavelength and the time after excitation. This results in a three-dimensional surface of data that allows me to monitor the temporal evolution of the fluorescence as well as to resolve the spectrally overlapping species by using different analysis methods or models like TRANES and DAS. The strength of TRANES is that it reveals spectrally separated emitting centers independently of the shape of the individual decay functions\textsuperscript{188}. While TRANES can identify the number of different emission centers in the solution, the DAS method can go beyond that and is able to reconstruct the steady state spectra of these centers if an appropriate spectral or temporal model is used\textsuperscript{189}.

Wavelength dependent time-resolved emission measurements were carried out at 321 nm excitation in all samples. Emission is measured in the 340-570 nm wavelength range with 10 nm steps. Decay curves free from excitation pulses’ distortion were reconstructed using deconvolution and then were used for TRANES and DAS analysis.

**Time resolved area normalized spectra analysis**

TRANES curves were derived by area normalization of TRES (Figure 3-16).

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure3-16}
\caption{Figure 3-16 an example of area normalization}
\end{figure}

I have found that the time-dependent spectra form a single isoemissive point in each sample that definitely implies two emission centers in my samples (Figure 3-17). This is intriguing because Kasha’s rule implies non-radiative recombination from the higher-level excited states toward the lowest energy excited state. If the higher energy excited states associated with the radiative decay are related to a surface group as expected from the steady state PL spectra and from theoretical calculations, changing the surface
chemistry should change the lowest energy states and an isoemissive point should not be found. If the emission is due to the recombination on different localized surface states then a decreasing number of isoemissive points should be observed by increasing the surface reduction degree. The presence of two emitters in all type of samples cannot be described with the usual relaxation theory.

**Decay associated spectra analysis.**

The DAS analysis method yields the individual spectra of the mixed fluorophores and the summation of these spectra reproduces the steady state PL. In order to fit the decay curves for DAS analysis of the three samples, 5-exponential fit was applied in all cases. For DAS analysis, fixed time constants have to be used in the global analysis (Figure 3-18). I assumed that these 5 exponentials do not directly imply at all that 5 individual emitters occur in my samples because SiC NPs have multi-exponential decay and DAS cannot deal with it. Therefore, these decay components are just a result of an excellent fit for non-monoexponential decay with chi-square of 1.0-1.5 at every wavelength. As a result, spectra and lifetimes given from DAS analysis have no exact physical meaning.

Figure 3-17 TRANES curves of the as-prepared, BH₄ reduced and the reoxidized SiC NPs samples
Nevertheless, by analyzing the shape and maxima of DAS, it is possible to draw some conclusions. By taking into account the variation of the emission wavelengths of a single type luminescent center in the model of the DAS method, DAS rather shows two different bands in all the three samples. From DAS analysis, using 5-exponential fit the as-prepared sample shows 3 broad features with maximum at 450-460 nm and 2 peaks at 410-420 nm. The NaBH$_4$ reduced sample has 4 peaks at ~435 nm with different lifetimes and one peak at 410-420 nm. In the case of the reoxidized sample, DAS fit gives 4 peaks with 410-420 nm peak maximum and one at 435 nm. Figure 3-19 shows the

Figure 3-18 The results of DAS analysis on different SiC NP samples. SUM represents the summation of curves associated to different life times. EEM is the curve from steady-state measurements.

reconstructed sub-spectra of the three samples. Curves with different lifetimes but same maxima are weighted together and this representation gives a very clear visualization of two different emitters.
In consistence with the result of TRANES analysis, DAS also indicates two emitters in all samples. DAS results imply that one of the emission centers does not change during the chemical modifications and has a short lifetime in all samples. The other one shifts with chemical modification. Combining this result with the FTIR spectra and ab initio theory it can be concluded that a common emitter forms in all the samples with wavelengths at 410–420 nm which may be associated with some defects on the oxidized SiC NP surface (ab initio calculations made by Bálint Somogyi from Gali’s group). Indeed, silicon dioxide (SiO$_2$) has numerous luminescent defects emitting at these wavelengths$^{191}$ and theoretical calculations made by our group prove that surface groups tailor the absorption band of the nanocrystal instead of forming individual localized emission centers, while Si – O defects create localized states and have “individual” absorption and emission peaks$^{192}$. These Si – O defect related emitters give little contribution to the overall emission in the as-prepared samples because SiO$_2$-like oxide is not the main compound on the surface and even smaller in BH$_4^-$ reduced samples where the oxygen bridges were slightly eliminated. However, they become dominant in reoxi-
Results and Discussion

ditized samples where carbon-oxygen groups were eliminated by the Zn/H\(^+\) reduction, the highly reduced surface reconstructed in water forming Si – O bonds on the fresh Si surfaces of SiC NPs, and some C-OH groups also reformed according to the FTIR spectra (see Figure 3-8).

Conclusions

The complexity of SiC NPs results in a subtle PL mechanism. First, NPs under 4 nm seems to be no size dependent optical properties with usual surface terminations. Elimination of both carboxyl and hydroxyl groups by reduction causes a dramatic blue shift in PL and by studying the pH dependent photoluminescence with the known solva-

![Figure 3-20. Band gap variation according to different sizes and surfaces. The horizontal lines represent the surface states that presumably show little quantum confinement effect. However, band edges do show quantum confinement effect, particularly, in the region of 4 and 6 nm. Such fraction of SiC NPs was not produced in our method. Larger NPs show band edge luminescence.](image)

![Figure 3-21 Surface dependent emission properties](image)
tochromism\textsuperscript{143}, it can be concluded that SiC NPs under 4 nm have surface state related emissions. Additionally, the identification of SiO\textsubscript{x} defect related color centers at the surface of SiC NPs gives more complexity the optical properties. From the experimental data I drew an illustration of size dependent (Figure 3-20) and surface dependent (Figure 3-21) optical properties as well. These results imply that the color centers introduced in the core of SiC NPs might interfere with the surface groups, thus careful surface engineering is inevitable in the fabrication of SiC NP based nanosensors.

Claim of contribution

In these broad research

- I synthesized and characterized the SiC NPs with different size distribution.
- all of the experiments in section 3.2, 3.3, 3.4 excluding size dependent properties are based on my individual research proposal to National Excellence Program (Grant no.: NPT-NFÖ-P-15-0052)
- I ran and characterized all of the steady state PL measurement.
- I carried out the titration experiments.
- I produced and characterized TRANES curves from TRES results and I suggested these methods for characterization (both TRES and TRANES).
- I made the theory for the use of DAS.
- I made the overall description of SiC NPs optical properties that was revised and modified with the theoretical results by Ádám Gali.
- Tibor Z. Jánosi ran the time resolved experiments and constructed the different spectra (TRES and DAS).

3.5 Emitters in SiC Nanocrystals

The rapid synthesis method I use for SiC powders with high surface area results in imperfect SiC crystals. However, imperfection can significantly change the optical and magnetic properties of the crystal. For example, point defects in SiC can be luminescent and paramagnetic. Luminescent point defects are also called color centers.
Room temperature single photon emission was observed by Castelletto’s group from SiC NPs that were synthesized by myself in our laboratory. The emission is broad with a zero-phonon line (ZPL) at 650 nm. These SiC NPs were significantly larger than I presented above. According to dynamic light scattering (DLS) characterization, the average particle size was about 110 nm (see Figure 3-22).

SiC NPs made by the synthesis of SiC powder in our laboratory from Si and activated charcoal. SiC powder was stain-etched-twice then was sonicated and centrifuged at 8000 rpm for 10 min. Supernatant was centrifuged through a 100 kDa Pall filter. Pellet was collected and redispersed in water.

SiC nanocrystals were dried on a glass coverslip. Room temperature confocal microscopy combined with AFM were used to characterize the nanoparticles. The emission from the NPs was sent to a spectrometer or to a Hanbury-Brown and Twiss interferometer to measure the second order correlation function g(2)(τ), that can be indicate if a color center is single photon emitter (g(2)(0) < 0.5), and identified as E-center (Figure 3-23). This E-center was previously associated with silicon vacancies, a missing Si-atom from the SiC lattice. However, PL associated with silicon vacancies in 4H and 6H-SiC polytypes occurs in the near-IR throwing doubt on this assignment. We identified these defect as a carbon antisite vacancy pair (C_{si}V_{c}) by theoretical calculations in Ádám Gali group.

![Figure 3-22 a) TEM image of individual SiC NPs, b) TEM image if SiC aggregates, c) size distribution of SiC NPs dispersed in water according to DLS measurement](image-url)
Variation of carbon vacancy concentration in SiC powder by varying the concentration of PTFE in the reaction mixture was already reported\(^{62}\). However, they measured the complex permittivity while single photon measurements and optically detected magnetic resonance method can identify many types of defect in SiC. Despite that detection of single photon signal from a particle with 80 nm of diameter is now not a world record, the simplicity and variability of such synthesis promise that we will be able to realize such defect in much smaller particles (there is no need to etch SiC for smaller particles). An apparatus for characterization of paramagnetic point defects is being built in our institute.

**Claim of contribution**

In this work I synthesized the SiC powder and prepared SiC NPs for the experiments. I characterized these particles with TEM recorded by Eszter Drotar (H.A.S. TTK) and DLS recorded by Eszter Fülöp (H.A.S. EK MFA) and FTIR. I carried out the FTIR measurements.
4 Outlook

In conclusion, I studied the size and surface dependent optical properties of SiC NPs, in order to understand the luminescence mechanism. I demonstrated that SiC NPs below 4 nm do not show quantum confinement effect and the emission is originated from the delocalized surface states. The very competition in this field is demonstrated by references in the results and discussion section. Indeed many papers were published within close proximity of ours with similar research interest. Parallel to the study of SiC NPs I made steps further to realize color centers in SiC NPs. I successfully synthesized SiC particles containing color centers with 110 nm average diameter. To realize these defect in molecular sized SiC NPs we have to increase the concentration of such emitters in SiC while quenching the surface state emission is also necessary.

At current time, aqueous solution of QDs is on the market under the name of QDot (Thermo). An easy method for doping is also reported\textsuperscript{195,196}. Despite the toxicity of Cd and Se, CdSe QDs are highly studied in clinical research\textsuperscript{197–199}. Thanks to the simplified synthesis of Si nanoparticles from HSQ (hydrogen silsesquioxane), this material is also intensively studied and marked as a potential biomarker\textsuperscript{200} and material for new generation solar cells\textsuperscript{201}. The intensive study of graphene led to the discovery of graphene and graphene oxide “quantum dots” and along with carbon dots, fluorescent carbon based materials with sizes of few nanometres are potential candidates for medical research\textsuperscript{202,203}, and most of the harvested knowledge from nanodiamond, carbon nanotubes and fullerenes can be applied here.

Even though it seems that Si and C alone can build up promising nanostructures, I believe that the potential of SiC is high in biological applications. Because of the higher
stability of graphite at ambient condition the surface of nanodiamond tend to reconstruct from sp$^3$ to sp$^2$ bonding structure which diminishes the superior properties of diamond$^{204}$. Silicon NPs with red luminescence can be prepared, but surface termination usually causes blue shift$^{205}$. While color centers in diamond (nitrogen vacancy center) has very interesting properties, similar defects can be realized in SiC too.

SiC NPs have a surface where traditional organic reactions can be applied while the stability of such nanoparticles promises realization of defects in it. While SiC is still a very interesting material and there are great potentials in SiC NPs, the improvement of the optical properties is necessary for biological application. At this time, the reported emission maximum is often around 450 nm and UV excitation is needed. Both should be avoided in biological research.
5 Thesis

The major conclusions of my Ph.D. work are summarized in the following thesis points. The results were published in five peer-reviewed papers that are referred as T1-5.

1. I synthesized 80-100 nm SiC particles with a single photon source called E center (T1).
2. I improved the synthesis method of SiC powders and I showed that the SiC prepared by this method
   a. increases the concentration of carboxyl moiety on the surface of SiC NPs made from them (T2)
   b. reduces the size distribution to 1-4 nm (T2, T4, T5).
3. I improved the stain etching synthesis method of SiC NPs by using a hydrothermal process (T2, T3, T4, T5). I demonstrated that
   a. the yield is increased by two times (T3)
   b. size distribution is reduced from 1-11 nm down to 1-6 nm (T3)
   c. and the average diameter reduced from 6 nm to 3 nm (T3).
4. I measured the titration curve of SiC NPs colloid and found three inflexion points with pka values of 4.7, 7.1 and 9.5. I associated these values to carboxyl, sylanol and hydroxyl groups (T2).
5. I demonstrated that SiC NPs smaller than 4 nm show no quantum confinement. (T2, T5)
6. I demonstrated that SiC in the range of 4-30 nm shows negligible quantum confinement. In addition I could show band edge luminescence and characteristic luminescence of stacking faults at room temperature. (T5)
7. I synthesized hydroxyl terminated, C-H terminated and SiOx terminated SiC NPs (T2).
   a. I showed that hydroxyl terminated SiC NPs have emission peak maximum at 435 nm, the C-H terminated SiC NPs have emission maximum at 380 nm.
   b. Furthermore, I demonstrated that C-H terminated SiC NPs are oxidized in aqueous solution and several Si-O-Si bridges are formed.
8. I identified a SiOx related localized luminescence centre in SiC NPs (T2), and I showed that carbon related surface groups form delocalized surface states (T2, T5).

5.1 Publications referring to my thesis points

5.2 Hungarian Publications


5.3 Conference Presentations

T10: E-MRS Spring Meeting and Exhibit, Lille, France (2016), Identification of Luminescence Centers in Molecular-Sized Silicon Carbide Nanocrystals


T12: MRS Fall Meeting, Boston, USA (2014), Surface Dependent Optical Properties of Silicon Carbide Quantum Dots


T14: 1st Innovation in Science, Szeged, Hungary (2014), Silicon Carbide Quantum Dots as a Non-toxic Probe for Bioimaging: Synthesis and Application

T15: Spring Wind Ph.D Conference, Debrecen, Hungary (2014), Szilíciumkarbid kvantumpöttyök időfelbontásos lumineszcencia-spektroszkópiás vizsgálata
Fabrication and characterization of silicon carbide nanoclusters

T16: NanoValid Training and Workshop, Zaragoza, Spain (2013), *Luminescence Silicon Carbide Quantum Dots*
T17: Spring Wind Ph.D Conference, Sopron, Hungary, Lumineszcerens Szilíciumkarbid Kvantumpötyök előállítása és jellemzése
T19: SIWAN5, Szeged, Hungary (2012), Luminescent Silicon Carbide Quantum Dots Prepared by Reactive Bonding and Subsequent Wet Chemical Etching: Characterization and Potential Applications
T20: XIX International Summer School Fluorescent Nanoparticles in Biomedicine, Miraflores de la Sierra (Madrid) Spain (2012), *Fluorescent Silicon Carbide Quantum Dots for Bioimaging And Sensing*
T21: SIWAN6, Szeged, Hungary (2014.), Time-Resolved Luminescence Spectroscopy of Silicon Carbide Quantum Dots
T23: Oláh György PhD. Conference, Budapest, Hungary (2014), *Szilíciumkarbid-alapú festékpróbák*
T24: ACIN2013 Namur, Belgium (2013), Preparation of small silicon carbide quantum dots by wet chemical etching
T26: MRS 2012 Spring Meeting, San Francisco, USA, Luminescent Silicon Carbide Quantum Dots Prepared by Reactive Bonding and Subsequent Wet Chemical Etching

5.4 Further Publications

T28: Zsolt Szekrényes, Bálint Somogyi, Dávid Beke, Gyula Károlyházy, István Balogh, Katalin Kamarás, and Adam Gali, Chemical Transformation of Car-


T30: David Beke, Anita Pongracz, Gábor Battistig, Katalin Josepovits, Béla Pécz, Selective Growth of Nanocrystalline 3C-SiC Thin Films on Si. AIP 2(1), 23-26 (2010).
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