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VEGÉSZMÉRNÖKI ÉS BIOMÉRNÖKI KAR
OLÁH GYÖRGY DOKTORI ISKOLA

FABRICATION AND CHARACTERIZATION OF SILICON CARBIDE NANOCCLUSERS

Ph.D Thesis

Author: Beke Dávid
Supervisor: **Gali Ádám**
Consultant: Horvölgyi Zoltán

MTA Wigner FK SZFI



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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

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 treatment¹⁻³. For *in vivo* imaging a fluorophore or fluorescent label or dye, i.e. a material is needed that is able to emit light and has to fulfill numerous criteria, for example, 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 microscopy⁴, 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.

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

2 THEORETICAL BACKGROUND

Synthesis and 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^{5,6}.

SiC nanoparticles made from porous SiC were first reported in 2005⁷. 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 luminescence was caused by quantum confinement of SiC nanoparticles, which will be revised in this dissertation.

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 process⁸

Both synthesis methods are based on a pore formation during an electrochemical process. Porous SiC then transformed to colloid SiC NPs by using ultrasonic bath.

Size distribution of colloidal SiC nanoparticles

The size distribution of the SiC particles was varied in the studies reported before the year 2011 between 1-10 nm and the main particle size was between 3 and 5 nanometers^{7,8}.

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 effect⁷. However, SiC nanoparticles in aqueous solution have peak maximum at about 450-470 nm that does not vary with SiC polytypes leading to the conclusion that surface states influence the optical properties (figure 2-1). 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.

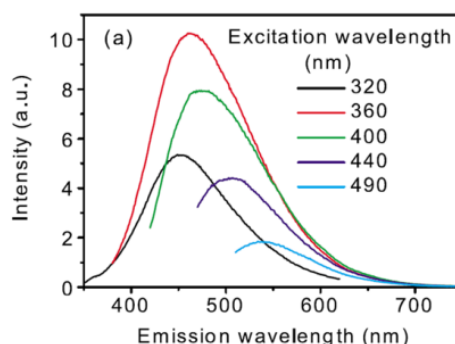


Figure 2-1. Excitation dependent emission of SiC NPs.

Surface chemistry

Silicon carbide is a covalent material therefore the surface has to be reconstructed after the etching. Infrared spectroscopic and X-ray photoelectron spectroscopic studies revealed that the surface of SiC nanoparticles is very rich in different moieties^{9,10}, for example carboxyl groups and oxygen bridges (C-O-C, Si-O-Si, C-O-Si) (Figure 2-2).

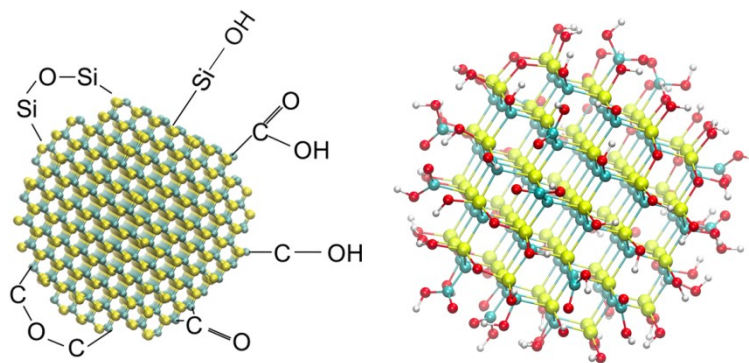


Figure 2-2 Surface reconstruction of SiC NPs. Left: surface groups represented by labels. Right: SiC crystal structure with surface groups represented by ball and stick model. green balls: Si, blue balls: C, red balls: O, white balls: H; this figure was made by Bálint Somogyi

Research objectives

Silicon carbide 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

3 MATERIALS AND METHODS

SiC powder synthesis

SiC synthesis was carried out in an induction furnace (figure 2-1). The induction generator operates at 400 kHz and the current is varied between 0.8 and 1.5 A.

The graphite crucible is 40 mm wide and 70 mm high, the wall thickness is 5 mm.

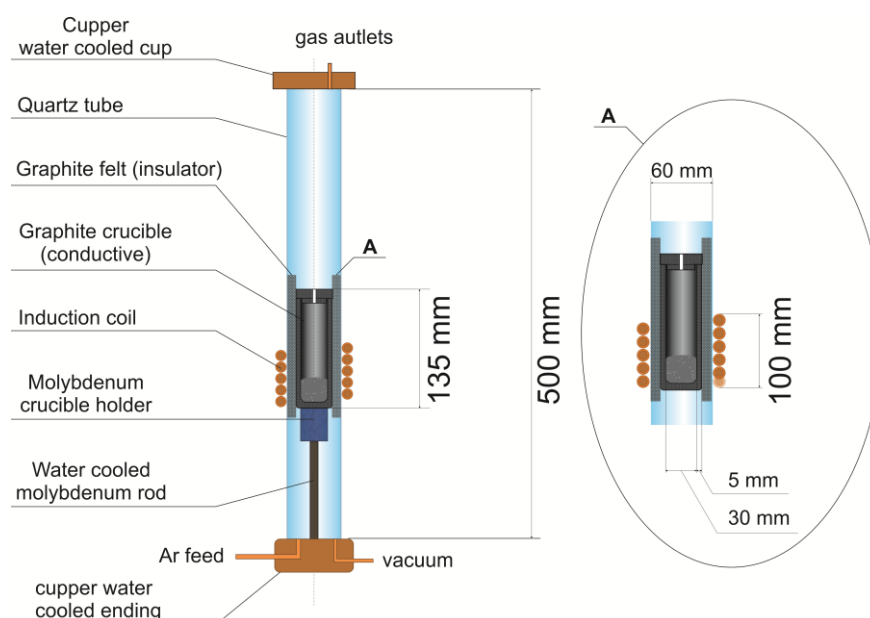


Figure 3-2 main parts of the induction furnace

For SiC synthesis we used Si wafer, Si powder (99%, 325 Mesh, Sigma) graphite powder (analytical grade, Reanal), and activated charcoal (Norit CA1, Sigma). In some cases, we also added PTFE to the mixture that propagates the reaction between silicon and carbon.

Stain etching of SiC

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.

For hydrothermal route, I used acid digestion bombs. The applied materials were hydrofluoric acid (HF) of 45%, analytical grade from VWR and nitric acid (HNO₃) of analytical grade from VWR, Sigma, or Reanal.

Infrared absorption measurements

Infrared absorption spectroscopy was used to study the surface properties of SiC NPs. I applied group frequency analysis on the recorded infrared spectra in order to follow changes on the surface during surface modification reactions.

Infrared measurements were carried out on drop-drying SiC NPs solutions at the surface of a

ZnSe multiple internal reflection crystal and measured in attenuated total internal reflection (ATR) mode.

I used Bruker Tensor 37 with 4 cm^{-1} resolution and DTGS detector. Spectra were recorded in the $700\text{--}4000\text{ cm}^{-1}$ range. The baseline was corrected by an adjusted polynomial function

UV-VIS and Photoluminescence Measurements

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.

Beside steady state emission spectroscopy, I used time resolved emission spectroscopy and decay associated spectra.

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 cases above, quartz cuvette with 1 cm path length was used.

Electron microscopy

I used scanning electron microscopy for visualizing SiC particles after synthesis and I used high resolution transmission electron microscopy or atomic force microscopy images for analyzing size distribution of the prepared SiC NPs.

Equipment: JEOL JEM-3010 HR-TEM with up to 300 kV acceleration

Atomic force microscopy

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. Both the concentration of the solution and the activation time are optimized for each sample. Size distribution was achieved by measuring the height of individual particles.

Equipment: Neaspec NeaSNOM AFM

4 RESULTS AND DISCUSSION

Improvement in the synthesis of SiC nanoparticles

Development on SiC NPs synthesis

Briefly, stain etching made under the following condition: $\text{HNO}_3\text{:HF}$ with a volume ratio of 1:3 at $100\text{ }^\circ\text{C}$ 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.

In the original method⁷ the mixture of SiC powder, HF and HNO_3 was heated up in an open sys-

tem like in a round flask made from fluorinated polymer. I transferred this reaction to a closed acid digestion system that can be heated up to 250 °C.

To compare the efficiency of the open and closed reaction conditions I prepared samples with the same conditions. Results can be found in table 4-1.

Table 4-1 Measured parameters of etched samples. Open vs. Closed reaction

Measurement	Open system	Closed system
Weight loss during etching	0.100 g	0.101 g
Weight loss during sonication	4.1 mg	3.8 mg
Total mass of NPs	2 mg	3.5 mg
Average size	5.8 nm	3.1 nm
PL Intensity (a.u.)	5×10^4	1.5×10^5

As can be seen in Table 4-1, 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. While the total mass of the particles in solution increased by 1.75 times, the PL intensity is increased by 3 times. Further reduction in size distribution can be achieved by applying mesoporous SiC powder as a SiC source for stain etching.

Synthesis of different surface terminated SiC NPs

To study how surface termination affects the emission properties I synthesized SiC NPs with different surface terminations.

As-prepared SiC NPs of diameter between 1-4 nm are terminated with a high concentration of carboxyl groups¹¹. For the preparation of -OH terminated SiC NPs as-prepared SiC NPs were reduced by NaBH₄ in aqueous solution. Hydrogen terminated SiC NPs were fabricated by reducing as-prepared samples dispersed in HCl by dissolving Zn powder. The oxidized sample ('reoxidized') was created by 2-hour illumination of the hydrogen terminated SiC NPs sample with 320 nm wavelength. The conversion degree was studied by FTIR and steady-state PL spectroscopy. These samples were used for studying the contribution of surface groups in optical properties.

Size and surface dependent optical properties

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

To study the size dependent optical properties of SiC NPs, I prepared nanoparticles with broad size distribution (1-30 nm). The recorded PL spectra of as-prepared SiC NPs are shown in Figure 4-1. We can observe 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 effect⁷.

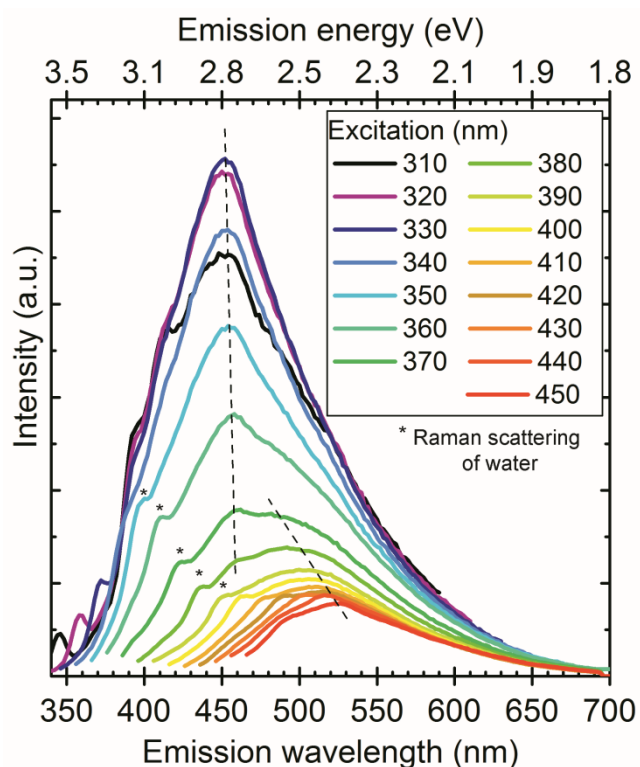


Figure 4-1. Photoluminescence spectra of 1-30 nm SiC NPs in water at different excitation wavelengths

A sample with broad size distribution was centrifuged through a 30 kDa PallTM macrosep filter. Figure 4-2 shows the size and atomic structure of retentate observed by HRTEM and AFM, whereas Figure 4-2(e) plots the corresponding PL spectra. The PL spectra of retentate 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 filtrate. 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). I attribute the 530-nm peak to the band edge luminescence of larger particles. 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 inclusions¹² whilst the other two may originate from their stacking faults¹³.

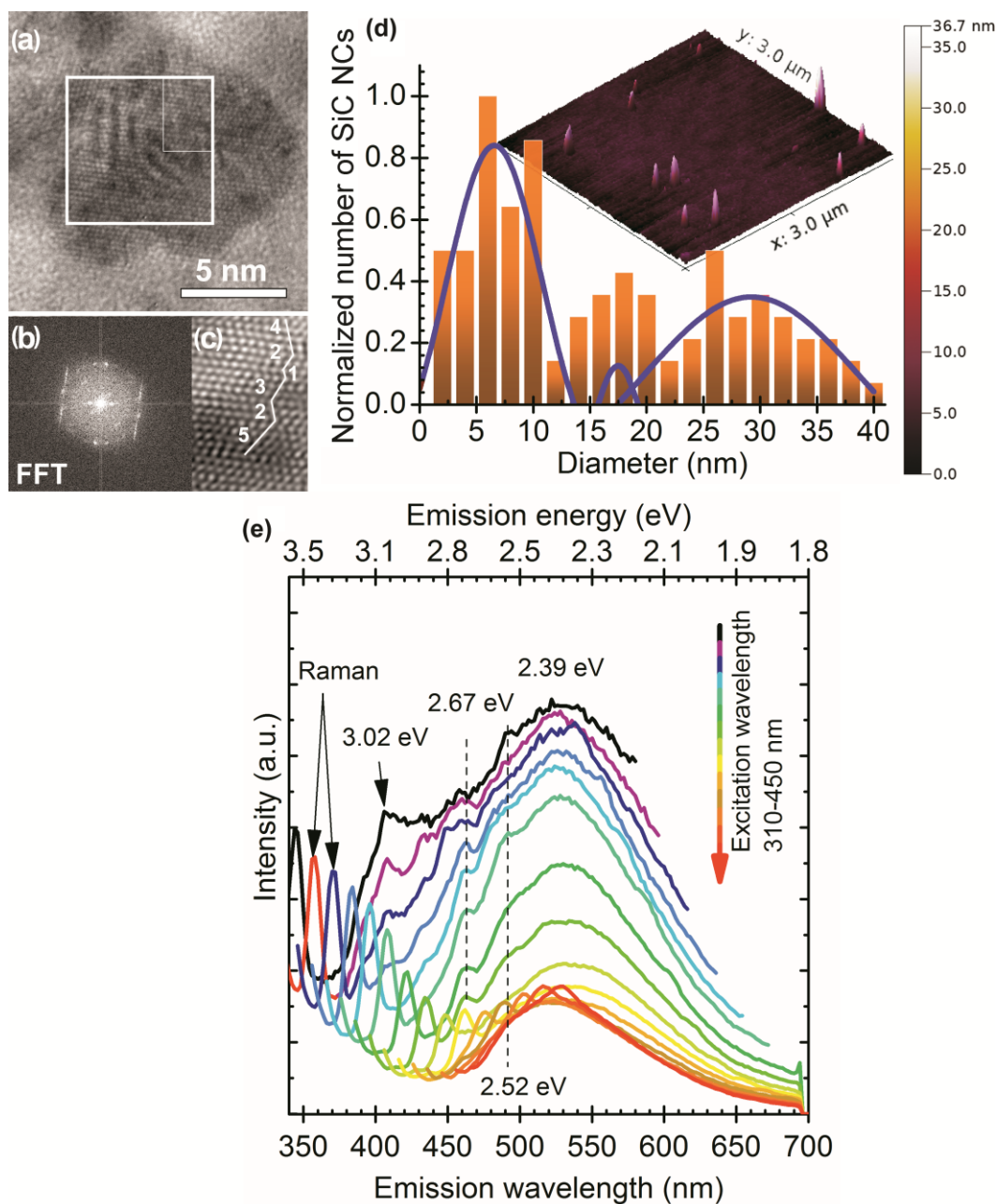


Figure 4-2 **(a)** HRTEM image of a ~ 10 nm SiC nanoparticle. **(b)** Fast Fourier transform (FFT) of the area marked with square in panel (a). **(c)** Fourier filtered HRTEM image of the area marked with a rectangle in the upper right corner of the square in panel (a). An irregular stacking sequence of 5-2-3-1-2-4 is indicated in the figure. **(d)** shows AFM image and the size distribution of sample II. **(e)** PL spectra of sample II (filtrate)

As shown in Figure 4-3, filtrate exhibits a similar peak maximum as the as-prepared sample, but there is almost no sign of changing the emission with excitation wavelength.

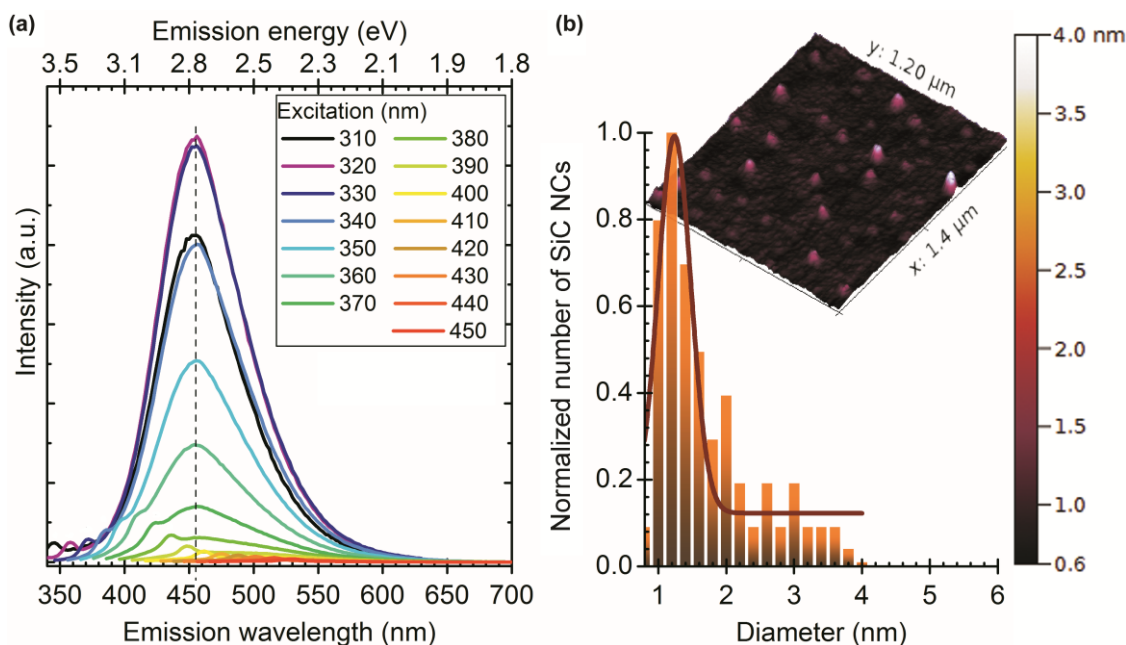


Figure 4-3. (a) shows the PL spectra of sample I (filtrate), (b) shows the AFM image and size distribution of sample I.

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.

Study of Surface Dependent Optical Properties

For these measurements I used SiC NPs with different surface termination.

pH dependent optical properties

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. The pK_a values were determined by derivation and line fitting methods. We found three dissociation processes with pK_a 4.2 (carboxyl group), 7.1 (hydroxyl group), and 9.5 (silyanol group).

By tracking the titration with PL, I 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. The titration curve with marked color changes is depicted in Figure 4-4.

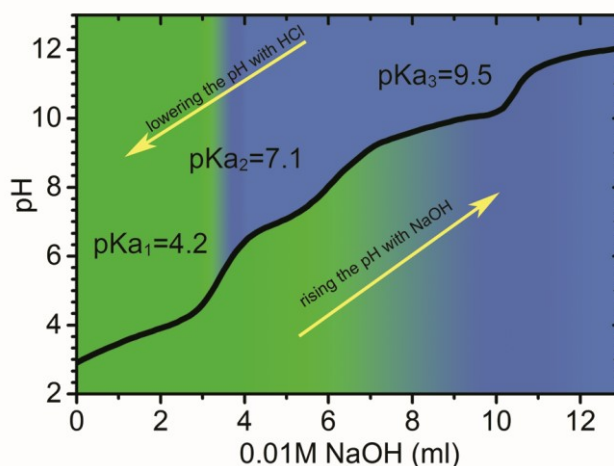


Figure 4-4. Titration curve of SiC NPs in the 2-13 pH range. Color changes below the titration curve represent the color changes of the solution when pH was changed from 2 to 13. Color changes above the curve represent the color changes of the solution when pH was changed from 13 to 2.

Wavelength dependent time-resolved emission spectroscopy studies

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 systems¹⁴⁻¹⁶. Time resolved emission spectra were recorded at the University of Pécs by János Erostyák and Zoltán Tibor Jánosi.

Time resolved area normalized spectra analysis

TRANES curves were derived by area normalization of TRES (Figure 4-5).

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.

Decay associated spectra analysis.

The DAS analysis method yields the individual spectra of the mixed fluorophores. In order to fit the decay curves for DAS analysis of the three samples, 5-exponential fit was applied in all cases. I assumed that these 5 exponentials do not directly imply at all that 5 individual emission centers occur in my samples because SiC NPs have multi-exponential decay and DAS cannot deal with it. As a result, spectra and lifetimes given from DAS analysis have no exact physical meaning. DAS rather shows two different bands in all the three samples. Figure 4-6 shows the 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 emission centers.

In consistence with the result of TRANES analysis, DAS also indicates two emitters in all samples. 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), while SiC NPs itself have surface related emission.

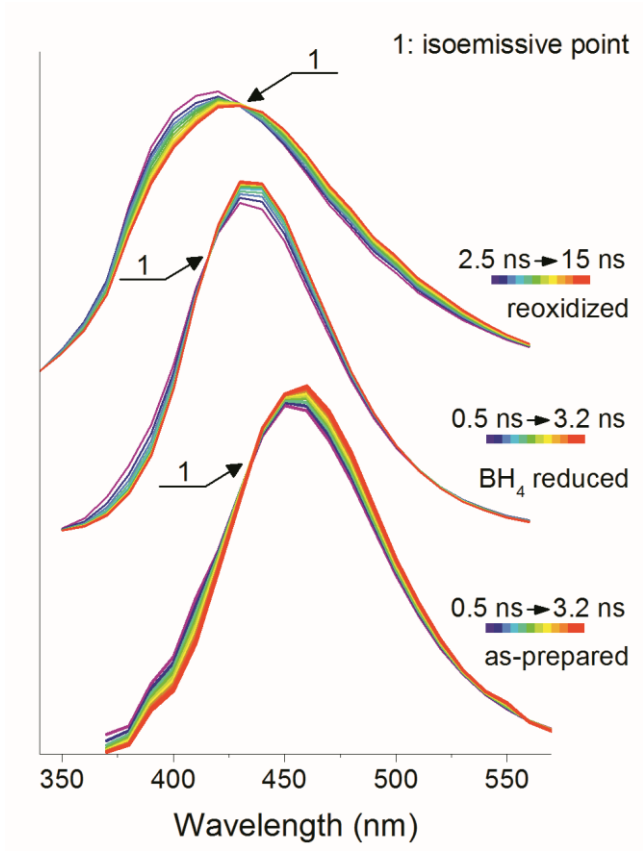


Figure 4-5. TRANES curves of the as-prepared, BH₄ reduced and the reoxidized form Zn/H⁺ reduced SiC NP samples

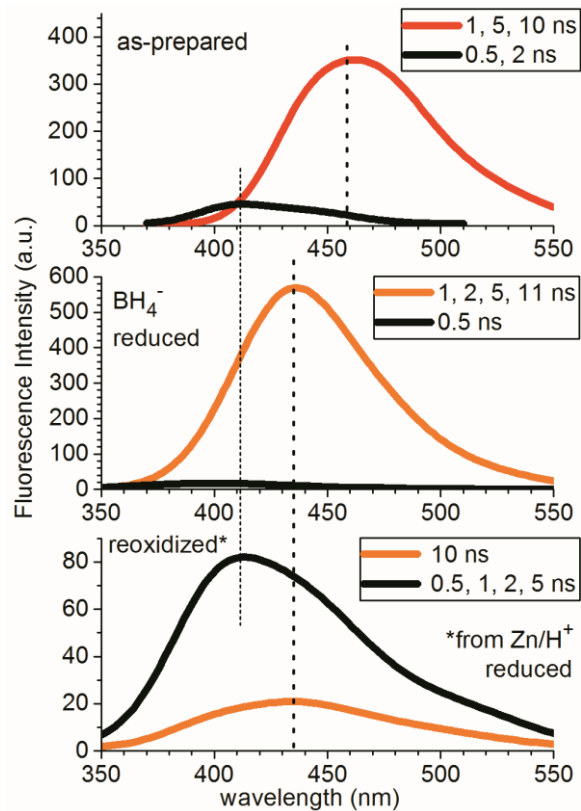


Figure 4-6. Decay associated spectra (DAS) of as-prepared and reduced SiC NP samples. Spectra having different lifetime components but the same maxima are weighted together

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 solvatochromism¹⁷, it can be concluded that SiC NPs under 4 nm have surface state related emissions. Additionally, the identification of SiO_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 4-7) and surface dependent (see Figure 4-8) optical properties as well.

crystals. However, imperfection can significantly change the optical and magnetic properties of the crystal. For example, point defect 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 I synthesized 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.

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.

5 FUTURE APPLICATION

The applicability of SiC NPs for bioimaging is already demonstrated in one of my publications and by other researchers as well. However the blue-green emission and the low quantum yield make SiC NPs inefficient compared to other fluorophores. Beside the stability and biocompatibility of SiC NPs, this material exhibits unique optical properties connected to some types of defects in its structure with excitation cycle that leads to the optical spin-polarization of high-spin defect ground state. Such systems are the most prominent objects for applications in new generation of supersensitive magnetometers, biosensors, single photon sources and so on. I already prepared SiC NPs with diameter of 80 nm that consist of such defect. I also unraveled the optical properties of SiC NPs with size below 4 nm. The next task is to realize known defect in molecular sized NPs.

6 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 developed a new synthesis method for 80-100 nm SiC particles with a single photon source called E center. This E center makes SiC nanoparticles a very promising candidate for *in-vivo* biological application and quantum information processing. (T1)
2. I developed a new SiC powder synthesis that serves as a starting material for SiC NPs synthesis. I showed that the properties of SiC NPs can be tuned by the SiC powder source. I showed that the concentration of carboxyl groups on the surface of SiC nanoparticles prepared by hydrothermal synthesis method from that SiC powder is increased compared to other SiC powder sources, and the size distribution of SiC nanoparticles is reduced down to 1-4 nm (T2, T4, T5). These properties improved the applicability of SiC NPs for *in-vivo* application.
3. I developed a hydrothermal stain etching synthesis method of SiC NPs (T2, T3, T4, T5). I showed that the yield is doubled in comparison to the stain etching applied previously by others while the size is reduced significantly (from 6 nm to 3 nm) and the size distribution narrowed (T3).
4. I showed by infrared absorption spectroscopy that the surface of SiC NPs prepared by hydrothermal stain etching consists of carboxyl and hydroxyl groups (T2, T3). I determined the titration curve of SiC NPs colloid contains SiC NPs below 4 nm for the first time and I associated the inflexion points on the titration curve to the dissociation of carboxyl, sylanol and alcohol groups (T2). These results prove that hydroxyl groups bond to both carbon and silicon atoms at the SiC surface of SiC NPs.
5. I developed a centrifugal filtration method to fractionate 1-30 nm SiC NPs prepared by hydrothermal stain etching method (T5). By studying the fractions of SiC NPs prepared by centrifugal filtration I showed that SiC NPs smaller than 4 nm show no quantum confinement and SiC NPs with size of 4-30 nm exhibit band edge luminescence and characteristic emission of stacking faults of SiC (T5).
6. I developed an aqueous synthesis route for hydroxyl terminated SiC NPs and for hydrogen terminated SiC NPs, and I synthesized SiO_x terminated SiC NPs by photo-oxidation of hydrogen terminated SiC NPs. I monitored the surface termination by infrared absorption spectroscopy. These SiC NPs have simplified surface chemistry that helps to analyze surface related optical properties (T2).
7. I studied the change in photoemission upon surface chemistry of SiC NPs by time resolved emission spectroscopy (T2). I developed an analysis method on time resolved emission spectroscopy that is able to distinguish different emitters with overlapping emission spectra in colloid solutions (T2). I showed on the synthesized model systems that

hydrogen terminated SiC NPs are oxidized in aqueous solution, despite the known chemical resistivity of SiC (T2). I identified a SiO_x related localized luminescence center in SiC NPs for the first time (T2) and showed that carbon related surface groups form delocalized surface states in SiC NPs with sizes below 4 nm (T2, T5).

Publications referring to my thesis points

T1: Stefania Castelletto, Brett Johnson, Cameron Zachreson, Dávid Beke, István Balogh, Takeshi Ohshima, Igor Aharonovich, and Adam Gali, *Room Temperature Quantum Emission from Cubic Silicon Carbide Nanoparticles*. ACS Nano. **8**, 7938–7947 (2014).

IF: 12.881; C: 25

T2: Dávid Beke, Tibor Z. Jánosi, Bálint Somogyi, Dániel Á. Major, Zsolt Szekrényes, János Erostyák, Katalin Kamarás, and Adam Gali, *Identification of Luminescence Centers in Molecular-Sized Silicon Carbide Nanocrystals*. J. Phys. Chem. C. **120** 685-691 (2016).

IF: 4.772; C: 4

T3: David Beke, Zsolt Szekrényes, István Balogh, Zsolt Czigány, Katalin Kamarás and Adam Gali, *Preparation of small silicon carbide quantum dots by wet chemical etching*. J. Mater. Res. **28**, 44–49 (2013).

IF: 1.647; C: 13

T4: David Beke, Zsolt Szekrényes, Denes Pálfi, Gergely Róna, István Balogh, Pal Andor Maák, Gergely Katona, Zsolt Czigány, Katalin Kamarás, Balazs Rózsa, Laszlo Buday, Beáta Vértessy and Adam Gali, *Silicon carbide quantum dots for bioimaging*. J. Mater. Res. **28**, 205–209 (2012).

IF: 1.647; C: 19

T5: David Beke, Zsolt Szekrényes, Zsolt Czigány, Katalin Kamarás and Adam Gali, *Dominant luminescence is not due to quantum confinement in molecular-sized silicon carbide nanocrystals*. Nanoscale. **7**, 10982–10988 (2015).

IF: 7.394; C: 7

Hungarian Publications

T6: Beke D, Szekrényes Zs, Róna G, Pálfi D, Vértessy B, Rózsa B, Kamarás K, Gali Á *Silicon Carbide Quantum Dots As A Non-Toxic Probe For Bioimaging: Synthesis And Characterization* In: Szilárd Szélpál (ed.) I. Innovation in Science - Doctoral Student Conference 2014: eBook of Abstracts. 207 p. (Doktoranduszok Országos Szövetsége,

Biológiai és Kémiai Tudományok Osztálya) Szeged: Magyar Kémikusok Egyesülete, 2014. pp. 30-31. (ISBN:978-963-9970-52-6)

T7: Jánosi TZ, Beke D, Szekrényes Zs, Kamarás K, Gali A, Erostyák J *Szilícium-karbid kvantum dotok fluoreszkáló centrumainak szétválasztása időemissziós mátrix analízisével* In: Ádám P, Almási G (ed.) Kvantumelektronika 2014: VII. Szimpózium a hazai kvantumelektronikai kutatások eredményeiről. P09. 2 p. (ISBN:978-963-642-697-2)

T8: Beke D, Szekrényes Zs, Kamarás K, Gali Á *Lumineszcens szilíciumkarbid kvantumpöttyök előállítása és jellemzése* In: Keresztes Gábor (ed.) Tavasz Szél, 2013: Spring wind, 2013. 659 p. Budapest: Doktoranduszok Országos Szövetsége, 2013. pp. 62-71. (ISBN:978-963-89560-2-6)

T9: David Beke: *Kvantumpöttyök – biológiai képkalkotás*, Természet Világa, **145(9)**, 396 (2014)

Conference Presentations

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

T11: [oral] Oláh György PhD. Conference, Budapest, Hungary (2015). *Szilíciumkarbid alapú nanoklaszterek előállítása és jellemzése*

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

T13: [oral] E-MRS Spring Meeting and Exhibit, Lille, France, (2014) *Silicon Carbide Quantum Dots: Properties and Application*

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

T15: [oral] Spring Wind Ph.D Conference, Debrecen, Hungary (2014), *Szilíciumkarbid kvantumpöttyök időfelbontásos lumineszcencia-spektroszkópiás vizsgálata*

T16: [oral] NanoValid Training and Workshop, Zaragoza, Spain (2013), *Luminescence Silicon Carbide Quantum Dots*

T17: [oral] Spring Wind Ph.D Conference, Sopron, Hungary, *Lumineszcens Szilíciumkarbid Kvantumpöttyök előállítása és jellemzése*

T18: [oral] Francelab Scientific Days, Budapest, Hungary (2013), *Lumineszcens szilícium-karbid kvantumpöttyök: jellemzés és lehetséges alkalmazások*

- T19: [oral] SIWAN5, Szeged, Hungary (2012), *Luminescent Silicon Carbide Quantum Dots Prepared by Reactive Bonding and Subsequent Wet Chemical Etching: Characterization and Potential Applications*
- T20: [oral] 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: [poster] SIWAN6, Szeged, Hungary (2014.), *Time-Resolved Luminescence Spectroscopy of Silicon Carbide Quantum Dots*
- T22: [poster] FQDots14, Oxford, UK, (2014.), *Surface-Dependent Optical Properties of Silicon Carbide Quantum Dots*
- T23: [poster] Oláh György PhD. Conference, Budapest, Hungary (2014), *Szilíciumkarbid-alapú festékpróbák*
- T24: [poster] ACIN2013 Namur, Belgium (2013), *Preparation of small silicon carbide quantum dots by wet chemical etching*
- T25: [poster] Oláh György PhD. Conference, Budapest, Hungary (2012): *Silicon Carbide Quantum Dots for bioimaging and Sensing*
- T26: [poster] MRS 2012 Spring Meeting, San Francisco, USA, *Luminescent Silicon Carbide Quantum Dots Prepared by Reactive Bonding and Subsequent Wet Chemical Etching*

Further Publications

T27: David Beke, Zsolt Szekrényes, István Balogh, Miklós Veres, Éva Fazakas, Lajos K. Varga, Katalin Kamarás, Zsolt Czigány, and Adam Gali, *Characterization of luminescent silicon carbide nanocrystals prepared by reactive bonding and subsequent wet chemical etching*. Appl. Phys. Lett. **99**, 213108 (2011).

IF: 3.302; C: 24

T28: Zsolt Szekrényes, Bálint Somogyi, Dávid Beke, Gyula Károlyházy, István Balogh, Katalin Kamarás, and Adam Gali, *Chemical Transformation of Carboxyl Groups on the Surface of Silicon Carbide Quantum Dots*. J. Phys. Chem. C. **118**, 19995–20001 (2014).

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T29: Gabriella Dravec, László Bencs, Dávid Beke, and Ádám Gali, *Determination of silicon and aluminum in silicon carbide nanocrystals by high-resolution continuum source graphite furnace atomic absorption spectrometry*. Talanta. **147**, 271–275 (2016).

IF: 3.545; C: 1

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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