Nonlinear Optical Properties of Silicon Carbide (SiC) Nanoparticles by Carbothermal Reduction

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ABSTRACT

SiC nanoparticles by carbothermal reduction show promising properties in terms of second harmonic and multiphoton excited luminescence. In particular, we estimate a nonlinear efficiency \(\delta = 17 \text{ pm/V}\), as obtained by Hyper Rayleigh Scattering. We also present results of cell labelling to demonstrate the potential use of SiC nanoparticles for nonlinear bioimaging by simultaneous detection of second harmonic and luminescence.

Keywords: Semiconductor Nanoparticles; Multiphoton Microscopy; Second Harmonic Generation; Cell Labelling

1. INTRODUCTION

In this paper we investigate Silicon Carbide (SiC) nanoparticles as potential biomarkers for multiphoton imaging. SiC is known as a wide bandgap semiconductor with excellent electronic characteristics that allow this material to be used in high-temperature, high frequency, and high-power electronic devices. Very conveniently, in view of applications, both silicon and carbon are abundant elements and SiC can be produced cost efficiently, a significant advantage compared to materials composed of noble metals and rare earths.\(^1\)

The original optical properties of SiC nanostructures have led to various promising applications as light-emitting agents.\(^1,2\) Contrary to bulk SiC materials, in the case of low-dimensional SiC NPs, the relatively high quantum efficiency of luminescent SiC NPs is mainly due to quantum confinement of photo-generated excitons in nanometer-scale crystalline structures. T. Serdiuk et al. have shown that small SiC NPs(\(\leq 5\text{ nm}\)) easily penetrate inside cells membranes and can be used for one photon excited fluorescence bioimaging.\(^3\) Measurements of the
nonlinear efficiency of bulk SiC suggest relatively high nonlinear SHG coefficients (≈ 10 pm/V).\(^4\) and commercial SiC NPs with size between 50-80 nm were first tested as multiphoton labels by the Fraser group.\(^5\)

In this paper, we investigate Second Harmonic Generation (SHG) and Two-Photon Excited Fluorescence (TPEF) from SiC nanocrystals by carbothermal reduction in order to describe their multimodal response. The results presented in this paper show that SiC nanoparticles have high optical nonlinear efficiency and are suitable imaging probes for SH imaging and benefits from the advantages related to this approach: signal photostability, wavelength flexibility, and narrow-band emission.\(^6\)

2. METHODS AND RESULTS

2.1 Synthesis

SiC NPs samples were obtained by carbothermal reduction from amorphous silica, sucrose, and citric acid (only for water quantity reduction). All the raw materials have been mixed in deionized water for 1 hour and dried to form white pellets which have then been carbonized at 240°C. As a result of the carbonization step, a dark brown powder was obtained. Finally, white nanostructured SiC nanopowder constituted by sub-micrometric NPs has been synthesised in a furnace after high temperature treatment of the carbonised powder at 1420°C in mid vacuum under Ar flow and continuous mixing.
2.2 Nanoparticles characterization

The X-Ray Diffraction and Raman spectra in Fig. 1 unambiguously associate to the sample a 3C crystal structure, which is associated with noncentrosymmetric 43m symmetry and therefore to a non vanishing second order susceptibility, $\chi^{(2)}$. Dynamic light scattering (DLS) shows that the mean size by number is approximately 160 nm.

Having a size larger than one hundred nanometers, the SiC nanoparticles used here are much larger than those NPs used before by T.Serdiuk et al. Contrary to TPEF from small(<10nm) SiC nanoparticles which is ascribed to quantum confinement and SH from <30 nm particles, which could be dominated by surface contributions, the SH and TPEF emission of this sample is expected to come essentially from bulk.

Figure 1D shows the linear absorbance and photoluminescence spectra of SiC nanoparticles in eV. For a reference, the maximum of one-photon absorption is at 300 nm, while the photoluminescence peak is located at 800 nm.

2.3 Determination of nonlinear efficiency on colloidal ensembles

Hyper Rayleigh Scattering is an experimental technique which has been recently used to characterize the second order nonlinear efficiency of several nanomaterials. Following the procedure described in references, HRS measurements were performed on SiC nanoparticles colloidal suspensions. The experimental set-up is based on a vertically polarized YAG laser ($\lambda=1064$nm) focused on the suspension. SHG intensity is collected at 90° from the excitation beam with a photomultiplier. For this set of measurement, a vertical polarizer is placed in front of the detector.

HRS results from the incoherent second harmonic signal emitted by each nanocrystal and is proportional to the nanoparticles concentration $N$. Moreover, in this analysis we assume that the second harmonic signal originates from the nanocrystal bulk contribution given their comparatively large size. As a result, HRS intensity is proportional to the squared nanoparticle volume, $V_{np}^2$.

$$I_{HRS} \propto N \langle d^2 \rangle V_{np}^2 I_{\omega}^2$$  \hspace{1cm} (1)

Knowing the mean particle size and suspension concentration from DLS and weighing measurements, the averaged SHG coefficient $\langle d \rangle$ was estimated at 17 pm/V. 3C SiC (43m point group) has only one nonzero nonlinear coefficient $d_{14}$. The average SHG experimental coefficient $\langle d \rangle$ is related to $d_{14}$ by

$$\langle d \rangle = \sqrt{\frac{12}{35}} \times d_{14}$$  \hspace{1cm} (2)

Thus, we can estimate the nanoparticle value at $d_{14} = 29$ pm/V pointing to a relatively strong SHG efficiency compared to other nanomaterials.

Two-photon microscopy of SiC HNPs

The imaging set-up we employed is based on a Nikon A1R-MultiPhoton inverted microscope coupled with a Spectra-Physics Mai-Tai tunable laser oscillator (100 fs, 80 MHz, 700-1100 nm). Four independent non-descanned detectors acquire in parallel the epi-collected signal spectrally filtered by four tailored pairs of dichroic mirrors and interference filters. In general, SiC nanoparticles show a strong nonlinear optical response. Figure 2 demonstrates that SiC nanoparticles simultaneously emit SHG and TPEF upon 720 nm excitation. Notice that, as SH emission is a non-resonant process, variable excitation wavelength can be used. The spectral density SHG at 485nm is approximately two orders of magnitude larger than that of TPEF (for a multiphoton excitation at 720 nm). Please note that according to the one-photon absorbance spectrum(Fig. 1D) 720 nm laser excitation is not the most efficient for TPEF generation of SiC. Practically, by adjusting the microscope detectors’ settings it is straightforward to simultaneously record the second harmonic signal and two-photon excited fluorescence of SiC nanoparticles. The possibility of emitting two spectrally different signals allow SiC nanoparticles to be used as correlative probes for multiphoton microscopy increasing selectivity against background.
Figure 2. Nonlinear microscopy image of SiC nanoparticles on a bare substrate. Excitation: 720 nm. A) blue (SH): 360/12 nm; b) green (TPEF): 485/20 nm; c) yellow (TPEF): 525/50 nm; d) red (TPEF): 607/70 nm

Figure 3 demonstrates the possibility of using SiC nanoparticles for cell labelling. For this assessment, we used 3T3-L1 fibroblast cells and SiC NPs at 0.25 mg/ml concentration. In this case laser excitation was set to 790 nm. In the images, blue corresponds to SHG (detected at 395 nm), and three combined colours (green - 485 nm, yellow - 525 nm, and red - 607 nm) correspond to TPEF from SiC nanoparticles and cells. The morphology of cells can be seen by their autofluorescence, in green. The fact that some SiC nanoparticles can be detected only...
Figure 3. Cells labelled with SiC P5 nanoparticles. Excitation 790nm. Blue corresponds to SHG signal (395 nm), other colors correspond to the two-photon luminescence. Cell autofluorescence in green.

by their TPEF signal can be explained by size dependence of second harmonic emission. As SHG is proportional to $V^2 \propto R^6$ and the TPEF signal is proportional to $V \propto R^3$ the smaller particles might yield a stronger TPEF than SHG. In addition, the SH signal strongly depends on individual HNPs orientation in space.\(^{16}\)

3. CONCLUSIONS

SiC nanoparticles show promising properties in terms of SHG and TPEF. SiC has a high nonlinear efficiency $\langle d \rangle = 17$ pm/V, as obtained by Hyper Rayleigh Scattering measurements. The first tests of cell labelling show the potential use of SiC nanoparticles for nonlinear bioimaging.

Further studies should address biocompatibility of SiC nanoparticles, obtained by carbothermal reduction method. Recent studies indicated that while SiC nanoparticles, obtained by laser pyrolysis or solgel methods do not exert cytotoxic effects, they can lead to proinflammatory response and/or oxidative stress.\(^{17,18}\) Such effects are related most probably to physicochemical features of the SiC NPs with size $< 10$ nm, which are known to interact differently than large ones with cell membranes. In fact, contrary to $>50$nm NPs which are actively uptaken by endocytosis small NPs can penetrate directly through the membrane. Interestingly, T. Serdiuk et.al. have shown that SiC NPs with size $< 10$nm can be selectively located in the nucleus or cytoplasm by modifying its surface charge.\(^3\)

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