

Probing the Optical Response of Functionalized Silicon Nanocrystals with Soft X-rays

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Introduction

The optical properties of silicon nanomaterials that result from quantum confinement effects have been shown to have great potential in a variety of applications [1]. In particular, silicon nanocrystals are expected to have superior biocompatibility in comparison to other compound semiconductor quantum dots and therefore are of notable relevance for *in vivo* imaging applications.

For incorporation into biological

applications, silicon nanocrystals require surface modification through functionalization reactions. However, in most reported cases, these surface-modification techniques have resulted in unpredictable changes in the optical properties. Surface effects such as surface oxides, aggregation and solvent-quenching are thought to alter their optical properties, however their significance and specific roles remain unresolved.

X-ray excited optical luminescence (XEOL) is a valuable technique in characterizing the origin of emission in luminescent materials. In particular, it has had a significant impact in characterizing the optical properties of silicon nanomaterials [2]. By providing a simultaneous comparison of X-ray absorption and optical emission data, it yields information on the local chemical and electronic structure of the sites that give rise to luminescence within a sample.

The Veinot Group at the University of Alberta has developed a facile synthesis for oxide-embedded silicon nanocrystals [3]. In addition, we have developed procedures for liberating and functionalizing these nanocrystals in a controlled and predictable manner. These functionalized materials provide the basis for a comprehensive study on surface chemistry's role in the optical properties of silicon nanocrystals using near-edge X-ray absorption fine structure (NEXAFS) and XEOL analysis. The spherical grating monochromator (SGM) beamline 11ID-1 is ideal for this investigation as it provides high energy resolution and photon flux over the 1s absorption edges of interest: 543 eV and 1839 eV for oxygen and silicon, respectively.

Experimental

Oxide-embedded silicon nanocrystals were prepared by the thermal processing of hydrogen silsequioxane (HSQ) [3]. In brief, solid HSQ was heated to 1100°C for 1 hour under a 5% H₂ and 95% Ar atmosphere. The resulting composite material was etched with hydrofluoric (HF) acid to yield freestanding, size-controlled silicon nanocrystals. Immediately following

etching, the nanocrystals were functionalized with styrene via a photochemically-initiated hydrosilylation reaction.

The X-ray fluorescence yield (FLY) was measured using a channel plate detector positioned at a 45° angle to the sample, at a step size of 0.1 eV with an exit slit width of 50 μm. All spectra were calibrated to a silicon wafer standard by setting the first derivative maximum of the Si *K*-edge absorption to 1839 eV. XEOL measurements were collected by setting the monochromator to 1841 eV and opening the exit slit width to 400 μm to maximize flux. Optical luminescence spectra were collected through a lens coupled to an Ocean Optics spectrometer with a detector range of 200-1000 nm. Freestanding samples were drop-coated from pentane solutions on to aluminium discs. Powder samples were mounted on carbon tape.

Discussion

Figure 1 shows the silicon *K*-edge NEXAFS spectra for a variety of freestanding and oxide-embedded silicon nanocrystals. Oxide-embedded silicon nanocrystals (trace A), show two key features, arising from an elemental silicon absorption (~1841 eV) comprising the nanocrystal core and an absorption corresponding to the SiO₂ matrix (~1848 eV). After dissolution of the matrix and etching of the nanocrystals with HF, the absence of any spectral feature apart from the elemental silicon edge (~1839 eV) suggests the complete removal of all oxide species in the liberated hydride-terminated nanocrystals (trace B). If exposed to ambient conditions, these nanocrystals

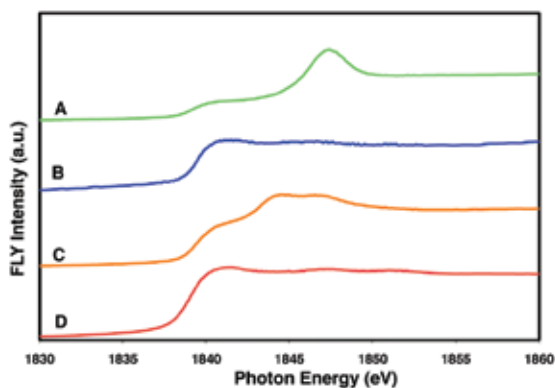


Figure 1: Normalized silicon *K*-edge NEXAFS spectrum (FLY) for A) oxide-embedded silicon nanocrystals, B) silicon nanocrystals etched with hydrofluoric acid, C) silicon nanocrystals functionalized with styrene and D) bulk silicon standard.

quickly oxidize, leading to an uncontrollable shift in their optical response. Functionalizing these hydride-terminated nanocrystals with styrene leads to a stable luminescence.

The functionalized nanocrystals show an elemental silicon absorption (~ 1841 eV), an absorption corresponding to SiO_2 (~ 1848 eV), along with a third feature at ~ 1844 eV (trace C). While the feature at 1848 eV suggests the formation of a SiO_2 -like surface-oxide on the nanocrystals during functionalization, the feature at 1844 eV may result from either the formation of suboxides (SiO_x , $0 \leq x \leq 2$) or from a new Si-C species formed during functionalization. The identification of this species is a topic of ongoing investigation.

Figure 2 shows the XEOL spectra of silicon nanocrystals excited at the elemental silicon *K*-edge absorption (1841 eV). Exciting oxide-embedded silicon nanocrystals results in an intense low-energy emission band centred at ~ 800 nm (trace A). Upon removal of the oxide matrix and reduction of the nanocrystal size via HF etching, this emission shifts to higher energy (~ 690 nm, trace B). Since elemental Si remains the only species present, as shown in the NEXAFS spectrum trace B, this shift as a function of decreasing crystal size is indicative of quantum confinement effects. After functionalization, the emission is further shifted to higher energy (~ 600 nm, trace C).

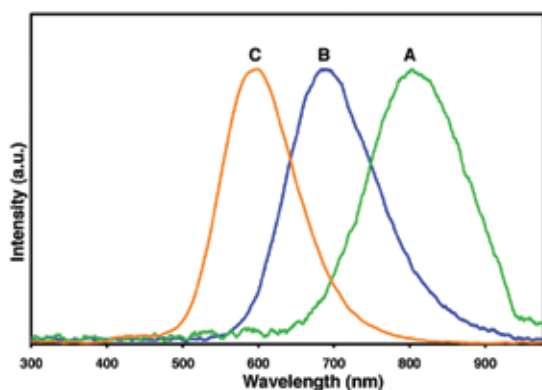


Figure 2: Normalized XEOL spectra of A) oxide embedded silicon nanocrystals, B) silicon nanocrystals etched with hydrofluoric acid and C) silicon nanocrystals functionalized with styrene. All samples were excited at 1841 eV, the energy corresponding to the elemental silicon *K*-edge absorption.

This shift may be a result of a combination of several factors: quantum confinement effects from the reduction in crystal size due to surface oxidation; the influence of organic surface species; and trapping of carriers in localized oxygen-related interfacial species have all been theorized to play a role in the optical response of functionalized silicon nanocrystals [4].

Conclusion

The use of soft X-rays as a probe for NEXAFS and XEOL spectroscopy has provided insight into luminescence from functionalized silicon nanocrystals. The identification of silicon species by FLY offers advantages over other techniques, including infrared spectroscopy and X-ray photoelectron spectroscopy, which suffer from interference effects and lower sensitivity, respectively. This report is believed to be the first silicon *K*-edge X-ray absorption study on functionalized silicon

nanocrystals. These preliminary results suggest that a variety of surface species are present, though the role these species play in luminescence is still unclear. Through further NEXAFS and XEOL analyses, we can understand the magnitude of these contributions, leading to new methods for a predictable and controlled optical response from functionalized silicon nanocrystals for *in vivo* applications.

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Acknowledgements

The Natural Sciences and Engineering Research Council (NSERC) of Canada supported this work through Discovery Grants to JGCV. We also thank Mr. Tom Regier and Dr. Robert Blyth for NEXAFS and XEOL measurements on the SGM beamline (11ID-1) at the CLS.