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Abstract

A solution method for preparing surface functionalized colloidal silicon quantum dots (SiQDs) is presented. SiQDs prepared by this method are reasonably monodispersed and can be further functionalized via thiol-ene click reactions to introduce specific functionalities (i.e. -NH₂, -COOH, -SO₃⁻, alkane, alkene).

Keywords

click, ene, thiol, via, chemistry, functionalization, one, surface, dots, quantum, silicon, colloidal, synthesis, pot

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COMMUNICATION

One-pot synthesis of colloidal silicon quantum dots and surface functionalization *via* thiol–ene click chemistry†Xiaoyu Cheng,^a Richard Gondosiswanto,^a Simone Ciampi,^a Peter J. Reece^b and J. Justin Gooding^{*a}

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A solution method for preparing surface functionalized colloidal silicon quantum dots (SiQDs) is presented. SiQDs prepared by this method are reasonably monodispersed and can be further functionalized *via* thiol–ene click reactions to introduce specific functionalities (*i.e.* $-\text{NH}_2$, $-\text{COOH}$, $-\text{SO}_3^-$, alkane, alkene).

Semiconductor nanocrystals, or quantum dots (QDs) with distinct optical features have attracted tremendous research attention in the past twenty years.¹ Major optical features of quantum dots include broad absorption spectrum, size-dependent emission spectrum, long fluorescence lifetime, high quantum yield and high stability against photobleaching.² QDs have therefore found potential applications in a range of technological fields, including optoelectronic devices, solar cells and fluorescent labelling agents in biomedicine.^{3–5} An issue for *in vivo* applications of conventional QDs is their potential toxicity, and therefore safety problems associated with the use of heavy metal elements in these nanoparticles.⁶ Short term cytotoxicity of conventional II–VI QDs (*e.g.*, CdS, CdSe, CdTe) has been controversial, with different levels of toxicity reported across the literature.⁶ Nonetheless, it was shown that QDs accumulate in organs such as liver, spleen and kidneys for at least 90 days once inside the body.⁷ It is therefore important to develop QDs with good optical properties but composed of materials with low cytotoxicities.

Crystalline silicon is bio-compatible in its various forms,⁸ and can be luminescent when its dimension approaches the exciton Bohr radius.⁹ These features make silicon nanocrystals one of the most promising candidates as benign QDs. Freshly prepared SiQDs surfaces are usually covered with Si–H bonds. These Si–H bonds degrade oxidatively in aqueous media,¹⁰ and surface modification is necessary to stabilise the SiQDs in order to retain their optical properties, while also allowing the introduction of further functionalities.¹¹ Among the various methods for preparation of nanocrystals, solution based synthetic procedures are attractive as they offer simultaneous control of particle size/shape

and surface chemistry. Most available solution methods for the preparation of functionalized SiQDs require surface hydrosilylation reactions, typically using an alkene moiety catalyzed with thermal or UV treatment.^{12,13} In these approaches, highly toxic materials and processes (*i.e.* etching with concentrated hydrofluoric acid solution) are often used.

Previously, Tilley and Yamamoto developed a reverse-micelle method for preparing SiQDs by reduction of halogenated silane precursors using LiAlH_4 , in which no highly hazardous materials were used.¹⁴ It has been shown that the gram scale of oxide-free SiQDs can be prepared by this approach,¹⁵ and the SiQDs are modifiable with molecules possessing a terminal alkene, a terminal group that can be further functionalized.^{16,17} This latter study by Zuillhof and co-workers¹⁷ is particularly relevant for the present study by showing the simple further functionalization of alkene terminated SiQDs using thiol–ene click reactions. Despite the good particle monodispersity, simple experimental procedures given by this procedure, monolayer surface coverage and purification from surfactants can both be problematic.^{16,18} To tackle these problems, Wang *et al.* advanced a method using hexyl-trichlorosilane as both the surfactant and the reactant, showing a fabrication strategy with simplified purification steps.¹⁹ However, the resultant monolayer coated SiQDs were terminated with methyl distal moieties; a surface functionality in which further modification is difficult at best. Therefore only hexane dispersible quantum dots with a hydrophobic surface were made, and the emission peak was restricted largely to the UV region.¹⁹

In view of the above mentioned issues, and using these previous methods as inspiration, we present an efficient one-pot method for fabricating colloidal SiQDs with a modifiable surface (Scheme 1). In particular, allyl trichlorosilane is used as both the surfactant and the reactant, self-assembling around halogenated silane precursors (SiX_4 , $\text{X} = \text{Cl}, \text{Br}$) in toluene (Scheme 1). The formed reverse micelle contains a SiX_4 core and allyl trichlorosilanes, which is then treated with LiAlH_4 to yield SiQDs with alkene groups covering the surface. We further demonstrate that SiQDs prepared by this method can be reacted with thiol bearing molecules, rendering the particles functionalized with a wide choice of distal groups, using the thiol–ene click reaction. By using a range of surface-tethered ω -functionalized alkanethiols, we show that the particles can be dispersed in either aqueous or organic phase, as well as having their emission properties altered.

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Scheme 1 One-pot synthesis of alkene coated SiQDs and further functionalization *via* thiol-ene click chemistry.

Fig. 1 Representative TEM images (a–c) and size distribution analysis (d) showing silicon nanocrystals in 50 nm (a), 20 nm (b) and 2 nm (nm) scale.

The obtained transmission electron microscopy (TEM) images (Fig. 1a–c) show that synthesized SiQDs are reasonably monodispersed, with only small amounts of aggregations seen across the grid. High resolution (HR-TEM) images (Fig. 1c) show lattice structures within the spheres (Fig. 1, middle), indicating that the obtained particles are crystalline. Based on the TEM results, size distribution analysis indicates the average particle size to be 3.68 ± 0.95 nm for allyl functionalized particles (Fig. 1d), with similar results observed for SiQDs with other functional groups (Fig. S1, ESI†).

To study the optical properties of the synthesized SiQDs, UV absorption and photoluminescence (PL) spectra were recorded. In particular, particles absorb mainly in the UV region below 400 nm (Fig. S2, ESI†). This is typical for SiQDs synthesized by similar approaches.¹⁴ The newly synthesized, allyl coated particles showed the emission peak in the UV region at 375 nm with a full width at half maximum (FWHM) of ~ 70 nm, upon excitation at 320 nm (Fig. 2), similar to that observed with similar approaches.^{16,17,19} The emission peak is red shifted with increasing wavelength of the excitation source, which is possibly due to the slight variation of particle size in the system. The high energy emission profile is comparable to what had been observed for oxide-free alkyl terminated quantum dots.² This suggests that the surface defect level is low in particles synthesized by this method, and the allyl group well protects the particle core against oxidation. After the thiol-ene click reaction, as surface alkanethiol molecules with polar or charged end groups are attached on the particle surface, the emission peak is red shifted for 50–70 nm, showing bright

Fig. 2 Photoluminescence (PL) spectra (upper) showing emission of SiQDs with different surface groups (a–e) excited at 320 nm. The lower picture shows change of fluorescence colour and hydrophobicity of the particles upon introduction of surface molecules. Images are taken with UV excitation (365 nm). Each vial contains hexane (upper layer) and H₂O (lower layer) with a particle concentration of 4 mg ml^{−1}.

blue luminescence upon excitation of UV at 365 nm (Fig. 2), the peaks are also broadened with a FWHM of ~ 100 –120 nm. These are in contrast to those of the butane thiol terminated particles, where no significant shift of the emission peak is observed.

To further investigate the effect of surface groups on fluorescence efficiency of SiQDs, the quantum yield (Φ) was obtained using a published method.²⁰ For these measurements the SiQDs fluorescence intensity was referenced against a solution of 2-(4-amidinophenyl)-1H-indole-6-carboxamide (DAPI) which has a reported quantum yield of 4.5%.²¹ The measured quantum yield of newly synthesized, allyl coated quantum dots is measured to be 2.5%. The quantum yield decreases to various extents as thiol groups are attached, with the most significant drop seen with $-\text{COOH}$ terminated particles to be only 0.9% (Fig. S3, ESI†).

Bulk silicon is an indirect band-gap semiconductor, in which direct radiative recombination of the electron–hole pair is difficult. This is due largely to the mismatch of energy states between conduction and valence bands in terms of a k vector in the Brillouin zone.²² However, such radiative processes can take place in nanocrystals, whose dimension approaches the exciton Bohr radius of 4.9 nm and quantum confinement becomes the dominant effect.²³ It has been shown that this process can be affected by a number of factors, including size/shape of the particles, surface structures and the presence of dopants.^{24–26} We therefore attribute the observed change of emission properties to the presence of alkanethiol molecules on the particle surface. For instance, attached alkanethiol molecules may lead to a change of energy levels of the quantum confined states in quantum dots, resulting in red-shifting of the emission peak, as well as a decrease in quantum yield. This is

Fig. 3 IR spectra showing surface thiol molecules.

particularly likely for carboxyl coated dots, which are covered with electron deficient carbon centres across the surface, a similar situation to what was observed recently.²⁷

It is known that surface groups affect the dispersity of nanoparticles in solvents, with good water solubility important in many applications, especially in biological contexts.²⁸ In our case, hexane and water were chosen as representative non-polar and polar solvents to investigate the effect of surface molecules on solvent dispersity. It was found that after being functionalized with alkanes or alkenes, SiQDs were dispersible only in the hexane phase. Upon the introduction of polar distal moieties, SiQDs became completely dispersible in water, with no fluorescence seen from the hexane layer (Fig. 2).

To characterize the alkanethiols attached onto the surface of SiQDs, IR and NMR measurements were performed. IR spectra show distinct bands from the surface molecules attached to SiQDs (Fig. 3). The peak at $\sim 1257\text{--}1268\text{ cm}^{-1}$ is typical for Si–C stretch and is seen in all spectra. After the thiol–ene click reaction, no typical S–H stretch in the region of $\sim 2530\text{--}2590\text{ cm}^{-1}$ is observed, while signature bands associated with the distal groups are seen in all spectra. For allyl terminated SiQDs, the peak at 1630 cm^{-1} indicates C=C stretch due to an allyl group on the surface. The peak disappears after thiol–ene click reaction, which is seen most clearly for butanethiol functionalized molecules. For amine functionalized SiQDs, the broad peak at 3470 cm^{-1} is due to the N–H stretch in the --NH_2 group. The peak at $\sim 1635\text{ cm}^{-1}$ is due to the N–H bending. For carboxyl terminated quantum dots, the peak at 1650 cm^{-1} and the broad peak at 3580 cm^{-1} are due to the C=O stretch and O–H stretch in the --COOH group. For sulfonate functionalized SiQDs, the peak at 1370 cm^{-1} is due to the S=O stretch in the --SO_3^- group. The surface chemistry is further confirmed by $^1\text{H-NMR}$ experiments (Fig. S4, ESI†). In general, the double bond signal that is seen for an allyl group disappears after grafting of alkanethiols, and the proton signal close to the thiol groups is seen after the thiol–ene click reaction. These results provide evidence that the surface molecules are attached to the SiQDs *via* covalent bonds.

In summary, we have shown an efficient one-pot synthetic method for fabricating colloidal silicon nanocrystals in solution. We have demonstrated that SiQDs synthesized by

this method are reasonably monodispersed, and can be further modified with a range of different thiol molecules. This process gives nanocrystals the surface groups in need and good dispersity in water. This advance is important as it provides a simple route by which SiQDs with a range of functionalities can easily be fabricated and we anticipate that such functionalized SiQDs quantum dots can be used for a number of future applications, including in nanomedicine.

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