Efficient one-pot synthesis of highly photoluminescent alkyl-functionalised silicon nanocrystals†

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The chemical reduction of micelles formed by mixing silicon tetrachloride and hexyltrichlorosilane in apolar solvent, where hexyltrichlorosilane serves as both reactant and surfactant, yields brightly luminescent silicon nanocrystals, and enables efficient synthesis of alkyl-functionalised silicon quantum dots (SiQDs) in a single step.

Semiconductor quantum dots have attracted great attention in the fields of industry and academy owing to their excellent optical and electronic properties such as broad absorption spectra, size-tunable and narrow fluorescent wavelength, high quantum yields, and very low photobleaching rate.1–3 Because of these unique advantages, quantum dots are obviously superior to organic dye in many applications including in lasers, medical biology and photodetectors.4–10 So far, group II–VI quantum dots such as CdX (X = S, Se, Te) have been well investigated due to their strong luminescence. However, their toxicity to cells11,12 limits their applications in biological areas.

Unlike traditional II–VI materials, the group IV semiconductor silicon is nontoxic, cheap, biocompatible, and electrochemically stable, and an essential material in the electronics industry. SiQDs are very useful for biological applications.13–16 Currently, a variety of physical and chemical methods have been reported for the synthesis of size-controlled and surface-functionalised SiQDs, such as chemical vapor deposition, plasma synthesis, electrochemical etching of crystalline silicon wafers, hydrofluoric (HF) acid etching from amorphous silicon oxide powders or pure silicon powders, and so on.13–18 However, these methods require specific chemicals, some of which are quite hazardous. In recent years, there have been a few researchers reporting the reduction of reverse micelles of SiCl4 by LiAlH4,17 resulting in almost monodispersed particles with Si–H terminated surfaces. The stability of the as-obtained nanoparticles can be improved by further modification generally using a Pt-catalyzed hydrosilylation process to form chemically robust Si–C bonds on the surface.19 This approach has a few advantages over others, e.g., no special apparatus is needed, and the use of extremely toxic HF is avoided. However, the removing of the abundant surfactant from the synthesised SiQDs is not a tribute job, and the adsorbed Pt2+, which is the catalyst for surface modification of SiQDs, is still toxic to cells. Efficient synthesis and stabilization of SiQDs to enable its wide applications is still challenging.

In this study, we demonstrate a one-step synthesis of highly monodisperse, alkyl-capped, brightly luminescent nanocrystals using hexyltrichlorosilane as both surfactant and reactant. The overall synthetic procedure is illustrated in Scheme 1. Hexyltrichlorosilane and silicon tetrachloride were mixed to form micelles in apolar solvents. Hexyltrichlorosilane, as a surfactant, self-assembled outside the SiCl4 core. Upon addition of the reductant, LiAlH4, the Si–Cl bonds in both SiCl4 and hexyltrichlorosilane were reduced and Si–Si bonds were formed in the micelles, while the Si–C bond in the hexyltrichlorosilane remained. Hexyl-capped silicon nanoparticles were therefore obtained from the room temperature reduction of Si–Cl bonds with LiAlH4. All the steps were carried out in an ultrasound sonication apparatus, and offered a route for the facile synthesis of alkyl-capped SiQDs. A large family of trichlorosilane with various alkyls and alkene or other group may be suitable for this procedure, resulting in the Si–C surface-bond capping of SiQDs with potential for further functionalisation.

Quantum-confinement effects can significantly enhance photoluminescence when the physical dimension of silicon nanoparticles is close to the bulk silicon exciton Bohr radius of about 4 nm.17,20 At this size scale, the ratio of surface to inner silicon atom is approximately one to the stability. The as-obtained

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Table of Contents Entry

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Scheme 1 Illustration for the procedure of the one-pot synthesis of hexyl-capped Si quantum dots.
The hexyltrichlorosilane/SiCl4 molar ratio was set to 1/1 for our experiment.

We first confirmed the formation of micelles in the pre-reacting solution by the dynamic light scattering (DLS) measurements shown in Fig. 1a, which revealed the presence of hexyltrichlorosilane/SiCl4 micelles in toluene. The size of the micelles was 7 ± 1 nm with narrow dispersion. The DLS data shown in Fig. 1b was obtained after the reduction of the micelles with LiAlH4 at room temperature. We noted the presence of two peaks and the peak ratio indicated that the size of the vast majority particles was 5.7 ± 2.1 nm in diameter including the alkyl surface, and this result agreed reasonably with transmission electron microscopy (TEM) measurements, as shown in Fig. 2a and b. The TEM images revealed that the alkyl-capped nanoparticles have an average diameter of 3 ± 0.5 nm, and the distribution of particle size was comparable with that obtained using a similar method, no aggregation of the nanoparticles was observed. Moreover, high-resolution TEM (HRTEM) measurements (Fig. 2b inset) showed that the small particles are crystalline.

If hexyltrichlorosilane was not added, although SiCl4 can still form micelles in toluene, the size distribution of the micelles was rather wide and was dependent on the sonication strength. On the contrary, the reduction of SiCl4 free micelle system, resulted in smaller SiQDs with diameters of 2 ± 0.5 nm and relatively narrow size distribution, as shown in Fig. 2c and d. This suggested that hexyltrichlorosilane alone formed smaller micelles in toluene and it is hypothesised that the sizes of SiQDs decreases as the hexyltrichlorosilane concentration increases.

The optical properties of the hexyl-terminated silicon nanocrystals were investigated using UV-visible and photoluminescence (PL) spectroscopy (Fig. 3 upper). The UV-vis spectrum of the silicon nanoparticles dispersed in hexane gives an absorption band ranging from 320 to 380 nm. The fluorescence emission spectra were collected for excitation wavelengths between 320 and 400 nm. A photoluminescence excitation (PLE) spectrum, which was collected by fixing the detection at 420 nm, is shown in Fig. 3 (upper). Several PLE bands were observed, as a result of a combination of factors including complex surface chemistry and crystal lattice structure. Photoluminescent quantum yields were determined by methods adapted from the work of Sankaram et al., using a comparative method which employs a quinine sulfate emission standard. PL emission spectra of quinine sulfate and hexyl-capped SiQDs were collected for various dilutions. The integrated emission intensity for each sample is plotted in Fig. 3 (lower) versus the corresponding UV-vis absorbance at the same excitation wavelength. The quantum yield of hexyl-capped SiQDs was determined by the comparative method using a quinine sulfate emission standard.

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**Fig. 1** DLS measurements of the (volume) distribution function of hexyltrichlorosilane/SiCl4 micelles (a) and hexyl-capped SiQDs (b) in toluene.

**Fig. 2** (a) and (b): TEM images of hexyl-capped SiQDs obtained from the reduction of hexyltrichlorosilane/SiCl4 micelles, inset of (b): a HRTEM image of an individual silicon nanocrystal. (c) and (d): TEM images of hexyl-capped SiQDs obtained from the reduction of hexyltrichlorosilane in toluene without adding SiCl4.

**Fig. 3** (Upper) Room temperature UV-vis absorbance, excitation wavelength dependence of PL emission, and detection at 420 nm of PL excitation spectra of hexyl-capped silicon nanocrystals dispersed in hexane. Inset, the photograph of the obtained SiQDs dispersed in hexane under illumination of UV light. (Lower) Integrated PL intensity versus absorbance for multiply diluted SiQDs in hexane and for various dilutions of quinine sulfate in 0.05 M H2SO4 under identical excitation conditions.
SiQDs at 340 nm was calculated to be 25% at room temperature from the ratio of the slopes of the linear fits to quinine sulfate and SiQDs, and the known quantum yield of quinine sulfate (54.6%) at 340 nm, as reported previously. It is as high as 23% which was reported in the literature about organic molecules terminated SiQDs. The exhibited excellent photoluminescent properties are not surprising and may contribute to the "in situ passivation" during the synthesis of the SiQDs, in which the hexyltrichlorosilane reduced to the corresponding heksylsilane and capped on the surface of SiQDs during its formation. This approach can potentially minimise the surface oxidation of SiQDs compared to the use of a conventional micelle method, in which the hydrogen-passivated SiQDs, inevitably exposed to oxygen, reduced the defect on the surfaces.

The surface chemistry of the hexyl-functionalised silicon nanoparticles was investigated by IR spectroscopy (Fig. 4). The spectrum reveals characteristic C–H stretching signals, with the symmetric CH2, antisymmetric CH2, and asymmetric CH3 stretching vibrations at 2854, 2925, and 2961 cm\(^{-1}\), respectively. Two peaks observed at 1461 and 1261 cm\(^{-1}\) are attributed to the scissoring and stretching vibration bands of Si–C bonds. These peaks indicate that the hexyl groups from the raw material are covalently attached to the surface of the quantum dots. However, owing to the polarity of the Si–O bond, the signals at 1097 and 1022 cm\(^{-1}\) were easily shown in the IR spectrum of alkyl-coated silicon nanoparticles. The surface oxidation may be resulting from the incomplete hexyl-passivation of the SiQDs, in which the hexyltrichlorosilane reduced to the corresponding heksylsilane and capped on the surface of SiQDs.

In summary, we have developed an efficient method for the preparation of monodispersed and alkyl-capped silicon quantum dots with high quantum efficiency. This procedure is very attractive because it offers a facile approach for the synthesis and surface modification with organic molecules of silicon nanocrystal in one single step. In addition, since this approach does not require any other surfactants or other toxic chemicals to be involved, isolation and purification of the resulting SiQDs is easier to perform. We envisage the method we reported here will expedite the application of SiQDs in a number of fields.

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Notes and references