PEGylated silicon nanoparticles: synthesis and characterization†

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**Silicon nanoparticles were prepared and functionalized with alkene-terminated poly(ethylene oxide) to impart amphiphilic solution properties to the particles.**

Semiconductor nanoparticles possess size dependent optical and electronic properties emanating from quantum confinement effects. Reports on the synthesis and properties of type II–IV (e.g., CdSe and CdTe) and III–V (e.g., GaN and InP) particles are extensive.[1,2] Technological applications of such particles include light emitting diodes, solar cells, single electron transistors, liquid crystals, and nanoscale fluorophores for biological imaging.[3–9] For fluorescent semiconductor quantum dots such as cadmium selenide, surface coverages consisting of small organic molecules or polymers, as well as lattice-commensurate inorganic coatings, are used to control solution properties and brightness, and mask the inherent toxicity of cadmium. The fluorescent properties of silicon nanoparticles are also of interest for sensing and tagging applications, and the lower toxicity of silicon makes such particles attractive.[10] However, far fewer reports center on silicon nanoparticles relative to other fluorescent particles. Here we describe efforts to apply surface functionalization, specifically PEGylation, to silicon nanoparticles, making them soluble in both organic solvents and aqueous environments.

Recently, silicon nanoparticles covered with alkyl groups, dispersible in organic solvents, were reported by Kauzlarich and co-workers,[11] and silicon nanoparticles covered with allyl amine groups, dispersible in water, were reported by Tilley and coworkers.[12] We are interested in developing a photostable, polymer encapsulated silicon nanoparticle with diverse utility derived from its solubility in both water and organic solvents. PEG-functionalization of nanoparticle surfaces provides such amphiphilic character.[13,14] As silicon nanoparticles are not generally amenable to metal–ligand coordination chemistry (as for example the cases of gold nanoparticles and quantum dots) a covalent functionalization of the Si–H groups, or micellar-like encapsulation with amphiphiles,[10] is required.

As shown in Scheme 1, the silicon nanoparticles used in this study were prepared by reduction of silicon tetrachloride using lithium aluminum hydride (LAH) in the presence of tetra-octylammonium bromide (TOAB).[12] To prepare the reactive PEG derivative, we chose etherification of PEG-1100 monomethylether with 1-undecenyl bromide to provide PEG with
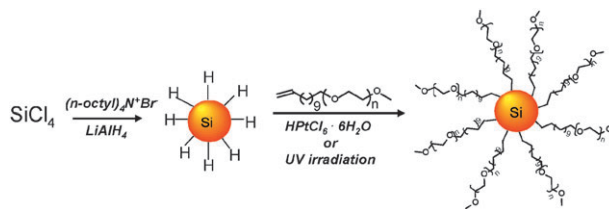
Scheme 1

an alkene chain end.‡ Hydrosilylation of the Si–H terminated silicon nanoparticles with alkene-terminated PEG-1100 was then performed by the two different methods shown in Scheme 1. In one case, the addition of olefins to the surface Si–H groups was carried out in the presence of chloroplatinic acid catalyst.[15] In the second case, a solution of silicon nanoparticles was irradiated at 290 nm in the presence of the PEG–alkene for two hours.[16] The exciton mediated addition of olefins to porous silicon was described in detail by Buriak and co-workers.[17] The PEGylated silicon nanoparticles obtained through these two methods were extracted into water and characterized by a variety of methods, including transmission electron microscopy (TEM), which shows low size dispersity, and average diameter $\sim$2 nm (synthesis of PEG–alkene‡).†

Successful nanoparticle PEGylation was suggested from the optically clear solutions obtained upon dissolving the particles in many good solvents for PEG, including water, methanol, and chloroform. Importantly, the PEGylated nanoparticles could be stored as solids, then redispersed readily into the same solvents. Fig. 1 shows fluorescence emission spectra recorded on solutions of the silicon nanoparticles after isolation from the reaction mixture. Aqueous particle solutions gave a broad UV–Vis absorbance spectrum, with a shoulder at 320 nm characteristic of silicon nanoparticles. The large blue shift ($\sim$0.4 eV) in the nanoparticle spectrum relative to bulk silicon is due to quantum confinement of electrons in the nanoparticles. Fluorescence spectroscopy of the PEGylated
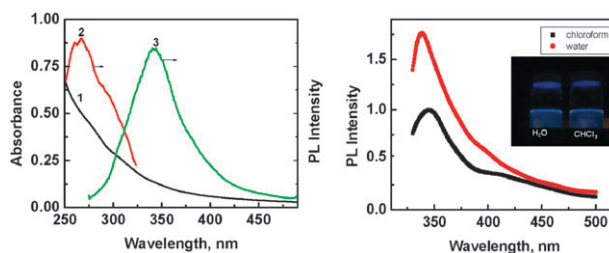

Fig. 1 left: absorption (1), excitation (2), and emission (3) spectra of PEGylated Si nanoparticles in water; right: fluorescence and photographs of aqueous and chloroform solutions of PEGylated Si nanoparticles.

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† Electronic supplementary information (ESI) available: TEM image of silicon nanoparticles. See DOI: 10.1039/b813025f
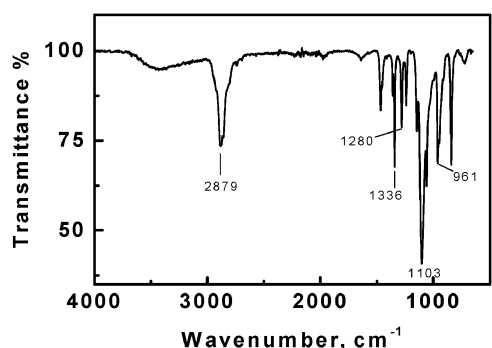
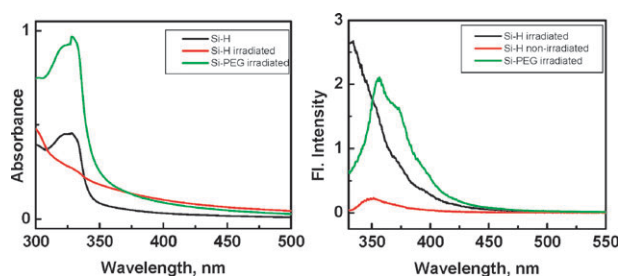**Fig. 2** FTIR spectrum of PEGylated silicon nanoparticles.

Fig. 3 Absorption spectra (left) and emission spectra (right) of silicon nanoparticles irradiated in the presence and absence of PEG–alkene **1**.

silicon nanoparticles in water revealed a blue luminescence centered at 350 nm. The fluorescence of these nanoparticles originates from the direct band gap optical transitions, and is consistent with predicted transitions for silicon quantum dots terminated with organic molecules.[18,19] The absence of a longer wavelength emission peak (>500 nm) indicates a homogeneity to the surface functionalization, and absence of substantial surface oxidation.

Covalent attachment of PEG to the nanoparticle surface, by the formation of C–Si bonds, was confirmed by FTIR spectroscopy, as shown in Fig. 2. The observed peaks at 1467 and 1280 cm^{-1} are attributed to vibrational scissoring and symmetric bending, respectively, of the Si–CH$_2$ group.[11] The spectral region between 1150 and 1050 includes vibrational bands due to C–O–C stretching from the PEG corona, and the PEG C–H stretching is seen at $\sim$2879 cm^{-1}.

The solution photostability of PEGylated Si nanoparticles was compared with particles containing the Si–H periphery following their synthesis (which surface oxidize over time). Two equimolar silicon nanoparticle solutions were prepared in quartz tubes, one containing PEG–alkene **1**, and the samples were irradiated at 290 nm (40 mJ cm^{-2}) for two hours in a nitrogen atmosphere. This led to a broadening of both the absorption and emission spectra of the unfunctionalized particles, as a result of ripening or aggregation. However, for the PEGylated particles prepared by this method, the breadth of the absorption and emission spectra changed little, and an increase in fluorescence intensity was observed, likely due to surface passivation effects associated with ligand functionalization. The PEGylated silicon nanoparticles retain their initial absorption and emission features even after continued irradiation for several hours. Fig. 3 compares these spectral properties of the silicon nanoparticles.

In summary, we have prepared and characterized photo-stable amphiphilic Si nanoparticles containing a PEG-corona. The rich application-base associated with PEGylation makes these particles promising for a diverse range of materials and cell culture applications.

Notes and references

‡ *Synthesis of PEG–alkene* **1**: A degassed aqueous NaOH solution (50%, 300 µL) was added slowly to PEG-1100 monomethylether (8.8 g, 8 mmol) under nitrogen atmosphere at 90 °C. Heating was continued for 45 min. 11-Bromo-1-undecene (95%, 3.6 mL) was added, and the mixture was refluxed for 12 h. The mixture was cooled and extracted into methylene chloride, then precipitated into hexanes to give a white solid, which was washed with hexane: ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.27 (m, 10H), 1.55 (q, 2H), 1.73 (s, 4H), 2.03 (q, 2H), 3.37–3.70 (m, 100H), 4.94 (m, 2H), 5.79 (m, 1H) ppm; ^{13}C NMR (400 MHz, CDCl$_3$) 25.9, 28.8, 29.0, 29.2, 29.4, 33.6, 58.0, 60.3, 69.4, 69.8, 71.0, 71.7, 114.2, 138.8 ppm.
Synthesis of PEGylated silicon nanoparticles: Inside a glove box, tetra-*n*-octylammonium bromide (1.5 g) was added to toluene (100 mL) and stirred for 5 min. SiCl$_4$ (100 µL) was added, and the solution was stirred for 1 h. A solution of lithium aluminium hydride in THF (1 M, 2 mL) was added slowly, and the mixture was stirred for 3 h. The silicon nanoparticles were collected by the addition of methanol (20 mL); and chloroplatinic acid hexahydrate (5 mg) and compound **1** (500 mg) were added, and the mixture was stirred for 3 h. The resulting nanoparticles were extracted into water with sonication, and unreacted **1** was removed by dialysis (cellulose acetate bag, Spectrum Laboratories, MWCO 2 kDa). For the irradiation experiment, the silicon nanoparticles were transfered to a UV irradiation chamber in a quartz tube containing **1** (50 mg). The mixture was irradiated for 2 h. Solvent was removed by evaporation, and the residue was sonicated with water (10 mL). The aqueous solution was filtered through a microliter syringe to remove TOAB and afford the PEGylated silicon nanoparticles.

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