Photothermal Aerosol Synthesis of and Photoluminescence from Silicon Nanoparticles

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The possibility of constructing optoelectronic devices, full-color displays, and optical sensors based on silicon has generated tremendous interest in the preparation and characterization of light emitting silicon nanoparticles. These particles also have exciting potential applications as fluorescent tags for biological imaging, as has been proposed for II-VI compound semiconductor nanoparticles. They can be brighter and much more stable to photobleaching than the organic dyes used in these applications, and they also have much broader excitation spectra, so that emission at multiple wavelengths (from particles of different sizes) can be excited by a single source. Although there are established methods for preparation of luminescent porous silicon, there are, to our knowledge, no reported methods for producing macroscopic quantities (i.e. more than a few milligrams) of luminescent silicon nanoparticles that are free from a substrate.

CO_2 laser pyrolysis of silane is an effective method of producing gram-scale quantities of silicon nanoparticles. It produces high-purity loosely agglomerated particles with controlled primary particle size and size distribution. While several groups have synthesized silicon particles with this and similar methods, the resulting particles showed little or no visible photoluminescence. In order to show efficient visible photoluminescence (PL), it is believed that silicon nanoparticles must be smaller than 5 nm, and their surface must be 'properly passivated'.

The size of silicon nanoparticles can be reduced by etching them in mixtures of hydrofluoric acid (HF) and nitric acid (HNO_3). We have recently discovered that a controlled HF/HNO_3 etching process can induce bright, visible photoluminescence in silicon nanoparticles produced by laser pyrolysis of silane that do not show significant photoluminescence before etching.

Upon initial synthesis in the laser-driven reactor, the silicon nanoparticles exhibit little or no visible photoluminescence (PL) either as a dry powder or dispersed in solvents. After etching with HF/HNO_3 mixtures, the particles exhibit bright visible PL. Powder samples and particle dispersions in water, methanol, and other solvents, with bright visible PL ranging from red to green have been produced. Figure 1 shows the spectra of the particles from a single experiment extracted after different etching times, presumably corresponding to different particle sizes.

While the PL of powder particles after etching is relatively stable over many weeks, PL from particles dispersed in solvents is less stable. The PL intensities typically decrease with time, on a time scale of hours to weeks. The peak positions of PL spectra also tend to shift with time. We found that chemical oxidization of the particles' surfaces using HNO_3 is one way to stabilize the PL spectrum. After 13 days, one sample treated with HNO_3 in chloroform kept 71% of its initial intensity, while untreated particles from the same experiment kept only 6.5% of their initial intensity.

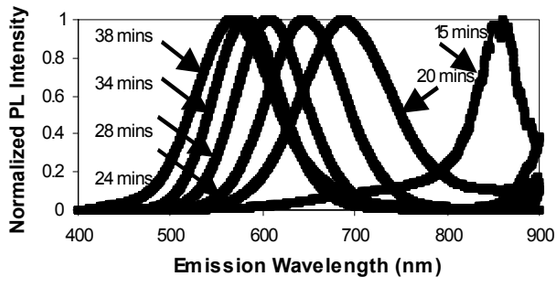

Figure 1: Normalized photoluminescence spectra of dry powder samples, showing the decrease in peak emission wavelength with increasing etching time.

The photoluminescence and dispersability of particles in different solvents were also studied. It was found that the emission of particles in chloroform is brighter than in water, methanol, and several other solvents tested. Dispersions in water, chloroform, and small alcohols are easily formed by shaking or mild sonication. However, these are not stable, and the particles agglomerate in these solvents on a time scale of hours to days. Dispersions in 1,2-propanediol, 1,4-butanediol, and glycerol, on the other hand, are stable indefinitely.

To summarize, silicon nanoparticles with an average diameter of about 5 nm were prepared by CO_2 laser-driven pyrolysis of silane (photothermal aerosol synthesis). After HF/HNO_3 etching, Si particles with controlled visible luminescence were produced. The wavelength of maximum PL emission from the nanoparticles was controlled from above 800 nm to below 500 nm by controlling the etching time and conditions. This method is unique in being able to produce macroscopic quantities (a few hundred milligrams in a few hours in our small bench-scale implementation) of Si nanoparticles with efficient visible photoluminescence. Si nanoparticle dispersions in water and methanol with bright visible PL were also produced and characterized. These dispersions usually exhibited changes in PL intensity for the first few days after preparation. PL of particles after etching in different solvents was also studied. It was found that PL in chloroform is the brightest among solvents we investigated so far. More stable dispersions were obtained for particles in diols and glycerol. PL from powder samples was generally stable with time. The PL from particles after etching can be stabilized by chemical oxidization using HNO_3.