A New Manufacturing Process for Non-Toxic, Silicone Photoluminescence Nano-Crystal Quantum Dots with Defined Spectral Properties

NIST scientists are developing non-toxic, stable Silicone (Si) crystal quantum dot (Qdots) nanoparticles that emit visible light with high quantum efficiency. A new manufacturing method involving post-production acid etching under 340nm light source is being explored to enable better fine control of crystal size to enhance the optical properties of the Qdots. This method is known as "photo-assisted tuning". These new detection tools are suitable for use in living systems, unlike current Qdots made from CdSe, CdS, InP, and GaAs. The new Si Qdots are expected to be very useful in association with biomolecular probes and enable new innovation in the drug discovery and development, and homeland security business sectors.

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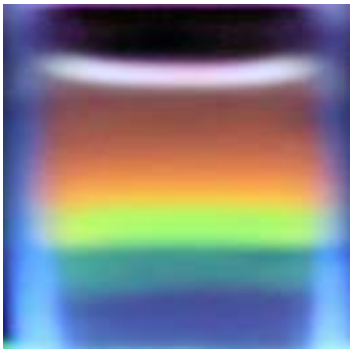
Quantum dots are nanocrystals of semiconducting material that emit light when excited by light or electric field. Qdots can be tuned to emit light at various wavelengths to create a wide variety of useful detection tools for biological investigations. They can be attached to biomolecules and used as probes for bioassays. Compound semiconductor quantum dots made from CdSe, CdS, InP, and GaAs have long been prepared with well-defined size, shape, and surface chemistry. Their main shortcoming for biological applications is their intrinsic toxicity that requires encapsulation in a thick shell, consequently compromising the main advantage of Qdots – their small size. On the other hand, Si is a bioinert semiconductor. Such particles will be tested as alternatives to organic fluorophores in biological assays.

Silicon is a material of choice in the semiconductor industry, but it is an extremely poor optoelectronic material. Fortunately, quantum confinement effects enable bright UV/VIS photoluminescence in 1 to 5 nm diameter Si crystals. Photoluminescent Si nanoparticles are actively explored by the photonics, solar power and biotechnology industries. Such particles are considered bio-inert and may lead to the development of biocompatible and smaller molecular tags than the well known metal chalcogenide-based quantum dots. However, current Si nanocrystal production procedures typically do not allow for the fine control of their particle size.

The work describe here is an efficient way to reduce the H-terminated Si nanocrystal diameter and narrow size distribution through the photo-catalyzed dissolution in the acid mixture. Photoluminescence and absorbance spectra, measured during the dissolution under UV exposure, show the gradual particle size decrease resulting in a monotonic photoluminescence blue shift. Simultaneous narrowing of the photoluminescence spectral bandwidth suggests that the dissolution rate varies with the particle size and allows for preparation of monodisperse Si nanoparticle suspensions. Moreover, quantum yields up to 60% were recorded for Si nanocrystal visible photoluminescence during dissolution, approaching the efficiency of the binary semiconductor quantum dots.



Multicolor photoluminescence pattern in the stationary Si nanoparticle suspension during the UV catalyzed acid dissolution reflecting median particle diameter variation from 3.2 nm (red) to 1.5 nm (blue).

Silicon is rather inefficient light emitter due to the indirect-band gap electronic structure, requiring a phonon to balance electron momentum during interband transition. Fortunately, momentum requirements are relaxed in 1to 5 nm diameter Si crystals as a result of quantum confinement effects and bright photoluminescence in the UV/VIS range is achieved. Photoluminescent Si nanocrystals along with C and SiC based nanoparticles are considered bio-inert and may lead to the development of biocompatible and smaller probes than metal chalcogenide-based quantum dots. Published Si nanocrystal production procedures typically do not allow for the fine control of the particle size. An accepted way to make H-terminated Si nanocrystals consists of anodic Si wafer etching with subsequent breakup of the porous film in an ultrasound bath. However, a rather polydisperse mixture is produced after the ultrasonic treatment leading to distributed band gap energies and degree of surface passivation. From the technological point of view, a homogeneous size nanoparticle mixture is highly desirable.

In conclustion, an efficient way to reduce H-terminated Si nanocrystal diameter and narrow size distribution through photo-catalyzed dissolution in the HF/HNO_3 acid mixture was demonstrated. Si particles were produced using lateral

etching of Si wafer in HF/EtOH/H_20 bath followed by sonication in a deaerated methanol. Initial suspensions exhibited broad photoluminescence in the red spectral region. Adding an HF/HNO_3 acid mixture to the suspension and exposing it to 340nm light carried out the photo-assisted etching. Photoluminescence and absorbance spectra, measured during the dissolution show gradual particle size decrease as confirmed by the photoluminescence blue shift. Simultaneous narrowing of photoluminescence spectral bandwidth suggests that dissolution rate varies with particle size. Photoluminescence quantum yields up to 60% were observed following acid treatment indicating efficient passivation of the nano-crystal surface states.

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