

Nanocrystalline Silicon Clusters For The Imaging Of Dynamic Cellular Processes.

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We report on the synthesis procedures and stability properties of nanocrystalline silicon clusters implanted on living tissue. We explain the preparation of the nanoclusters, their morphological and photoluminescence (PL) properties and the stability of these properties once implanted in biological material. We finally present our conclusions about the applicability of such nanostructures for imaging of dynamic cellular processes.

Si nanoparticles were initially synthesized following the top-down protocol used for the preparation of Porous Silicon¹ (PSi). Crystalline Si wafers with resistivities between 0.5 Ωcm and 1.5 Ωcm were electrochemically etched in a Teflon cell and with an electrolytic solution made with 25% HF, 50% H₂O and 25% Ethanol (per volume). A 50mA/cm² electrical current density was applied between the anode (the Si wafer with an Al ohmic contact at the bottom) and the cathode (Platinum electrode) The anodization time was 50 minutes. We produced PSi films with thicknesses of the order of 200 μm and 0.5cm² in area. By the application of a high voltage pulse we could disengage the porous films from the Si wafers. The so resulting free-standing porous films were then washed in Ethanol and dried using the critical point method². Several films so prepared were finally immersed in Ethanol and sonicated in an ultrasonic bath during 30 minutes, until a suspension of Si nanoclusters were obtained. Figure 1 shows a TEM image of a collection of Si nanoclusters obtained by this method. The figure shows a broad clusters' size distribution. A reduction in size dispersion is obtained by decantation and centrifugation.

Figure 2 shows the normalized PL spectra of: (a) the dried PSi film previous to sonication and (b) Si nanoclusters in ethanoic suspension after sonication. It is worth to mention that PL is quenched by Ethanol in fresh sonicated nanoclusters but it is recovered by keeping the clusters suspended in ethanol for more that 12 hours. It has been explained³ that for Si nanoparticles with sizes between $\sim 1\text{nm}$ and $\sim 3.5\text{nm}$, the quasi-indirect gap nature of the electronic transitions responsible for the PL makes the PL quantum yield of such nanostructures is strongly dependent on any change in their surface passivation conditions. Si nanoparticles surrounded by its oxide show intense and stable PL as in the case of n-Si/SiO₂ composites. The above-mentioned aging step is considered responsible of the formation of an oxide layer that improves the PL intensity and stability by isolating the Si cores from the external environment. The improved PL stability of such clusters benefits their applicability for marking purposes and becomes a key factor for the use of our nanostructures when implanted in biological tissue. Figure 3 shows the image of one nanocluster from an aged suspension. Each cluster is made of several to many nanoparticles. Raman spectroscopy of the dried PSi films here described is consistent with a size distribution of silicon nanocrystalline cores with an average diameter of $\sim 2.7\text{nm}$ ⁴. The analysis of the optical absorption spectrum of the nanoclusters showed that they can be effectively stimulated by using light sources with wavelengths below 500nm.

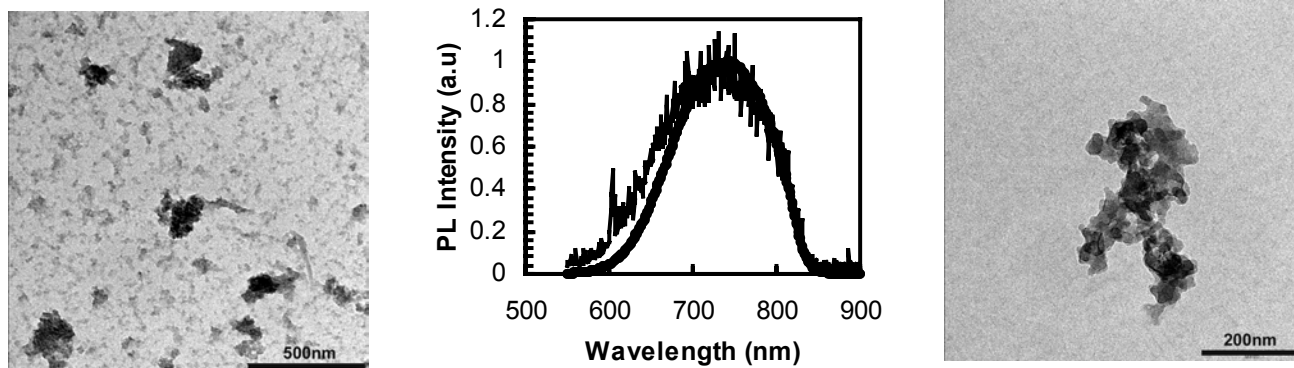


Figure 1. TEM image of Si nanoclusters from sonicated PSi.

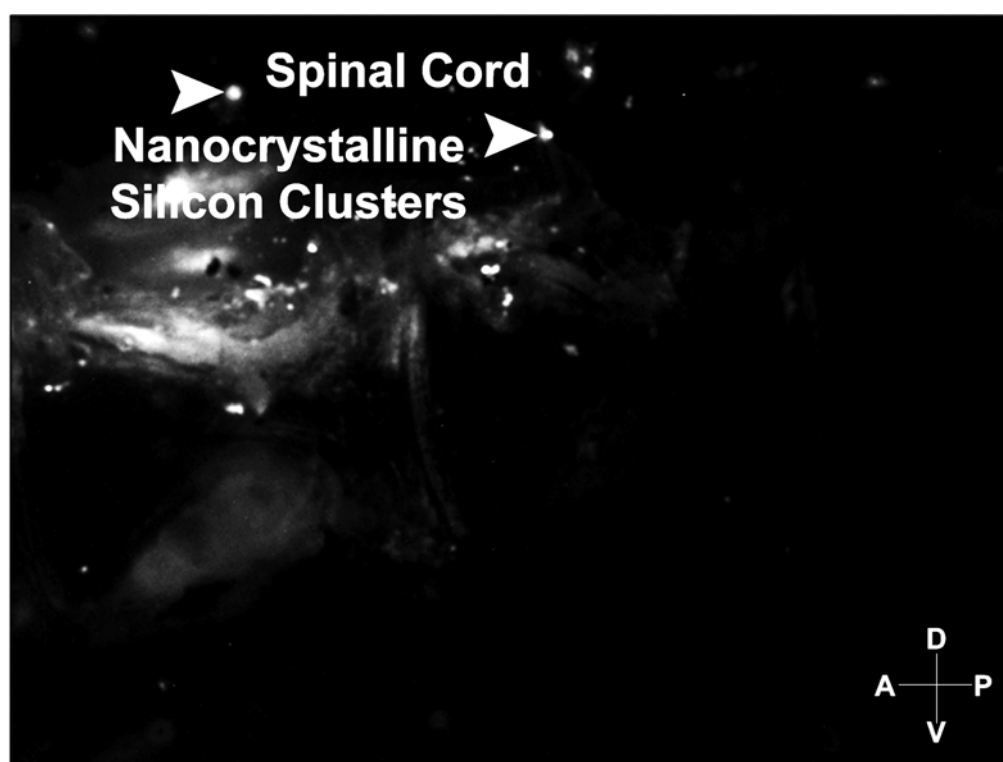


Figure 4. The implantation of the silicon nanoclusters in the living tissue was carried out by impregnating Polyethylene tubes of 13mm in length and with 2mm inner diameter with the nanoclusters by vacuum drying of the Ethanoic suspension and using the gene gun technique.

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