Supporting Information

for

"Improved opto-electronic properties of silicon nanocrystals/polymer nanocomposites by microplasma-induced liquid chemistry"

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SI.1 X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy of electrochemically etched silicon nanocrystals (SiNCs)

The dry powder produced by electrochemical etching consists of SiNCs which are often aggregated and with a degree of oxidation. The SiNCs are relatively stable in air whereby no changes were observed in the surface chemistry (analyzed by Fourier transform infra-red spectroscopy) and in their photoluminescence properties after a few months of storage.[1] We have performed extensive material characterization and analysis of the optoelectronic properties; see the main manuscript for related references. Here we report unpublished XPS and TEM results that complement and confirm all our previous findings. For the XPS analysis a PHI XPS TFA system was used with an Al-monochromatic X-ray beam with

energy resolution of 0.6 eV. The analysis area was 0.4 mm in diameter and the estimated analyzed depth was about 4 nm.

We have first analyzed a sample of dry powder of SiNCs, which we fixed on carbon adhesive tape. The binding energy scale was referenced to the energy of *C 1s* spectrum at 248.8 eV.

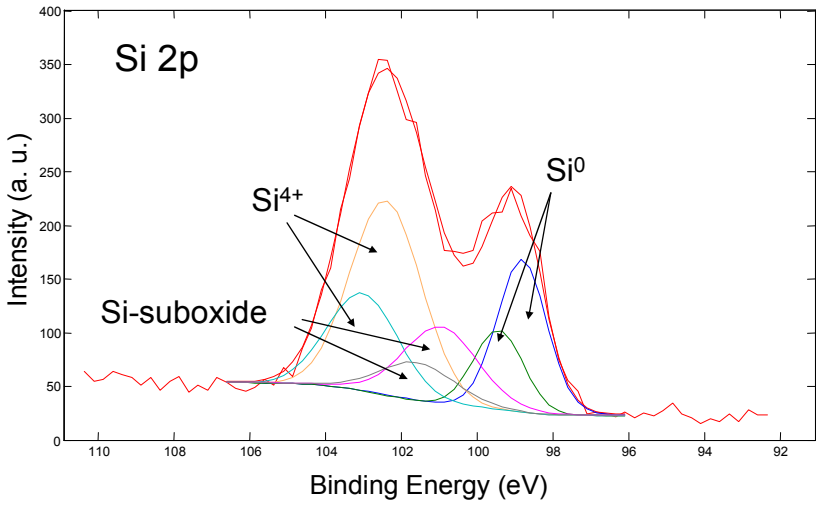

Figure S1. X-ray photoelectron spectrum Si 2p of dry silicon nanocrystal powder.

In figure S1 the *Si 2p* spectrum is shown. It has been fitted with corresponding *Si* $2p_{3/2}$ and *Si* $2p_{1/2}$ doublets separated by 0.6 eV. In particular the Si^0 metallic (at 98.8 eV for *Si* $2p_{3/2}$ and at 99.3 eV for the *Si* $2p_{1/2}$) and the Si^{4+} (at 102.4 eV for the *Si* $2p_{3/2}$ and at 103 eV for the *Si* $2p_{1/2}$) components are clearly visible indicating the presence of Si-Si bonds attributed to SiNCs and to the presence of an oxide possibly resulting from the partial oxidation of SiNCs when exposed to air. The peaks at 101 eV (*Si* $2p_{3/2}$) and 101.6 eV (*Si* $2p_{3/2}$) correspond to sub-oxide possibly at the oxide/Si interface. These results with the analysis reported in[1] confirm the stability of SiNCs in air.

When the SiNCs are dispersed in water, further oxidation is initiated as we have previously observed.[1] We have performed XPS analysis of a sample of SiNCs that has been stored in water for 3 days and following drop-casted on a graphite substrate.

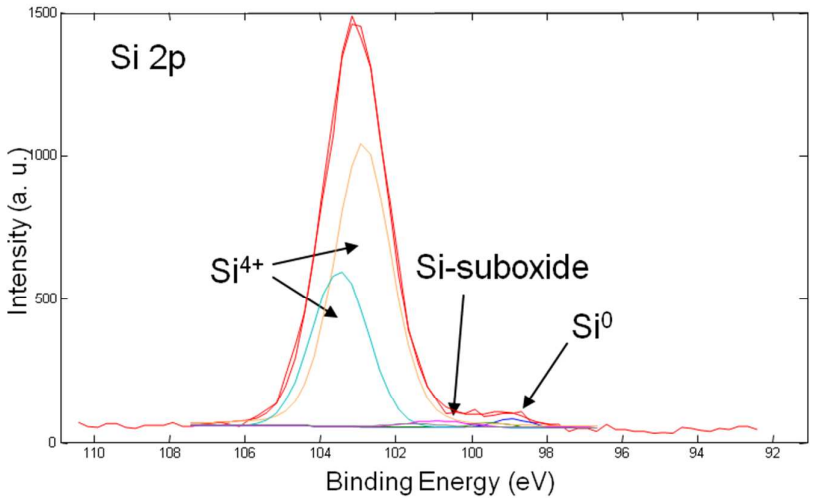

Figure S2. X-ray photoelectron spectrum Si 2p of silicon nanocrystal powder stored in water for about 3 days.

In figure S2 the same fitting procedure has been followed as for the *Si 2p* spectrum given in figure S1. The *Si 2p* spectrum consists mainly of Si^{4+} doublet (102.9 eV for $Si\ 2p_{3/2}$ and 103.5 eV for $Si\ 2p_{1/2}$). Only a small presence of sub-oxide at 100.9 eV ($Si\ 2p_{3/2}$) was recognized in this spectrum. It follows that after storage in water for a few days, extensive oxidation has taken place which fully correlates with the optical properties of the SiNCs. In figure S2, it is however still possible to observe the peak related to Si-Si bonds (98.8 eV and 99.3 eV), which indicates an oxide layer of less than 10 nm and still some non-oxidized silicon. Based on the SiNCs photoluminescence, we can suggest that extensive oxidation takes place after several hours.[1] Therefore the work reported in the main manuscript was initiated within 10-15 minutes, after SiNCs dispersion, and the whole process was completed within 40-45 minutes; within this timeframe, the SiNCs optical properties are very little degraded/modified suggesting limited oxidation.

The limited oxidation and the ability of the plasma process to stop inward oxidation are confirmed by TEM analysis of the SiNCs samples that were plasma-treated in the polymer/water colloid.

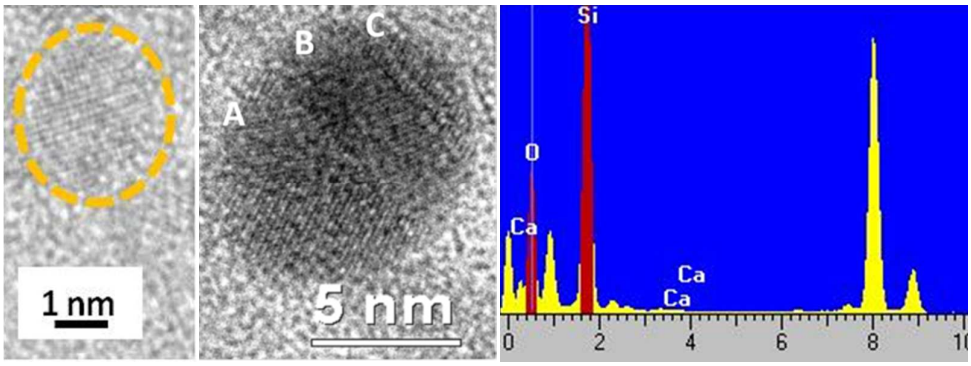

Figure S3. High resolution transmission electron images of SiNCs (left and middle) exhibiting typical fringes of crystalline structure; on the right energy dispersive spectroscopy of the particle in the middle image.

Figure S3 (left and middle) shows high resolution images of SiNCs corresponding to figure 2c of the main manuscript, which confirm the silicon crystal structure. In some cases (middle of figure S3), a silicon crystal structure with twin defects is observed, dividing the particle into three regions as marked by A, B, and C. The measured d-spacing in A is 2.03 Å, that in B and C are 2.09 and 2.12 Å, respectively. These atomic fringes can be indexed to the (220) of cubic silicon with the unit cell parameter a = 5.43 Å, but their values are slightly larger than the standard value (1.92 Å). It was also noticed that the crystal structure in C has been significantly disturbed. We believe these defects are related to a partial oxidation. Finally, energy dispersive spectroscopy (right of figure S3) of the NC in the middle of figure S3 confirms silicon elemental composition with some oxide being present.

References

1. Mariotti, D.; Švrček, V.; Hamilton, J. W. J.; Schmidt, M.; Kondo, M. *Adv. Funct. Mater.* **2012**, *22*, 954–964.