Electronic Supporting Information

Resolving the source of blue luminescence from alkyl-capped silicon nanoparticles synthesized by laser pulse ablation

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1. Experimental details:

The scheme for femtosecond laser ablation of a Si target in 1-octene performed in this study is shown in Fig. S1a. A Piranha cleaned, n-type Si (111) etched wafer was immersed vertically in 4 mL of neat 1-octene inside a $10 \times 10 \times 40$ mm guartz cuvette. Laser ablation was carried out using 35 fs, 100 µJ laser pulses centered at 790 nm generated by a titanium-sapphire-based chirped-pulse amplifier operating at a 1 kHz repetition rate. Before being focused into the sample cuvette, the 35 fs pulses were simultaneously spatially and temporally focused (SSTF) using a homebuilt apparatus as illustrated in Fig. S1b.¹ The set up consisted of a pair of 1200 lines/mm gratings in a single-pass configuration followed by an f = 4-cm aspheric lens. The purpose of the SSTF apparatus is to minimize energy deposition in the cuvette and solvent; no attempt was made to re-compress the pulse after the grating pair, resulting in a pulse duration of \sim 36 ps at the sample.¹ In this way the spectrally dispersed components of the laser pulse are simultaneously focused in space and time, and the temporal profile (chirped by the gratings in this case) is restored when all of the spectral components are recombined at the focal point.¹ SSTF has been shown to provide precise control of the position of the laser focus and to minimize nonlinear pulse distortions in the solvent media and the quartz cuvette before and after the focal point. It has been shown that laser irradiation of liquid using SSTF can reduce the nonlinear optical effects occurring in the liquid before reaching the target.¹ The cuvette was mounted on a computer-controlled stage and translated vertically at a speed of 2 mm per second during irradiation so that each surface spot was irradiated by ~10 laser pulses (the beam waist is 20 µm).



Figure S1a-b: (a) Schematic of femtosecond laser ablation of Si wafer in 1-octene and (b) the principle of SSTF adapted from Ref 1.

2. Laser irradiation time dependence on luminescence of Si NPs:

The properties of the synthesized Si NPs were not observed to change for irradiation times between 80 seconds and 5 minutes (Fig. S2). We report results for an irradiation time of 80 seconds, which was chosen to ensure that the optical density of the solvent does not change significantly during the course of the ablation period. In fact, the luminescence recorded for the 80 sec irradiation time was more intense than recorded for longer irradiation. This is because longer irradiation time generated more of the solvent by-product which could have quenching effects on the emission from Si NPs.



Figure S2: Luminescence of the separated Si NPs after two different laser irradiation times of 5 min and 80 s, when excited at 280 nm.

3. TEM of as-ablated samples:

Representative TEM images of the as-ablated samples (Fig. S3), show Si NPs ranging from \sim 8 to \sim 2 nm in size with an average size of 3.3 nm. A closer look at the TEM reveals the presence of grey, film like objects, in addition to the dark spherical Si NPs (Fig. S3a). The EDS analysis of the as-ablated sample shows the presence of high intensity of C peak in addition to Si peak (Fig S3c).



Figure S3a-d: Representative TEM image of as-ablated products (a) and (b) size distribution analysis performed on 250 particles from the three images. (c) EDS spectra taken on a region containing Si NPs and carbon by-product, shown as red box in inset image.

4. Laser power dependence on the optical properties of the ablation products:

To test the effect of laser power on the luminescence properties of the Si NPs generated by femtosecond laser ablation, the ablation was carried out using four different laser pulse energies: 20 μ J, 50 μ J, 100 μ J, and 250 μ J. The luminescence spectra of the separated Si NPs were recorded as a dilute solution of the particles in dichloromethane. We observed that the emission from the Si NPs at four different excitation wavelengths were the same, with no change in position or width of emission (Fig. S4a-d). This indicates that changing the laser power does not influence the optical properties of the synthesized Si NPs.



Figure S4a-d: Luminescence from separated Si NPs at laser energies of (a) 20 μ J (b) 50 μ J (c) 100 μ J, and (d) 250 μ J.

5. PL of separated carbon by-product.



(b) PL spectra of separated carbon by-product (solid lines) compared with that from control sample (dashed lines). All samples were dispersed in dichloromethane (DCM). The star symbols indicate the scattered 2nd order diffraction peaks of the excitation photons.

6. SAED analysis of separated Si NPs



7. Spectroscopic analysis of 1-octene irradiation control sample:

The IR absorption spectra of the 1-octene control sample (Fig. S7a) was essentially featureless, except for a peak at 1592 cm⁻¹ which is assigned to the C=C vibration stretch, suggesting the possible presence of graphitic matter. The IR spectrum of the separated carbon by-product on the other hand, did not show any peaks (Fig. S7b). This is most likely due to the absence of any aromatic or aliphatic species. If there is some graphitic/carbon particulate species present, similar to the case of the 1-octene control sample, then its concentration must be very low. The Raman spectra of the 1-octene control under 325 nm excitation (Fig. S7c) shows intensity at 1612 cm⁻¹, which is similar to the G band of graphite but may be shifted due to presence of graphene, as reported previously.³ Under 532 nm excitation the spectra were overwhelmed by a strong luminescence from the carbon by-product with a small intensity peak appearing at 1580 cm⁻¹ corresponding to amorphous carbon band (Fig. S7d). Although, a thorough analysis of the carbon by-product remains to be performed, preliminary analysis suggests the presence of graphene-like or other carbon nanomaterial, as reported previously for ablation in toluene.⁴



Figure S7a-d: (a, b) IR spectra of the 1-octene irradiated product and the separated carbon product. (c, d) Raman spectra of the 1-octene irradiated product with 325 nm and 532 nm excitation, respectively.

References:

1. Tangeysh, B.; Moore Tibbetts, K.; Odhner, J. H.; Wayland, B. B.; Levis, R. J., Gold Nanoparticle Synthesis Using Spatially and Temporally Shaped Femtosecond Laser Pulses: Post-Irradiation Auto-Reduction of Aqueous [AuCl₄]⁻. *J. Phys. Chem. C* **2013**, *117* (36), 18719-18727.

3. Jung, N.; Crowther, A. C.; Kim, N.; Kim, P.; Brus, L., Raman Enhancement on Graphene: Adsorbed and Intercalated Molecular Species. *ACS Nano* **2010**, *4* (11), 7005-7013.

4. Yang, S.; Zeng, H.; Zhao, H.; Zhang, H.; Cai, W., Luminescent hollow carbon shells and fullerenelike carbon spheres produced by laser ablation with toluene. *J. Mater. Chem.* **2011**, *21* (12), 4432-4436.