

## Electronic Supplementary Information

### Band-Gap Engineering by Molecular Mechanical Strain-Induced Giant Tuning of the Luminescence in Colloidal Amorphous Porous Silicon Nanostructures

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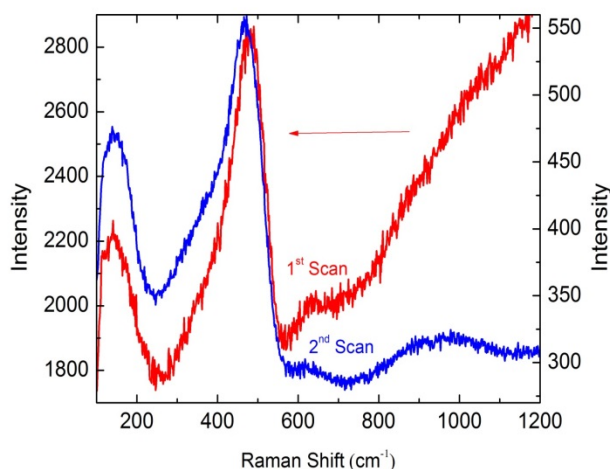
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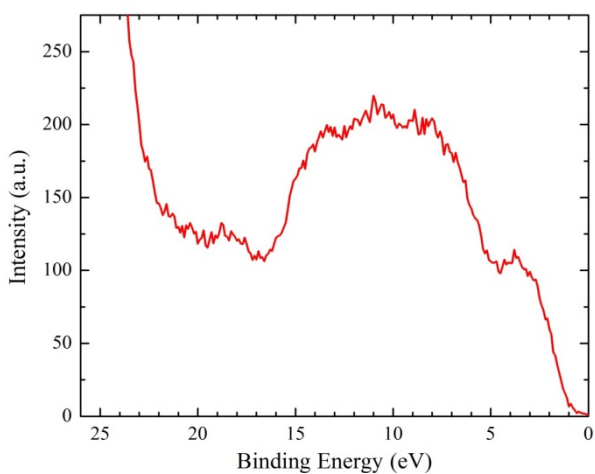
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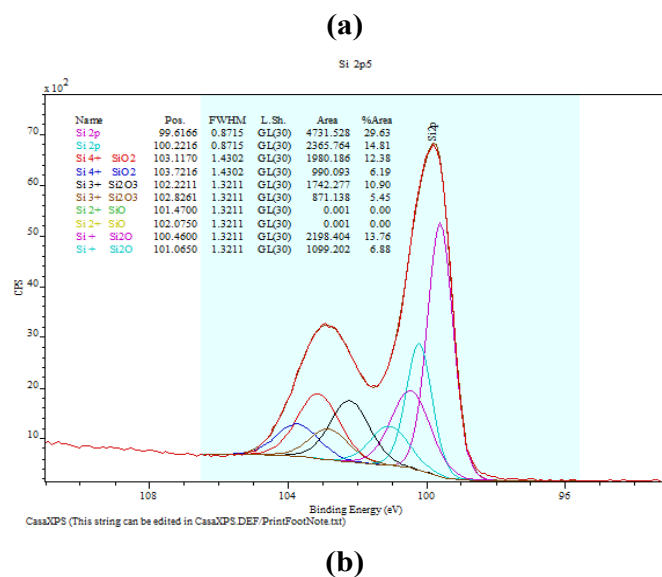
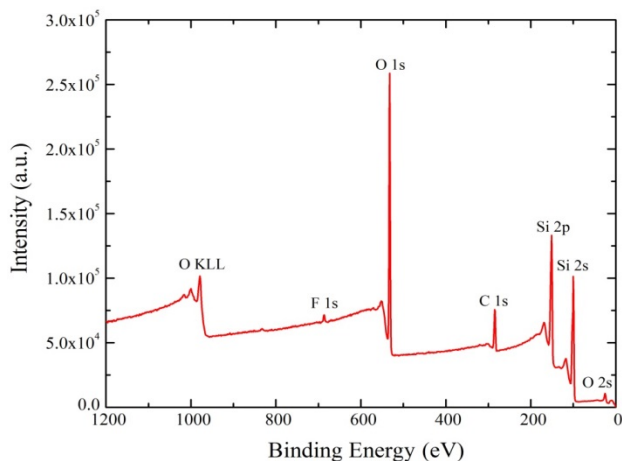
Nano-silicon is a nanostructured material in which quantum or spatial confinement is the origin of the material's luminescence. When nano-silicon is broken into colloidal crystalline nanoparticles, its luminescence can be tuned across the visible spectrum only when the sizes of the nanoparticles, which are obtained via painstaking filtration methods that are difficult to scale up because of low yield, vary. Bright and tunable colloidal amorphous porous silicon nanostructures have not yet been reported. In this letter, we report on a 100-nm modulation in the emission of freestanding colloidal amorphous porous silicon nanostructures via band-gap engineering. The mechanism responsible for this tunable modulation, which is independent of the size of the individual particles and their distribution, is the distortion of the molecular orbitals by a strained silicon-silicon bond angle. This mechanism is also responsible for the amorphous-to-crystalline transformation of silicon.



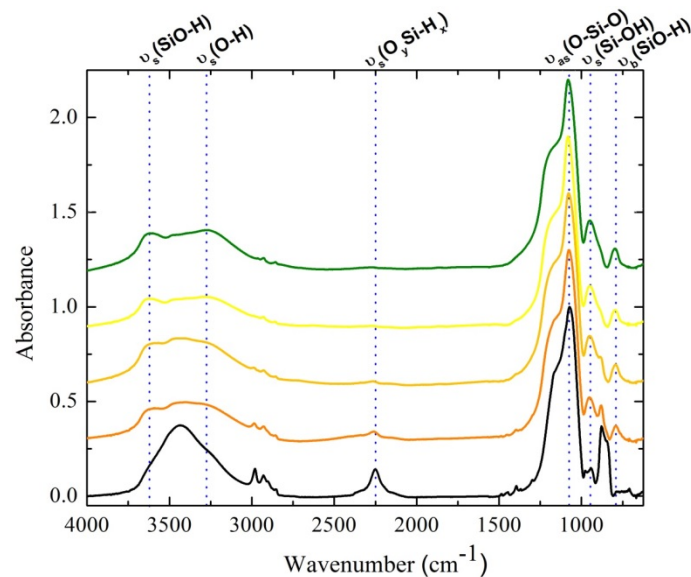
**Fig. S1** Raman spectra of the amorphous nanostructured particles. The second scan shows the appearance of Si-O bond vibrations at 800-1000  $\text{cm}^{-1}$ . The decrease in spectrum intensity for Raman shifts greater than 700  $\text{cm}^{-1}$  is probably due to photobleaching. Further excitation can also remove surface-bonded hydrogen/oxygen, creating non-radiative dangling bonds that also increase the disorder. The wavelength used in the scanning was 473 nm.



**Fig. S2** XPS valence band spectrum verifying the existence of an amorphous Si structure. The spectrum consists of a broad peak between 15 and 5 eV as well as a shoulder around 3 eV, further confirming the presence of an amorphous phase.



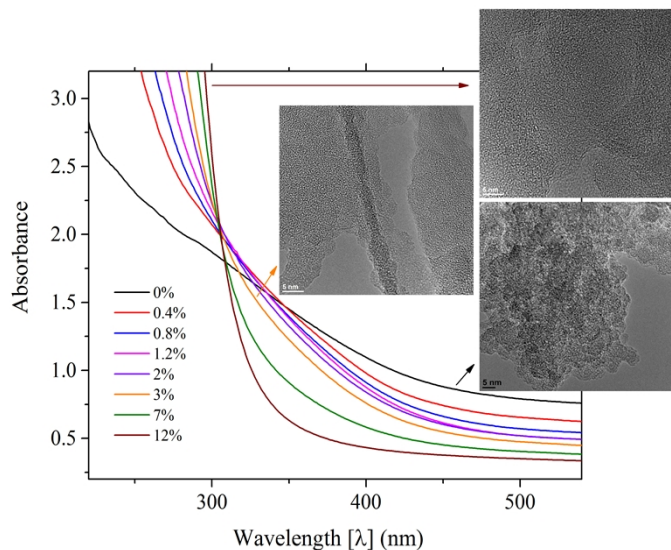
**Fig. S3** (a) XPS wide scan spectrum of amorphous porous silicon nanostructures showing that Si and O are the primary elements detected, with only traces of C present on the surface. (b) Deconvoluted Si-2p core level spectrum of ap-SiNsts (the Si-2p XPS peaks were analyzed by means of Gaussian peak).



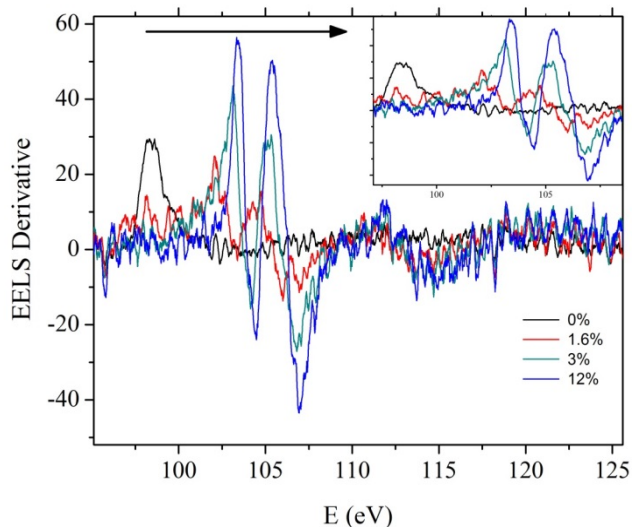
**Fig. S4** Evolution of the FT-IR absorbance spectra of the ap-SiNsts colloidal suspensions as more peroxide is added. The black spectrum corresponds to a colloidal suspension in toluene with no peroxide added. The orange spectrum corresponds to 0.4% in volume of peroxide added. Brownish orange corresponds to 1.2%. Yellow corresponds to 3% and green corresponds to 12%.

As shown in Fig. S4, the disappearance of the peak at 880  $\text{cm}^{-1}$  is a contributor to the disappearance of the very weak shoulder at 2100  $\text{cm}^{-1}$  that corresponds to stretching modes of SiH and which increases linearly with hydrogen content.<sup>32</sup> Upon addition of peroxide, the 880  $\text{cm}^{-1}$  peak that corresponds to bending modes, slowly decreases with increasing peroxide concentration and becomes a faint shoulder. The absence of a band at 840  $\text{cm}^{-1}$  when a peak at 2100  $\text{cm}^{-1}$  is indicates the presence of hydrogenated silicon.<sup>33</sup>

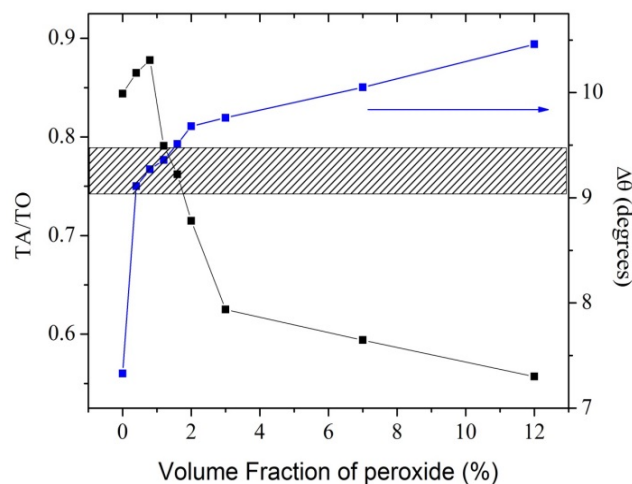
The absence of this shoulder is due to the oxygenation of the SiH bond. The peak at  $3440\text{ cm}^{-1}$ , typical of OH stretching bonds, splits upon addition of peroxide into a peak at  $3260\text{ cm}^{-1}$ , which corresponds to 2-trihydride silicon connected by an oxygen ( $\equiv\text{Si-O-Si}\equiv$ ) which correlates well with the disappearance of the  $2250\text{ cm}^{-1}$  peak that corresponds to a hydride peak with three oxygen atoms ( $\text{O}_3\text{SiH}$ ),<sup>34</sup> and a peak at  $3630\text{ cm}^{-1}$ , which is a signature of the appearance of silicon oxide. The peaks at  $2980\text{ cm}^{-1}$  and at  $1400\text{ cm}^{-1}$  are typical CH and CC from toluene.<sup>1</sup>



**Fig. S5** Uv-Vis absorption spectra as a function of added hydrogen peroxide volume fractions. Notice the abrupt decrease with further oxidation. The long tails are reminiscent of quantum confinement.



**Fig. S6** Derivative spectra of the  $L_{2,3}$  edge absorption from amorphous silicon nanostructured particles with various oxidation states. The arrow points to the direction of the spin-orbit peaks. The black spectrum corresponds to non-oxidised ap-SiNsts. The percentages are of the added volume fractions peroxide. Notice the shift in the  $p_{3/2}$  peak.



**Fig. S7** The disorder parameter, TA/TO, as well as the deviation of the bond angle ( $\Delta\theta$ ) are plotted as a function of the percentage of volume fraction of peroxide. Notice the drop in the value of the ratio after 1%. The shaded box is where the structure changes as per UV-Vis and TEM observations.

## Notes and References

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<sup>1</sup><http://webbook.nist.gov/cgi/cbook.cgi?Spec=C108883&Index=8&Type=IR&Large=on>

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