Supplementary information

Carbogenically coated silica nanoparticles and their forensic applications

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Experimental Section

Synthesis and characterization of C-SiO_2

3 ml of colloidal silica nanoparticles (Ludox HS 30 from Sigma-Aldrich) with a mean diameter of 18 nm were treated with 3g of Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride (Sigma-Aldrich), in acidic media (1 ml of 1M HCl) at 60 °C for 10 min. The dispersion was neutralized with 0.1 M NaOH, was left for 24h at room temperature and was dialyzed against deionized water using snakeskin pleated dialysis tubing membrane with a molecular weight cut-off of 3500 Da. TGA characterization (Mettler Toledo TGA 1 STAR system) under nitrogen atmosphere and heating rate 10 ^{o}C/min indicate that the surface-modified silica nanoparticles have 34 wt% organic content. Subsequently, the nanoparticles were pyrolysed at 250 ^{o}C for 3h before being subjected to surface oxidation via HNO_3 (3M) at 100 ^{o}C and dialysis against water. Finally, the C-SiO_2 were treated with ethylene diamine (Sigma-Aldrich) at 80 ^{o}C for 1h followed by dialysis.

Elemental analysis (Flash 2000 CHNS-O Analyzer calibrated using methionine) of C-SiO_2 thus received suggests the presence of 26% C, along with minor amounts of H and N (4 and 5%, respectively).

Fourier Transform Infra-Red (FTIR) spectra were recorded using a Nicolet IR2000 spectrophotometer (32 scans from 3500-700 cm^{-1} with a resolution of 8 cm^{-1}).

Fluorescence imaging

The fluorescence microscopy images were obtained using a Zeiss Axio Scope A1 microscope equipped with band-pass filters. Three excitation wavelengths were used with 350, 395 and 590 nm.

Transmission Electron Microscopy (TEM) images were obtained by A FEI T12 Spirit operated at 120 kV. A droplet of a dilute suspension (0.05mg/mL in water) was deposited on a carbon coated cupper grid (Agar Scientific, USA) and dried under air.

Scanning Electron Microscopy (SEM). The microstructure of the nanotags generated on a sticky SEM pad was investigated using a FEI Quanta 200.

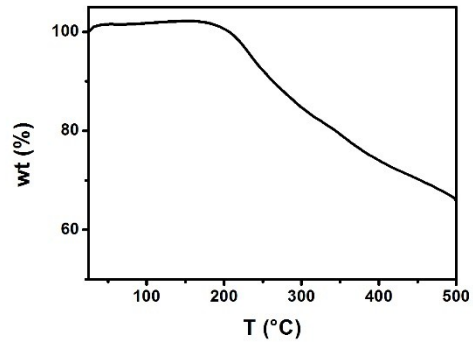
Photoluminescence spectra of 13 mg/ml aqueous dispersion of C-SiO_2 under different excitation wavelengths were recorded at room temperature using a Horiba Jobin Yvon FluoroMax-4 spectrofluorometer.

Dynamic Light Scattering. The hydrodynamic diameter of C-SiO_2 of the nanoparticles were measured on well-filtered suspensions (Nylon membrane filters with porosity 0.45 μm) using a Malvern Zetasizer Nano-ZS (Malvern Instruments, England) package which includes a 4 mW He–Ne laser operating at λ=633 nm.

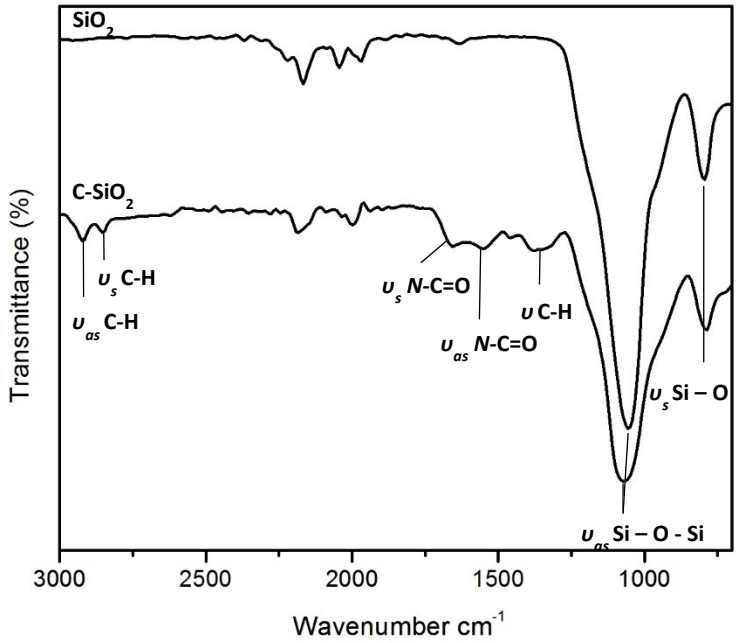
Fingerprint collection and development

A squirrel-hair brush was used to apply the powders to fingerprints deposited on a variety of surfaces. In the first stage, one fingermark donor was used and the results were later confirmed using a pool of two more donors. The donors' hands were washed thoroughly, and then the right index finger was rubbed on the forehead as to have both eccrine and sebaceous sweat. The marks were developed 24 h after their deposition. Natural fingerprints were also collected and the results (not shown here) were similar to those observed for the charged ones. The standard white fingerprint powder (WFP) was obtained from Crime Scene Investigation (Instant white Powder). The fluorescent fingerprint powder was obtained from Foster and Freeman.

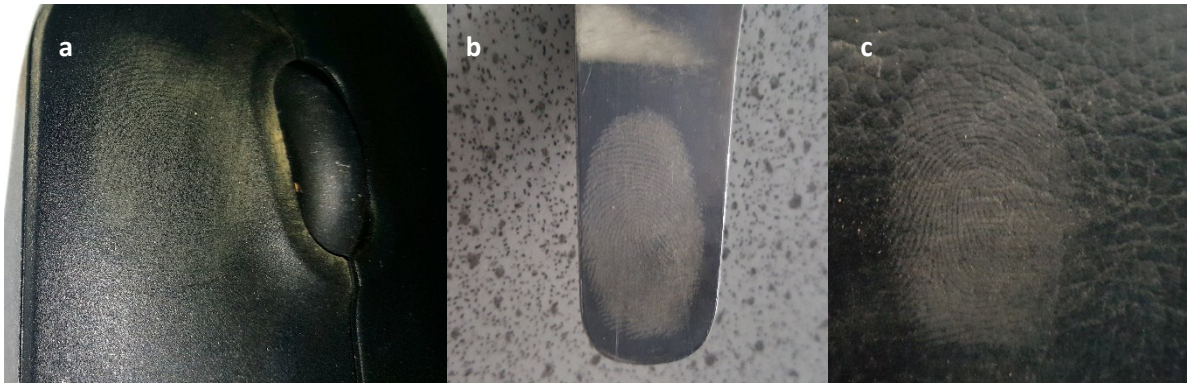
Figures



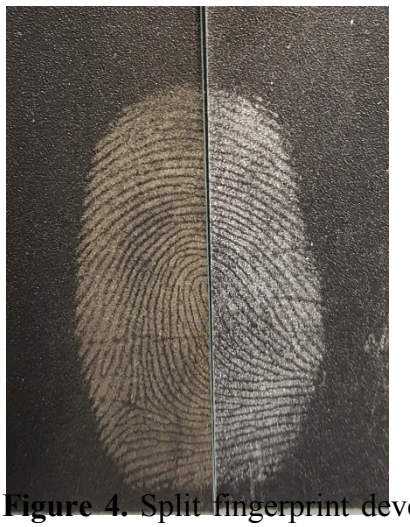
S.I. Figure 1. TGA thermograph of the surface treated silica nanoparticles before carbonization.



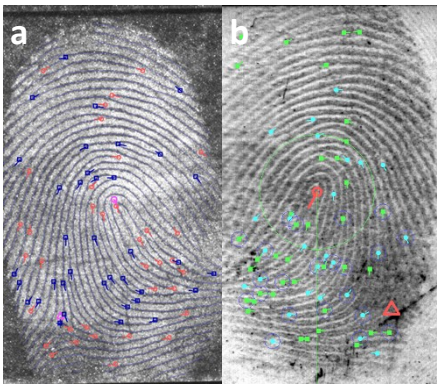
S.I. Figure 2. FTIR spectra of the colloidal SiO_2 and C-SiO_2. (υ_s and υ_{as} stand for symmetric and anti-symmetric stretching vibration, respectively).



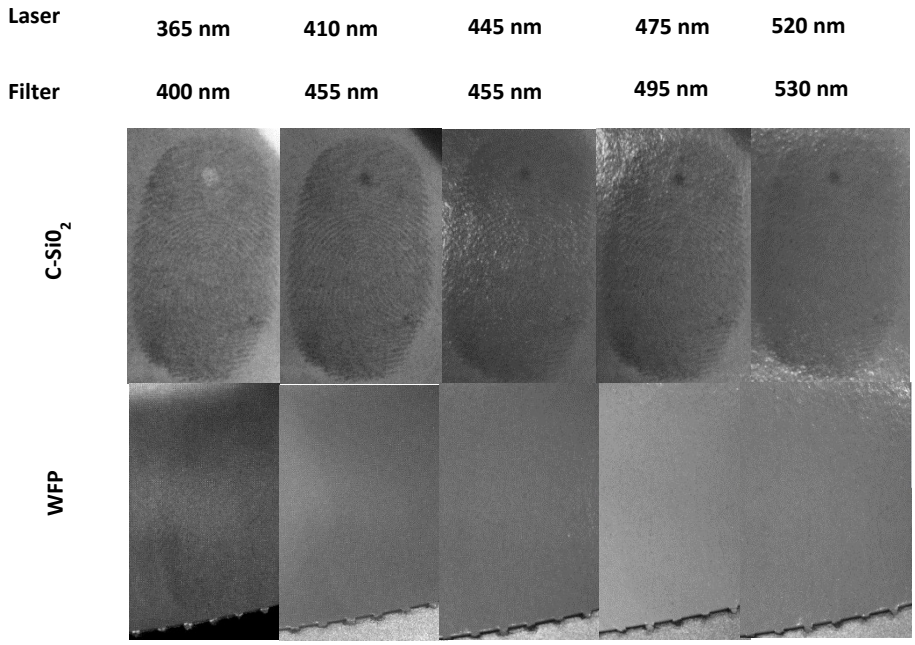
S.I. Figure 3. Fingerprints developed with C-SiO_2 nanoparticles on various surfaces: (a) computer mouse, metallic spatula and (c) a rough plastic surface. The images were captured under white light.



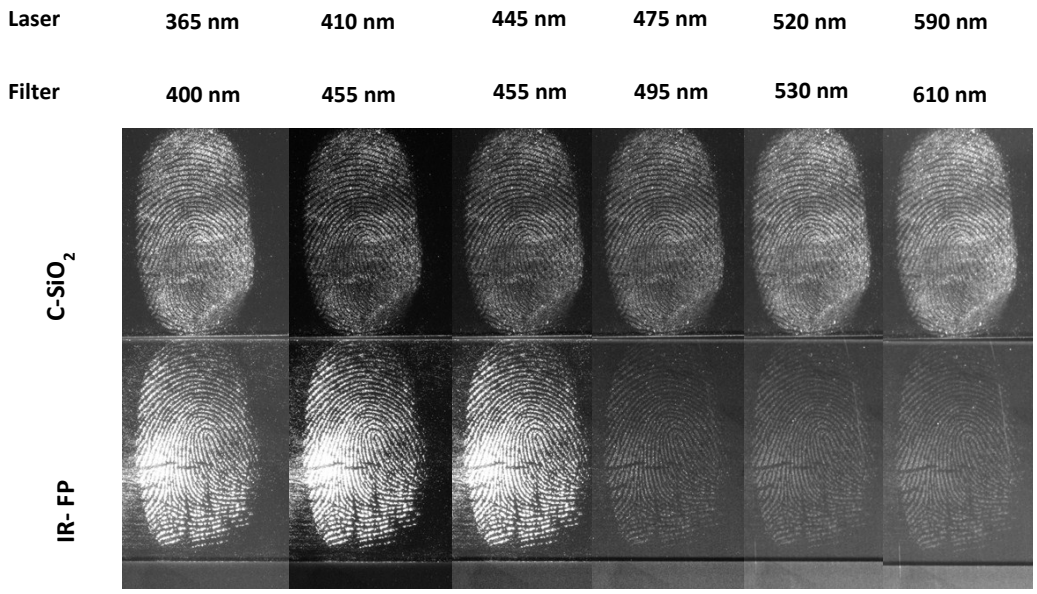
S.I. Figure 4. Split fingerprint developed with C-SiO_2 nanoparticles (left half) commercial WFP (right half). The image was captured under white light.



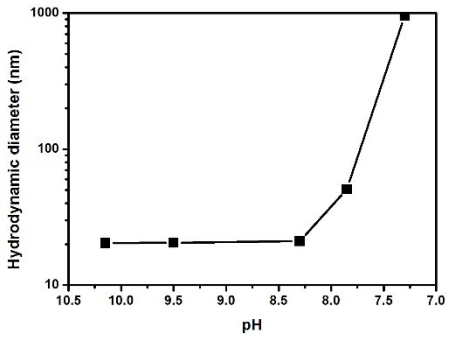
S.I. Figure 5. AFIS analysis of a fingerprint developed with (a) C-SiO_2 nanoparticles and (b) commercial WFP showing 73 and 65 minutiae, respectively.



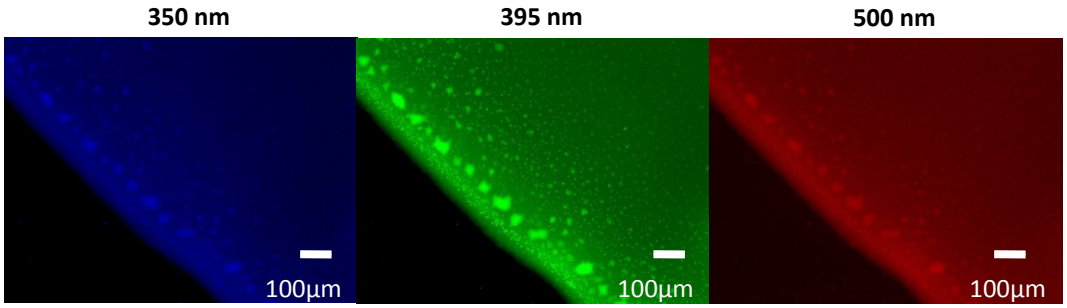
S.I. Figure 6. Comparison between the C-SiO_2 (upper images) and a commercial instant white fingerprint powder on a glass slide investigated on a crime lite imager.



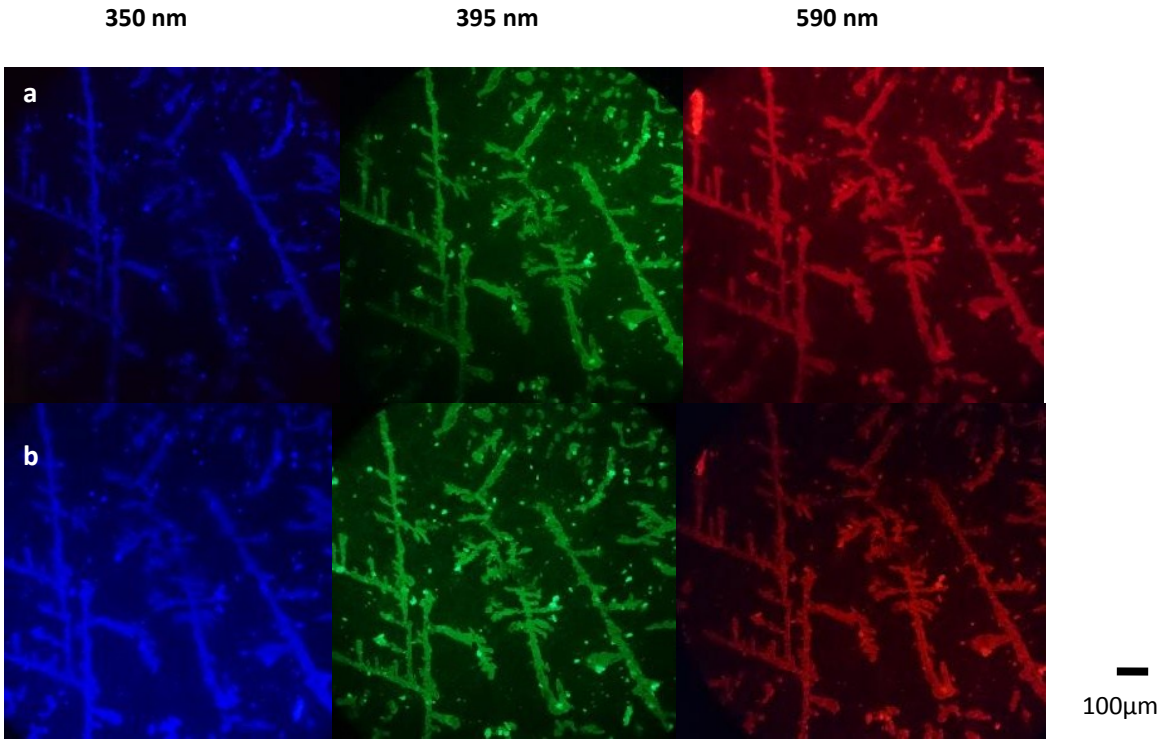
S.I. Figure 7. Comparison between the C-SiO_2 (upper images) and a commercial fluorescent fingerprint powder on a glass slide investigated on a crime lite imager.



S.I. Figure 8. Hydrodynamic diameter of 0.1wt% C-SiO_2 in water as a function of pH.



S.I. Figure 9. Fluorescence microscopy images (under three excitation wavelengths) of air-dried aqueous dispersions of C-SiO_2 with pH=10, indicating the absence of structured PL motives, in strong contrast to the behavior observed when pH=7.



S.I. Figure 10. Fluorescence microscopy images (under three different excitation wavelengths) of self-assembled motives of C-SiO_2 generated on a glass surface before (a) and after (b) being heated to 100°C for several hours.