

Electronic Supplementary Information

On determinative impact of hydrofluoric acid on surface states of as-prepared and chemically modified Si nanocrystals

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Fabrication of Si nanocrystals (Si NCs)

P-type boron-doped (0.2 and 17 $\Omega\cdot\text{cm}$) double-side polished (100)-oriented silicon wafers with an Al backside ohmic contact were used for electrochemical fabrication of Si NCs. The electrochemical process was performed in a Teflon cell with an Au counter electrode and a backside Cu electrode. The etching of the silicon substrates was carried out in a solution containing 1:1 volume mixture of HF (49%) and anhydrous ethanol. The etching process took place during 60 minutes at 50 mA/cm^2 of anodic current density. Permanent stirring of the etching solution was applied for evacuation of hydrogen bubbles formed during the anodization process. After the etching, the samples were washed several times with anhydrous ethanol and naturally dried in ambient air. The drying step results in exfoliation of the formed highly nanoporous Si layers with formation of Si NCs-based powder which was collected without any mechanical grinding for following chemical modifications.

Fabrication of meso-porous Si (meso-PS)

P-type boron-doped (0.02 – 0.03 $\Omega\cdot\text{cm}$) double-side polished (100)-oriented silicon wafers were used for electrochemical fabrication of meso-PS free layers. The electrochemical process was performed in a Teflon cell with an Au counter electrode and a backside Cu electrode. The etching of the silicon substrates was carried out in a solution containing 1:1 volume mixture of HF (49%) and anhydrous ethanol. The etching process took place during 6 minutes at 150 mA/cm^2 of anodic current density. Permanent stirring of the etching solution was applied for evacuation of hydrogen bubbles formed during the anodization process. At the end of the etching anodic current impulse with 1 A/cm^2 current density was applied for 5 seconds to tear off the

obtained porous layer from the Si wafer. After that, the samples were washed several times with anhydrous ethanol and naturally dried in ambient air.

HF-free standard hydrosilylation procedure

As-prepared Si NCs powder (10 mg) was transferred into a Schlenk-type reactor containing a magnetic stirrer and 1.5 mL of neat 1-octadecene (to form sample Si-C₁₈H₃₇ NCs) or 10-undecylenic acid (to form sample Si-C₁₀H₂₀COOH NCs). The contents of the reactor were degassed using at least three flash-pump cycles and sonicated (Elma sonic P30H ultrasonic bath, 130 W, 37 kHz) to disperse the NCs-based powder. However, it was almost impossible to form a stable colloidal dispersion and the reactor contents always appeared to be cloudy. The reactor was illuminated by Hg lamp (B-100AP, Blak-Ray, 100 W) without filter for 5h in N₂ atmosphere under continuous stirring. Water bath was used to keep temperature below 35°C. At the end, the reaction mixture was centrifuged for 60 min at 14000×g and the precipitated Si NCs were washed three times with the mixture of toluene and methanol (1:3 v/v) to remove the alkenes residues. Finally, the functionalized Si NCs were mixed with 1.5mL of n-hexane (in the case of Si-C₁₈H₃₇ sample) or ethanol (in the case of Si-C₁₀H₂₀COOH sample), sonicated for 10 min and centrifuged again for 20 min at 14000×g. Further work was produced using the separated liquid layer.

HF-based modified hydrosilylation procedure

Si NCs powder (10 mg) was put in a transparent polypropylene vessel containing magnetic stirrer, 1 ml mixture (1:1 v/v) of HF (49 wt %) and a co-solvent (tetrahydrofuran). Ambient air in the vessel was removed by continuous nitrogen flow. The vessel was sealed and its content was sonicated to ensure the most homogeneous dispersion of the reagents. The whole mixture was

illuminated by Hg lamp without filter for a period from 0.5 to 1.5 hours under continuous stirring. Then, 1 ml of 1-octadecene (to form sample Si-C₁₈H₃₇ NCs) or 10-undecylenic acid (to form sample Si-C₁₀H₂₀COOH NCs) was added. The air was again removed by the nitrogen flow and the vessel was resealed. The reaction mixture was set under Hg lamp without filter for a period from 2 to 5 hours under vigorous stirring. Water bath was used to keep temperature below 35°C. After that, the reacted mixture was diluted with 2 ml of deionized water, the organic phase was separated and rinsed with deionized water three times to remove HF residues and centrifuged for 60 min at 14000×g. The precipitated chemically modified Si NCs was rinsed three times with mixture of toluene and methanol (1:3 v/v) to remove alkenes and water residues. At the end, the Si NCs were mixed with 1.5mL of n-hexane (in the case of the Si-C₁₈H₃₇ NCs sample) or ethanol (in the case of the Si-C₁₀H₂₀COOH NCs sample), sonicated for 10 min and centrifuged for 20 min at 14000×g. Further work was produced using the separated liquid layer.

Measurement methods

Fourier transform infra-red (FTIR) spectra of the Si NCs embedded into KBr pellets were recorded in transmission measurement mode in 400 – 4000 cm⁻¹ spectral range in ambient conditions using Bruker Vertex 80 spectrometer. FTIR spectra of the free layers of meso-PS were recorded in transmittance measurement mode in 400 – 8000 cm⁻¹ spectral range in ambient conditions.

For all PL experiments all the investigated sols of the Si NPs were put in an UV transparent 1 ml quartz cuvette and all spectra were corrected using the spectral response function of whole PL system.

PL spectra (steady-state and lifetime) were collected using Edinburgh Instruments Ltd. FLS920 spectrometer. Xe lamp (150W, Hamamatsu) was used as the excitation source for steady-state spectra and picosecond pulsed laser EPL-375 (377.2 nm, 76.4 pulse width, 50 us period) was used for PL lifetime measurements. Relative QY was measured according to procedure described in literature ¹ using fluorescein in 0.1M NaOH as QY standard.

Absolute QY was measured using 6'' integrating sphere Labsphere RTC-060-IG according to the described in literature common methodology ² with the self-absorption correction ³. The third harmonic (343 nm) of the pulsed laser Mikan (Amplitude Systemes, 3W, 1000-1100 nm) was used as the excitation source. Liquid nitrogen-cooled CCD camera CCD-1024x256-OPEN-1LS HORIBA Jobin Yvon with the iHR 320 HORIBA Jobin Yvon monochromator was used as the detector. The PL registration time did not exceed 30 seconds.

REFERENCES

- 1 C. Würth, M. Grabolle, J. Pauli, M. Spieles and U. Resch-Genger, *Nat. Protoc.*, 2013, **8**, 1535–1550.
- 2 J. C. de Mello, H. F. Wittmann and R. H. Friend, *Adv. Mater.*, 1997, **9**, 230–232.
- 3 T. S. Ahn, R. O. Al-Kaysi, A. M. Müller, K. M. Wentz and C. J. Bardeen, *Rev. Sci. Instrum.*, 2007, **78**, 086105.