Supplementary Information

Synthesis of Hollow Silica Nanostructures using Functional Hairy Polymer Nanofibers as Templates

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Experimental Details

Materials. Polystyrene-*block*-poly(4-vinyl pyridine) was procured from Polymer Source, Canada. The PS-*b*-P4VP purchased had Mn =18500 and Mn = 40500 for PS and P4VP, respectively, and a polydispersity index of 1.10. The calculated volume fractions of the PS and P4VP blocks were 0.3 and 0.7, respectively. The Tetraethylorthosilicate (TEOS), chloroform and methanol were purchased from Aldrich and were used as it is. Highly polished single-crystal silicon wafers of {100} orientation were used as substrates. The silicon wafers were cleaned with dichloromethane in an ultrasonic bath for 20 min and then further in a 1:1:1 mixture of 29% ammonium hydroxide (Acros), 30% hydrogen peroxide (Merck) and deionized water for 1.5 h at 65°C *(Warning: This solution is extremely corrosive and should not be stored in tightly sealed containers)*, rinsed several times with distilled water and finally dried in an argon flow.

Preparation of Polymer Nanofibers. PS-*b*-P4VP block copolymer was dissolved in chloroform (a common solvent for both PS and P4VP) at room temperature. Solution was then kept in a saturated vapor atmosphere of chloroform in a closed chamber with a very small opening for slow solvent evaporation. After complete evaporation of the chloroform, block copolymer film was then dissolved in methanol which is a selective solvent for P4VP block. The nanofibers so obtained in the methanol solution were then immobilized on silicon substrates by spin-coating.

Fabrication of Nanospheres from Nanofibers. The nanofibers prepared from the block copolymer self-assembly could be transformed to nanospheres by refluxing the dispersion of nanofibers in methanol. The nanofibers (1 mg/ml) were dispersed in the methanol (selective solvent for P4VP) in a 100 ml round bottom flask fitted with a condenser tube. The solution was heated on a hot plate at the boiling point of the methanol for 48 hours. The solvent vapors were made to condense by the circulating water in the condenser. After refluxing for 48 hours the

dispersion was stored in the glass vial. The dispersion was then spin coated over the cleaned silicon wafer. The nanospheres expected to form were analyzed using SEM, TEM and DLS.

Fabrication of Silica Nanofibers and Nanospheres. Two different approaches were used to fabricate the silica nanofibers and the nanospheres, vapor and the solution approach. In the vapor approach, the silica deposition over the nanofibers/nanospheres was carried out in the vapor phase. The pre-requisite of this approach is the presence of the block with functional group which should be sufficiently nucleophilic to undergo the hydrolysis and condensation. In our system we have 4-vinylpyridine block, where the nitrogen of the pyridine unit provide the sufficient nucleophilicity to undergo the hydrolysis and condensation at the neutral pH. In the solution approach, two different procedures were adopted for silica deposition both of which involved a prior preparation of the sol followed by depositing the silica in the form of the sol over the nanofibers/nanospheres either in their ethanol dispersion or after immobilizing it on silicon substrate. The methods employed for fabricating the silica nanofibers/nanospheres are dealt in brief. In the first approach for fabricating the silica nanofibers/nanospheres, the silicon wafers with the immobilized polymer nanofibers/nanospheres were treated with the vapors of the tetraethylorthosilicate at the neutral pH. The silicon wafers with immobilized nanofibers/nanospheres were kept together with TEOS and water in the closed assembly inside the oven at 60° C for 12 hours. In the second approach the sol is formed first by mixing the TEOS, ethanol, water in the molar ratio of 1:4:16 and 3ml of the 2M solution of HCl in the 100 ml round bottom flask. The solution is placed on the magnetic stirrer and refluxed at 60^oC for 2 hours. The silicon wafers with the immobilized polymer nanofibers/nanospheres were treated with the sol for 10 minutes followed by the washing of the superfluous silica with the methanol followed by drying the silica wafer under the high pressure air. In another procedure, the sol was

directly mixed with the ethanol dispersion of the polymer nanoobjects and then further stirred for 30 minutes. Then this mixture was drop/spin casted over the silica wafer. The drop casted wafers were washed with the ethanol to remove any excess of sol over the substrate and dried with high pressure air. The silica deposited polymer nanofiber/nanosphere samples were then calcined in the air furnace at 400° C for 2 hours.

Characterization. Scanning electron microscopy (SEM) images were obtained with FEI Quanta 200F with Oxford-EDS system IE 250 X Max 80 equipped with field-emission gun (FEG) electron source. The samples prepared on silicon substrates were viewed under the SEM without any additional coating. Conventional Transmission Electron Microscopy (TEM) was performed using a JEOL JEM-2100F transmission electron microscope at an accelerating of 200 kV. Energy-Filtered TEM (EFTEM) analysis was performed on Zeiss Libra200 TEM equipped with Omega-type energy filter at 200kV acceleration voltage using 3-windows method. For mapping of Si, N, C, O the energy windows of 10 eV, 20eV, 30eV, 30eV were used, respectively at the K-ionisation edges of N, C, O and L_{23}-ionisation edge of Si. The samples for TEM imaging were prepared on the carbon coated copper grid and on silicon or silicon oxide thin films supported by silicon frame (TEMwindows^{TM}) by drop casting method. Dynamic light scattering (DLS) measurements were performed with Zetasizer Nano S, (He-Ne-laser 4 mW, 632.8 nm, back scattering, NIBS Technology, Malvern Instruments).
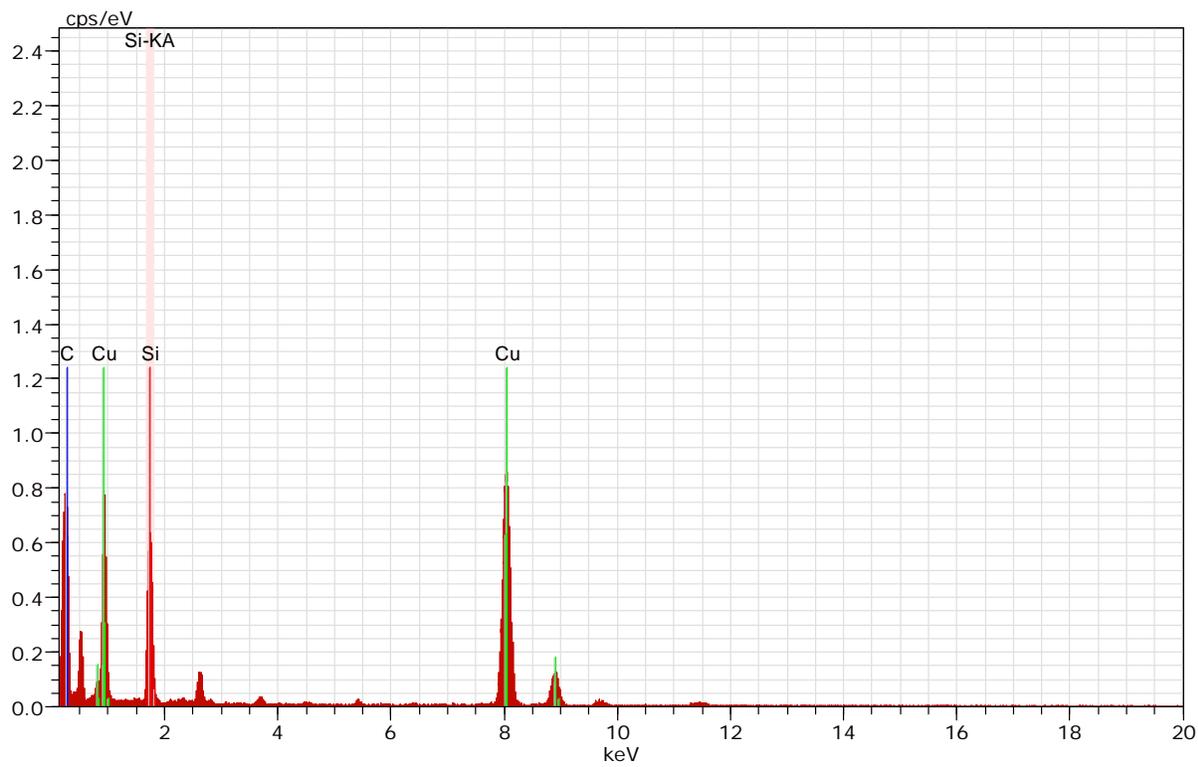
Figure S1: EDX spectra of silica deposited polymer nanofibers obtained during TEM

measurements. The corresponding peaks for silicon could be clearly seen in the spectra.
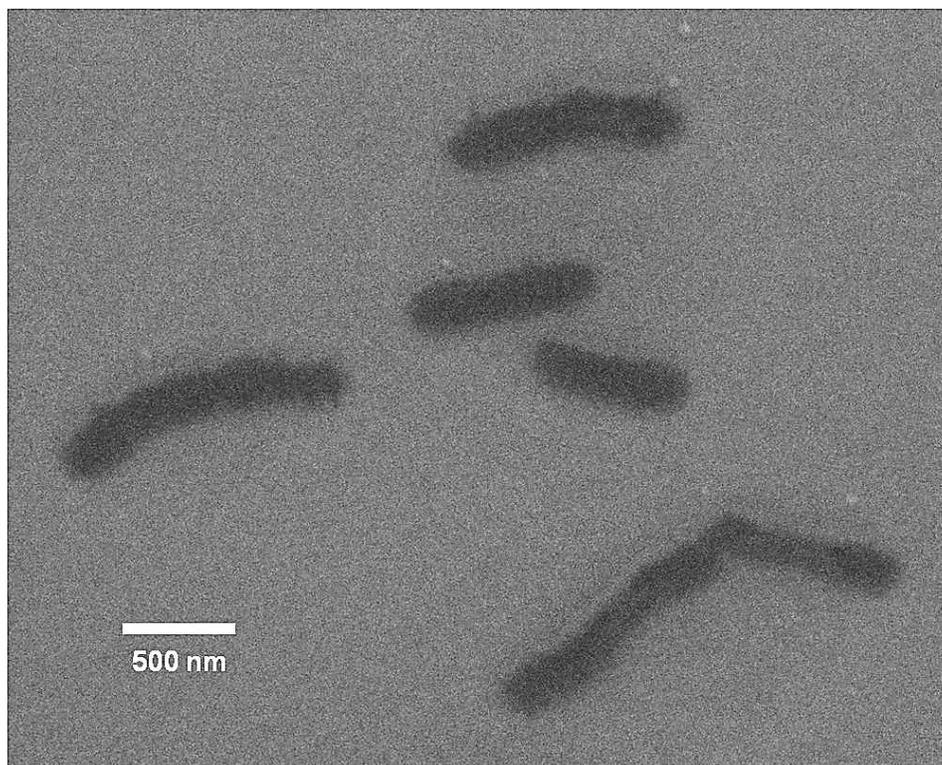
Figure S2: Figure S2: SEM image of Silica/polymer hybrid nanofibers obtained from the vapor phase deposition method. The diameter of the nanofibers increased from ca. 80 nm (as-prepared NF) to around 150 nm after treatment with TEOS vapor, which clearly indicated that silica deposition was successful on the nanofiber.
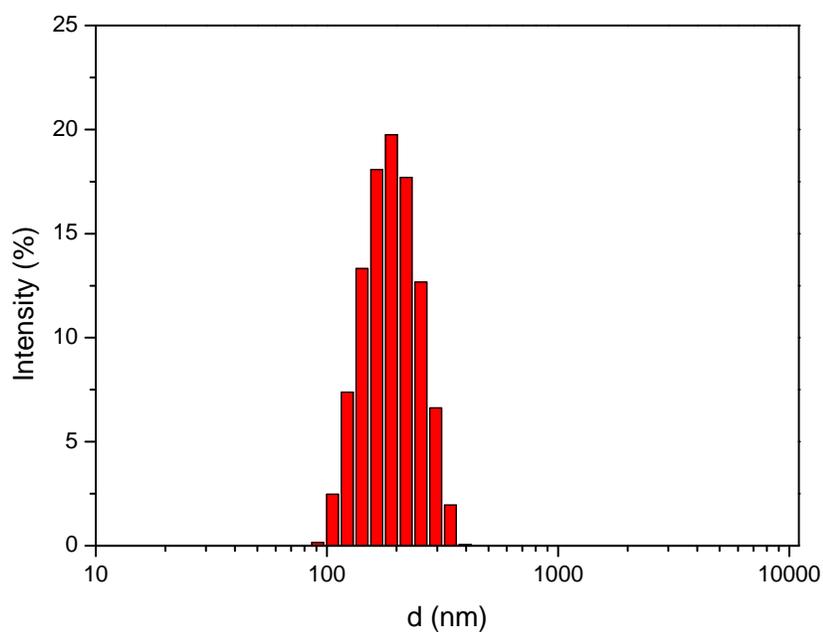
Figure S3: Size distribution histogram of polymer nanosphere obtained from DLS measurements. The average diameter of the nanosphere in methanol was found to be ~ 169 nm with a PDI of 0.150. It must be noted that since in ethanol the P4VP chain will be in a stretched conformation, hence, the diameter as measured using DLS is much larger than that using SEM or TEM of dry samples.
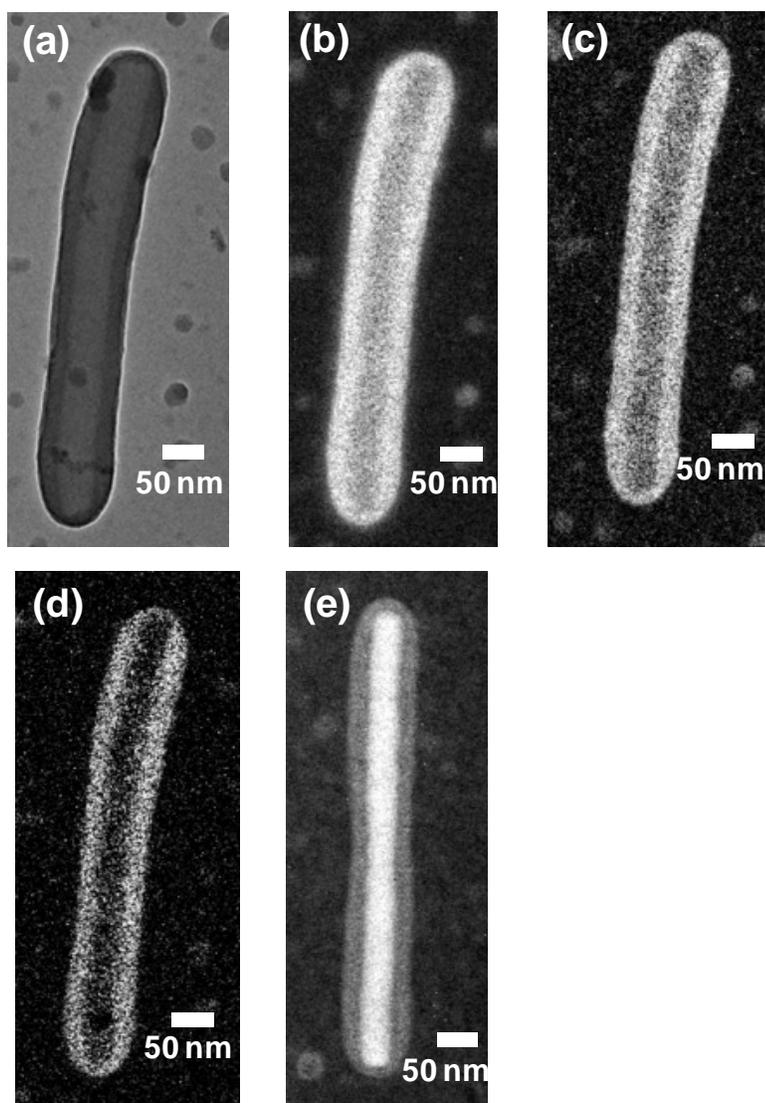
Figure S4: EFTEM images of silica deposited polymer nanofibers (a) and (d) original TEM image of the nanofiber; (b,c,e,f) shows the distribution of different elements in the nanofibers (b) silicon map, (c) oxygen map, (e) nitrogen map, (f) carbon map. The EFTEM analysis clearly shows the homogenous silica deposition on the polymer nanofibers and carbon-reach internal part of the nanofibers composed of PS core. (Note: the carbon mapping was done on different nanofiber due to technical reasons)
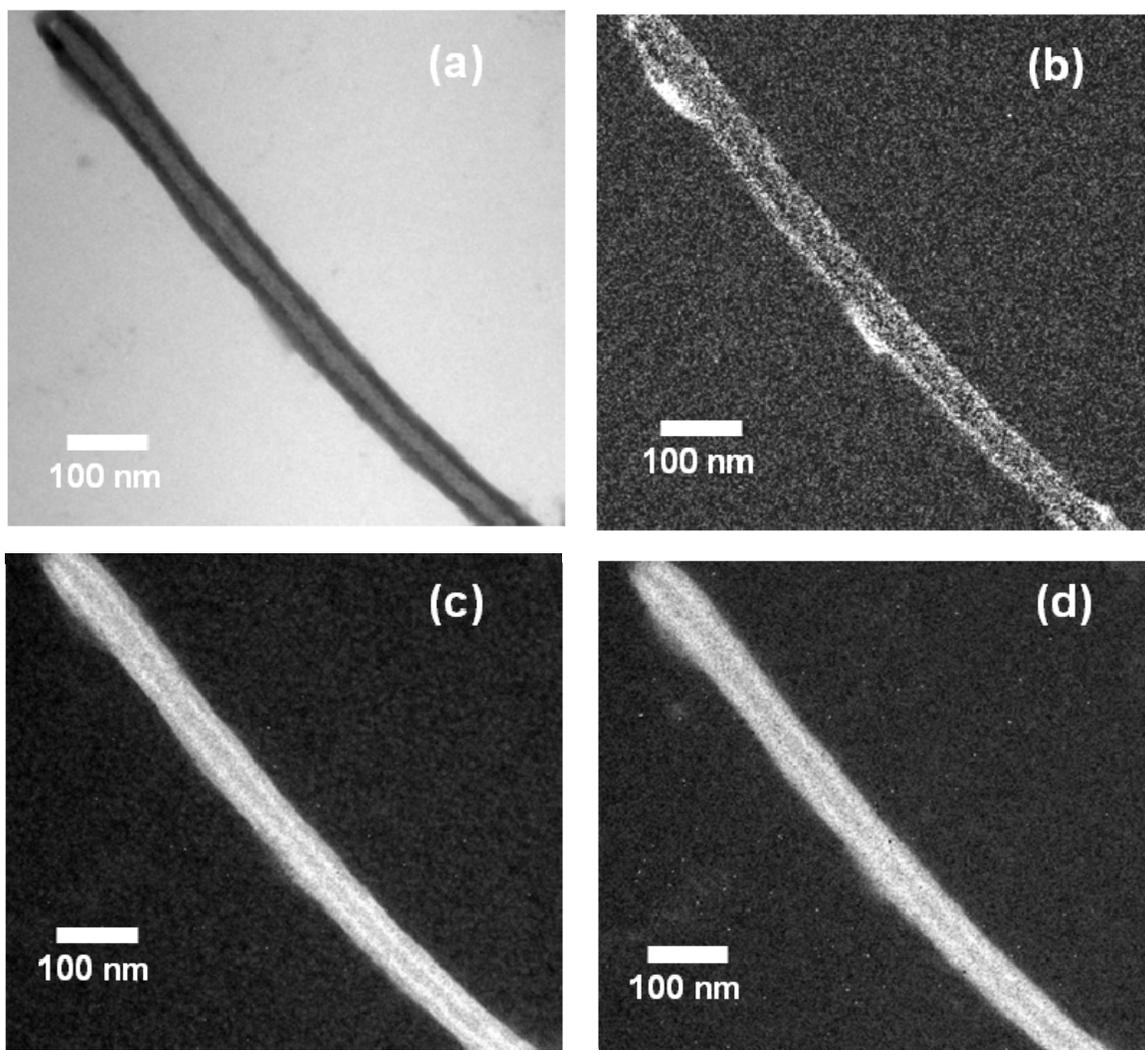
Figure S5: EFTEM images of silica deposited polymer nanofibers after calcination (a) original TEM image of the nanofiber; (b-d) shows the distribution of different elements in the nanofibers (b) carbon map, (c) silicon map, (d) oxygen map. The EFTEM analysis shows that most of the carbon was removed during the calcination process. The presence of carbon traces suggests that a higher residence time during calcination might be necessary for complete removal of carbon.
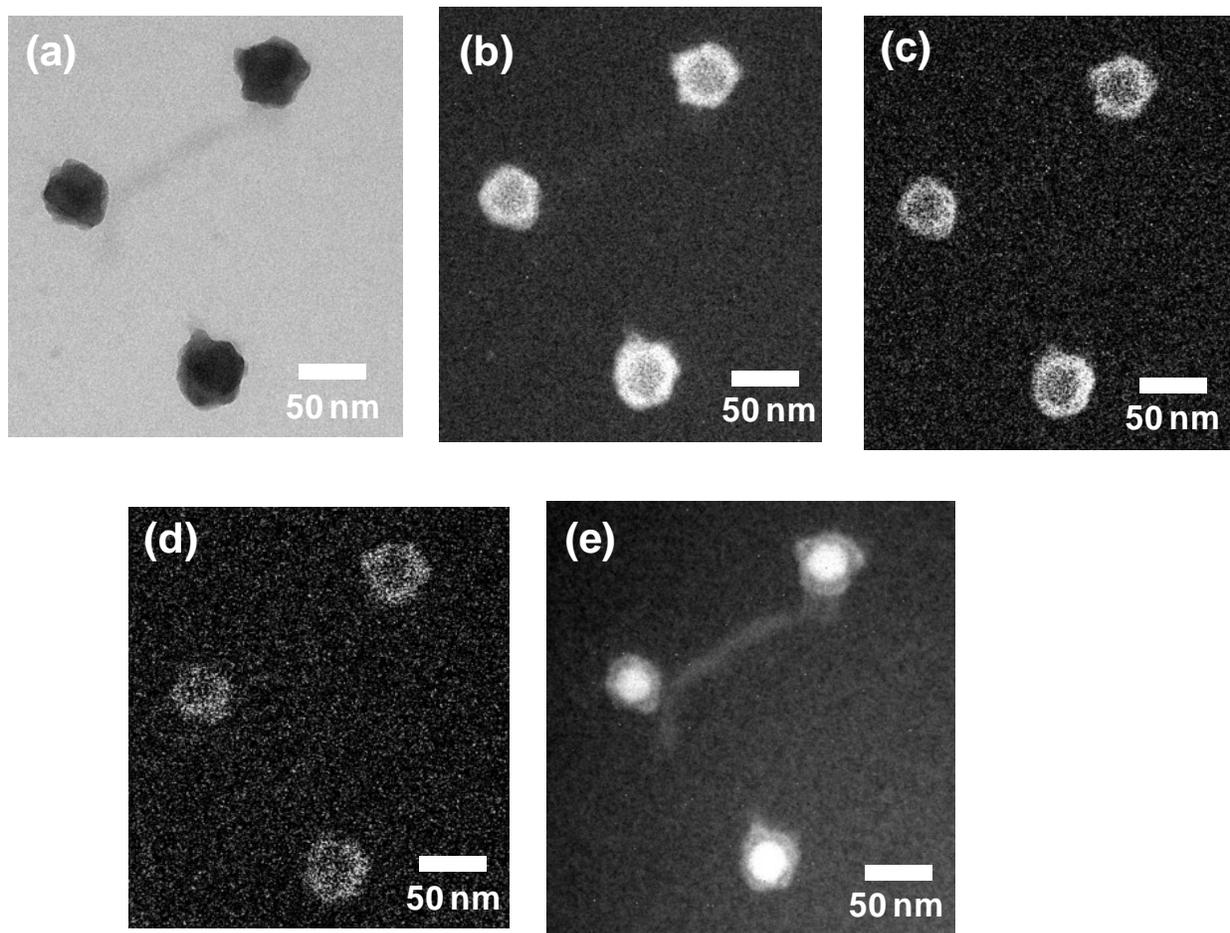
Figure S6: EFTEM images of silica deposited polymer nanospheres (a) original TEM image of the nanosphere; (b-e) shows the distribution of different elements in the nanospheres (b) silicon map, (c) oxygen map, (d) nitrogen map, (e) carbon map. The EFTEM analysis clearly shows the homogenous silica deposition on the polymer nanospheres.
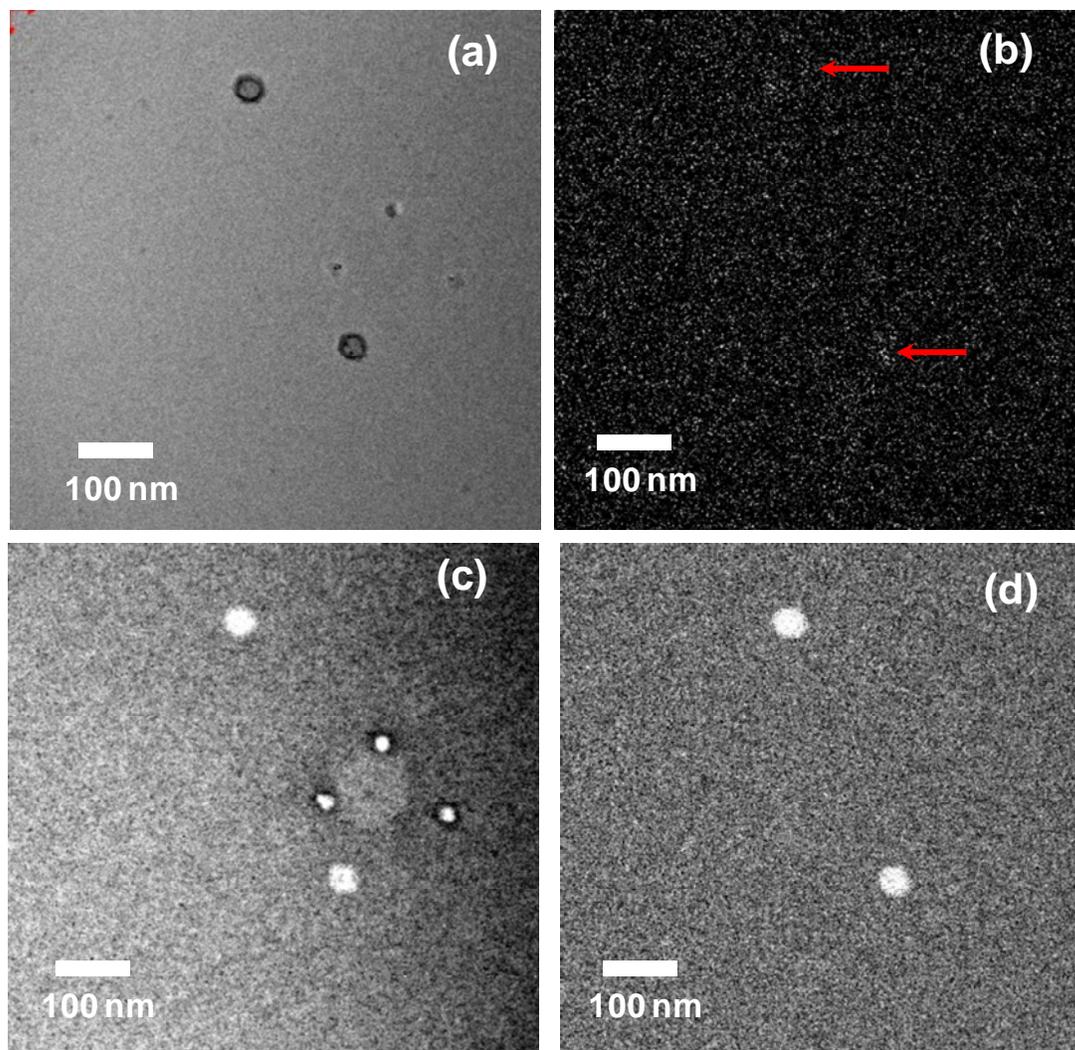
Figure S7: EFTEM images of silica deposited polymer nanospheres after calcination (a) original TEM image of the silica nanosphere; (b-d) shows the distribution of different elements in the nanofibers (b) carbon map, (c) silicon map, (d) oxygen map. The EFTEM analysis shows that almost all carbon was removed during the calcination process. Red arrows on EFTEM image (b) point out traces of carbon signal at silica deposited nanospheres.
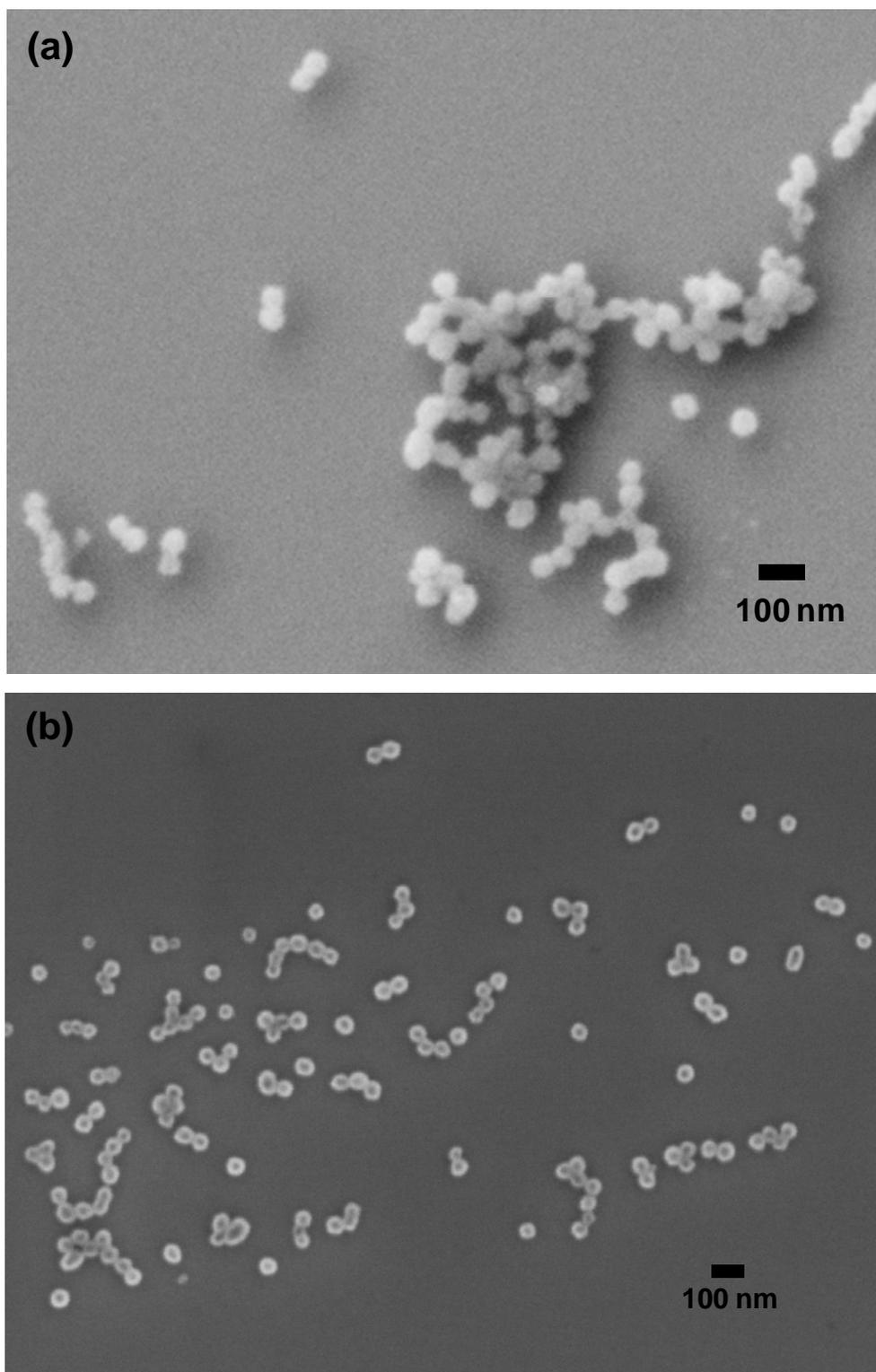
Figure S8: SEM images of silica nanopshere immobilized on a silicon substrate (a) before calcinations; (b) after calcination. The SEM results clearly show that silica coated nanospheres retain their spherical shape after calcination.