

Electronic Supporting Information

Heterogeneous deposition of noble metals on semiconductor nanoparticles in organic or aqueous solvents

Jun Yang,^a Larissa Levina,^b Edward H. Sargent^b and Shana O. Kelley*^a

^a *Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, Massachusetts 02467. Fax: 1-617-552-2705; Tel: X1-617-552-3121; E-mail: shana.kelley@bc.edu*

^b *Department of Electrical and Computer Engineering, University of Toronto, 10 King's College Road, Toronto, Canada M5S 3G4.*

Experimental protocols:

Synthesis of PbS nanoparticles. PbS nanoparticles were synthesized by a previously reported solution method (ref. 17). Briefly, the lead oleate precursor was prepared in advance in situ by heating PbO in oleic acid (OA) at concentrations 0.05~0.2 M under Ar at 150°C for 1 hour. A solution of bis(trimethylsilyl)sulfide (TMS) in octadecene (ODE), a non-coordinating solvent, corresponding to a molar ratio of 2:1 Pb/S was injected into the vigorously stirring lead oleate solution at 150°C. A typical synthesis involved 90 mg PbO dissolved in 4 mL OA, into which 42 μL TMS in 2 mL ODE was injected. The heating mantle was lowered away from direct contact to the reaction flask immediately after injection of the TMS solution. The heating mantle was turned off and then replaced under the reaction flask once the temperature dropped to 125-130°C for slow cooling. After the reaction is completed, methanol was used to precipitate nanoparticles and isolate them from growth solution, starting materials, and side products. Nanoparticles were dispersed in 4 ml of toluene. The average size of the PbS nanoparticle was about 5 nm.

Phase transfer of PbS nanoparticles from toluene to water. 0.2 mL of PbS organosol was diluted 4 mL of toluene, and then 200 μL of MPA was added; the mixture was vortexed for 30 seconds, followed by addition of 4 mL of H₂O. The mixture was vortexed again for 1 minute. The supernatant was removed after complete precipitate of PbS nanoparticles, and the PbS precipitates were resuspended in 4 mL of H₂O, followed by addition of 60 mg DMAP. A clear PbS hydrosol was obtained.

Phase transfer of noble metal ions from water to toluene. The transfer of HAuCl₄ and AgNO₃ (aqueous solution, 1 mM) from water to toluene followed a previous procedure (ref. 19, 20). Typically, 6 mL of 1 mM aqueous HAuCl₄ solution (or AgNO₃ solution) was mixed with 6 mL of ethanol containing 240 μL of dodecylamine. After 3 minute of stirring, 6 mL of toluene was added and stirring continued for 1 more minutes. Phase transfer of Au (or Ag) ions from water to toluene would then occur quickly and completely, as evinced by the complete bleaching of the color in the aqueous phase (for Au). The Au (or Ag) ion concentration in toluene assuming complete transfer of the ions from water was therefore 1 mM. The Au and Ag ions in toluene were separated from the aqueous phase and saved for further experiments.

Deposition of noble metals on semiconductor in organic phase. For the deposition of Au on PbS nanoparticles, 12.5 μL of PbS organosol in toluene obtained above was diluted with 250 μL of toluene, followed by mixing with 1 mL of AuCl_4^- solution in toluene. The mixture was aged for 3 hours to complete the deposition reaction. The deposition of Ag on PbS is similar. The only difference is the reaction time is 6 hour.

Deposition of noble metals on semiconductor in aqueous phase. First, 1 mL of PbS hydrosol prepared using the phase-transfer method was mixed with 4 mL 1 mM aqueous HAuCl_4 solution, followed by addition of 400 μL of aqueous PVP solution ((poly(N-vinyl-2-pyrrolidone), MW = 8000, 100 mM in monomer units). Then under vigorous stirring, 200 μL of aqueous NaBH_4 solution (100 mM) was slowly added dropwise with 5 μL of each drop. The deposition of Au on PbS could be confirmed using TEM, as described in detail in the text.

TEM characterizations. A JEOL JEM2010 microscope with field emission was used to obtain TEM and HRTEM images of the nanoparticles. For TEM measurements, a drop of the nanoparticle solution was placed onto a 3mm copper grid covered with a continuous carbon film. Excess solution was removed by an adsorbent paper and the sample was dried under vacuum at room temperature.