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† Electronic Supplementary Information

Direct synthesis of metal nanoparticles with tunable porosity

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Experimental Section

Chemica** (high solute concentrations)**: Solutions of 50 mM $HAuCl_4$, 150 mM $AgNO_3$ and 600 mM PVP were separately prepared at room temperature by dissolving 85 mg of $HAuCl_4$ (Aldrich), 128 mg of $AgNO_3$ (Merck) and 333 mg of PVP (weight-average molecular weight ~24000, Aldrich), respectively, each in 5 ml EG under stirring with a Teflon-coated magnetic stir bar.

***Synthesis of porous bimetallic nanoparticles**:* Typically, 2 ml of 50 mM $HAuCl_4$, 2 ml of 250 mM $AgNO_3$ and 3 ml of 600 mM PVP were taken from the aforementioned solutions, using 3 different glass pipettes and manually injected at the same time into 3 ml of EG initially preheated for 1 hour at 160^{o}C in a 50 ml beaker. The solution was further heated under magnetic stirring for 15 to 60 minutes, depending on the desired dimension of nanoparticles. A gradual change in color of the solution takes place within the first 3-5 minutes, where a stable opaque purple color appears.

Phase separation: The solution is transferred into a 25 ml glass flask and aged for one day at room temperature in order to allow the metallic nanoparticles to precipitate to the bottom of the flask. EG was then separated from the precipitate, which was further cleaned twice in acetone and twice in demineralised water under magnetic stirring at room temperature. Between each cleaning step, the solution was aged at room temperature for a few hours in order to separate the metal nanoparticles from the solvent by precipitation.

Microstructural characterization: The precipitate was dispersed in methanol (which evaporates quickly) and brought onto an aluminum specimen holder of a scanning electron microscope. An ultra-high resolution scanning electron microscope (UHR-SEM Philips-XL30S SEM-FEG) was used to investigate the porosity under acceleration voltages ranging between 5 and 20 kV and an environmental scanning electron microscope (Philips XL30 ESEM FEG) was used to investigate the alloy composition of the nanoparticles by energy dispersive X-ray spectroscopy (EDS) under an acceleration voltage of 20 kV.

Optical absorption spectra: A spectrometer *(Perkin-Elmer Lambda 900 UV-Vis-NIR Spectrometer)* was used to investigate the absorption spectra of pure Ag and Au-Ag alloys nanoparticles, both

prepared from intermediate solute concentrations (Quasi-uniform nanoparticles required for optical characterization are preferably synthesized from low and intermediate solute concentrations. When the concentration of the reaction reagents is too high, the nanoparticles are not uniform as shown in the SEM image below).

Effect of the synthesis time on the microstructure of the nanoparticles: The synthesis time affects both the nanoparticle size and the average size of ligaments and pores as follows:

(i) The longer the synthesis time, the bigger the particle size. This is a typical behavior which is also observed on non-porous nanoparticles.

(ii) Since the synthesis of the metallic nanoparticles takes place at a relatively high temperature (160^{o}C), the longer the synthesis time, the bigger the average size of ligaments and pores. This is a typical behavior observed in nanoporous metals. This behavior is associated to the severe thermal coarsening of the ligaments and pores in nanoporous metals *(ref. 15)*.

Additional Figure:

Left: Low resolution scanning electron micrograph showing the various types of porous microstructures formed during the one-step synthesis process. Right bottom: Corresponding image at a higher magnification. The difference in ligament size among the nanoparticles can be distinguished. Right top: It can also be seen that the porous microstructure exists inside the nanoparticles.