Electronic Supplementary Information

Gold nanoparticles encapsulated in porous carbon

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Experimental details

 $HAuCl_4 \cdot 3H_2O$ and sucrose are used as the precursor for gold and carbon respectively. NaNO₃ is added as catalyst and as porogen (i.e., pore formation agent). As shown in Fig. S1, a 1.7 MHz piezoelectric transducer was used to nebulize a precursor aqueous solution (e.g. 5 mM HAuCl₄, 0.5 M sucrose, and 1 M NaNO₃) into a mist with micrometer-sized droplets. The mist was then carried through a furnace (500-700 °C) by argon gas at 1 SLPM. The materials were collected in water in bubblers and then washed with water/ethanol (1:1 vol) solution 4 times. The washed product was then dried in a vacuum oven overnight at ~60 °C. As a control, porous carbon without gold was prepared at 700 °C using the same condition as Au/C except no HAuCl₄·3H₂O was added in the precursor solution.

For comparison, the conventional wet impregnation method was used to make Au-loaded on activated carbon (Darco[®] G-60): 0.1 g activated carbon was added to 5 mL HAuCl₄ solution, stirred magnetically at RT for 4 h, dried in vacuum overnight at ~60 °C, and reduced under a flow of 5% H₂ in N₂ at ~300 °C for 3 h. The conventional catalyst so obtained (referred to as Au/AC) has the same loading (3.3 wt% Au) as the USP Au/C catalyst.

Catalytic activity tests for all the chosen nitroaromatic compounds were carried out at 25 °C. 0.2 mL of an aqueous suspension of 1mg/mL USP Au/C or other control catalysts were added to 3 mL 0.1 M NaBH₄ aqueous solution and the mixture was stirred with magnetic stirring for 10 min. 0.1 mL 2.5 mM nitroaromatic compound aqueous solution was then added. The reaction was carried out with magnetic stirring and UV-Vis spectra were collected every 1.5 min and the absorptions at fixed wavelengths were measured every second.

Characterization

Transmission electron microscopy (TEM) micrographs were obtained on a JEOL 2100 Cryo microscope with an accelerating voltage of 200 kV. Scanning electron microscopy (SEM) micrographs were obtained on a Hitachi S-4800 microscope operating at 15 kV. An image analysis software package, ImageJ, was used to measure nanoparticle sizes. Elemental analysis was performed with a CE 440 CHN Analyzer and inductively coupled plasma-mass spectrometer by the Microanalysis Lab of the School of Chemical Sciences at UIUC. Elemental analysis for USP Au/C: Au (3.3 wt%), C (65.5 wt%), O (24.0 wt% by difference), N (4.8 wt%), and H (2.4 wt%). Elemental analysis of USP C without Au: C (61.8 wt%), O (31.1 wt% by difference), N (5.0 wt%), and H (2.1 wt%). Elemental analysis of conventional Au/AC: Au (3.1 wt%), C (89.3 wt%), O (7.3 wt% by difference), N (0.1 wt%), and H (0.2 wt%). Powder X-ray diffraction (XRD) patterns were obtained on a Siemens/Bruker D-5000 XRD using Cu Ka radiation. X-ray photoelectron spectra (XPS) were collected on a Physical Electrons PHI 5400 X-ray Photoelectron Spectrometer using Mg K α radiation. FTIR spectra were acquired on a Thermo Nicolet Nexus 670 FTIR spectrometer using a KBr pellet from 4000 cm⁻¹ to 800 cm⁻¹ at room temperature. Three point Brunauer-Emmitt-Teller (BET) specific surface areas and nitrogen adsorption isotherms were measured using a Quantachrome Nova 2200e system. Pore-size analysis was performed using the Barrett-Joiner-Halenda (BJH) method. The UV-Vis measurements were performed on a Cary 50 UV-Vis spectrophotometer.

HAuCl ₄ initial concentration	Au wt% in catalyst	$\boldsymbol{k}_{\mathrm{app}}~(\mathrm{s}^{-1})$	$\boldsymbol{k}'_{\text{gold}} (\text{s}^{-1}\text{g}^{-1})$
5 mM	3.3%	1.0 x 10 ⁻²	$1.5 \ge 10^3$
20 mM	4.3%	1.7 x 10 ⁻²	2.0×10^3
50 mM	38.5%	4.1 x 10 ⁻²	5.3 x 10

Table S1 Comparison of catalytic activities of USP Au/C with different gold loadings.

Table S2 Comparison of USP Au/C and Au-loaded on activated carbon synthesized using impregnation method.

Catalyst	Surface area (m²/g)	Au NP diameter (nm)	Au wt%	k_{app} (s ⁻¹)	$\mathbf{k'}_{gold}$ (s ⁻¹ g ⁻¹)	$k'_{\text{surface gold}}$ (s ⁻¹ cm ⁻²)	$k''_{\text{surface gold}}$ (s ⁻¹ mol ⁻¹)
USP Au/C	770	33	3.3%	1.0 x 10 ⁻²	1.5×10^3	9.1 x 10 ⁻³	6.3 x 10 ⁶
Au/AC*	340	61	3.1%	2.5 x 10 ⁻³	$4.0 \ge 10^2$	2.1 x 10 ⁻³	1.5 x 10 ⁶

 * Au/AC refers to the catalyst prepared by conventional wet impregnation of HAuCl₄ on activated carbon, described in the Experimental Details section above.



Fig. S1 Ultrasonic spray pyrolysis (USP) experimental apparatus.



Fig. S2 TEM images of USP Au/C microspheres at high and low magnifications. (a) and (e) USP Au/C prepared at 700 °C, (b) and (f) at 600 °C, (c) and (g) at 500 °C. (d) Low magnification SEM image of Au/C microspheres synthesized at 700 °C. The porosity of the carbon support is substantially greater at 700 °C than at lower temperatures. (h) TEM image of porous carbon particles synthesized without Au at 700 °C.



Fig. S3 Size distribution of Au nanoparticles within the carbon spheres synthesized at 700 °C according to TEM images; 116 Au nanoparticles sized using ImageJ image analysis software.



Fig. S4 Pore size distribution of porous carbon support of USP Au/C prepared at 700 °C.



Fig. S5 FTIR of (a) USP Au/C synthesized at 700 °C and (b) USP porous carbon without gold. The presence of similar polar surface functionality (e.g., surface hydroxyl or carboxylic acid groups) is clearly evident both in the absence and presence of Au.



Fig. S6 (a) C 1s, (b) O 1s and (c) Au 4f XPS spectra and peak fitting of Au/C synthesized at 700 °C. In (b), the specific types of oxygen atoms are shown in red.



Fig. S7 UV-Vis spectra of control experiments. (a) a solution of 4-nitrophenol and NaBH₄ without catalyst as initially prepared and after 24 hours (same concentrations as Figure 3). (b) a solution of nitrobenzene and NaBH₄ at the same concentrations as Fig. S10. (c) a solution of 4-nitrophenol and NaBH₄ with porous carbon without Au added; no reactivity is observed over 15 min.



Fig. S8 TEM images of USP Au/C synthesized at 700 °C with different Au loadings. Increasing the initial HAuCl₄ concentrations in the nebulized precursor solution increases the amount of Au in the final catalysts, but also increases the Au nanoparticle size. (a) 5 mM HAuCl₄ in the precursor solution, (b) 20 mM HAuCl₄ and (c) 50 mM HAuCl₄. In all cases the aqueous precursor solution contained 0.5 M sucrose and 1.0 M NaNO₃.



Fig. S9 TEM image of conventionally prepared wet impregnation Au-loaded on activated carbon. The mean Au NP size is 61 nm, as measured using ImageJ.



Fig. S10 (a) Time-dependent UV-vis absorption spectra of the reaction mixture (nitrobenzene and NaBH₄) catalysed by USP Au/C prepared at 700 °C. (b) Plot of $ln(C_t/C_0)$ versus reaction time. C_t/C_0 is calculated based on the absorbance of nitrobenzene at 275 nm.