ESI for

Monolithic Hierarchical Gold Sponges for Efficient and Stable Catalysis in a Continuous-flow Microreactor

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Experimental Section

Preparation of Au Sponges: p(METAC-co-MPTS) was prepared according to the literature[1]. PU sponges were cleaned by water and ethanol for several times, and dried at 80 ºC for 1 h. The precleaned PU was dip-coated into the ethanol solution of p(METAC-co-MPTS), and then the copolymer-coated PU Sponges were dried at 80 ºC for 5 min to remove the solvent. After that, samples were immediately incubated in an ammonia (95% humidity) atmosphere for ~20 min at room temperature, and sequentially baked at 80 ºC for 5 min. And then, the copolymer-coated PU sponges were successively immersed into an aqueous solution of $(NH_4)_2PdCl_4$) (0.5 mM) and deionized water (DI) for 20 min, respectively.

The electroless deposition (ELD) of Au was conducted by first activating the $PdCl_4^{2-}$-loaded substrate in the Cu ELD solution for 5 min, followed by immersing in

the Au plating bath at 65 ºC for about 5 min. After ELD, all samples were rinsed by DI water and dried by compressed air. The Cu ELD solution consists of a 1:1 mixture of freshly prepared solution A and B. Solution A contains NaOH (12 g/L), $CuSO_4 \cdot 5H_2O$ (13 g/L), and $KNaC_4H_4O_6 \cdot 4H_2O$ (29 g/L) in DI water. Solution B is a HCHO (9.5 mL/L) aqueous solution. The Au ELD solution contains $HAuCl_4$ (16.95 g/L), NaOH (2.0 g/L), $NH_2OH \cdot HCl$ (34.75 g/L), Na_2HPO_4 (55 g/L), $Na_2S_2O_3 \cdot 5H_2O$ (80 g/L) and Na_2SO_3 (200 g/L) in DI water.

Catalytic Reduction of 4-NP with $NaBH_4$: In a typical catalytic reaction, the Au sponges were employed as the catalyst for the reduction of 4-NP at room temperature. An aqueous solution of 4-NP (0.005 M, 0.16 mL) was added to water (10 mL), followed by the rapid addition of a freshly prepared solution of $NaBH_4$ (0.5 M, 0.80 mL). The absorption spectrum of the reaction mixture was measured on a UV-vis spectrometer. The peak intensity at 392 nm was assigned as A_0. The Au sponges were then placed in the reaction solution. After the reaction solution was kept under gentle magnetic stirring for proper time, the absorption spectrum of the mixture was measured again. The peak intensity at 392 nm was assigned as A_t. The conversion efficiency was calculated according to the equation $C = (1-A_t/A_0) \times 100\%$.

For the continous-flow catalytic reduction of 4-NP, the as-prepared Au sponges were firstly sealed in a PDMS box with the inlet and outlet (diameter = 1.0 mm). Then, 500 mL of the reaction solution was slowly injected into this microfludic reactor, and the flow rates were controlled by a peristaltic pump. The whole process was conducted in a dark place.

Characterizations: The morphology and energy dispersive spectroscopy (EDS) of PU and Au sponges were investigated by scanning electron microscopy (SEM) (TM3000, Hitachi). Atomic force microscopy (AFM) was performed with XE-100 (Park Systems) in non-contact mode to characterize the surface morphology of Au films and sponges. UV-vis spectra were recorded by a UV-vis spectrometer (PerkinElmer Lambda 18). X-ray diffraction (XRD) spectra were carried out by using a Bruker D8-Advance X-ray powder diffractometer with Cu Kα radiation (λ = 1.5418 Å).

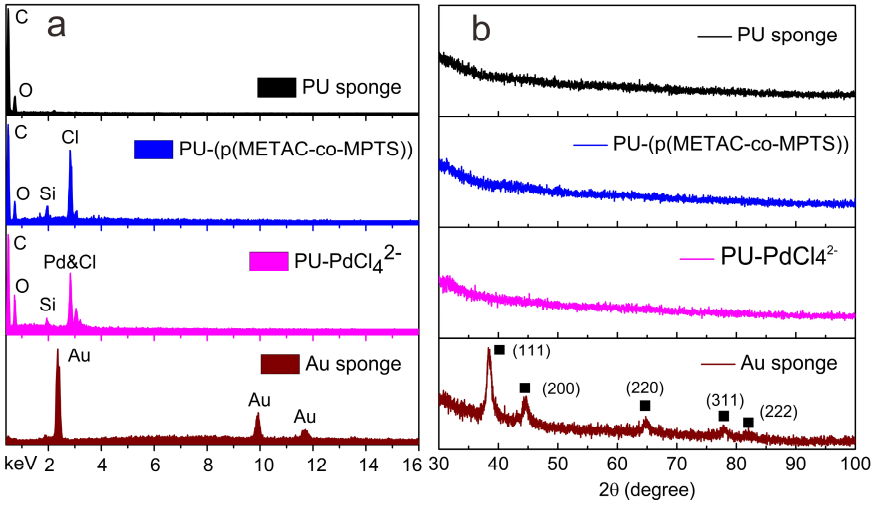

Figure S1. EDS (a) and XRD (b) spectra of PU sponge, PU-(p(METAC-co-MPTS)), PU-$PdCl_4^{2-}$, and Au sponge, respectively.

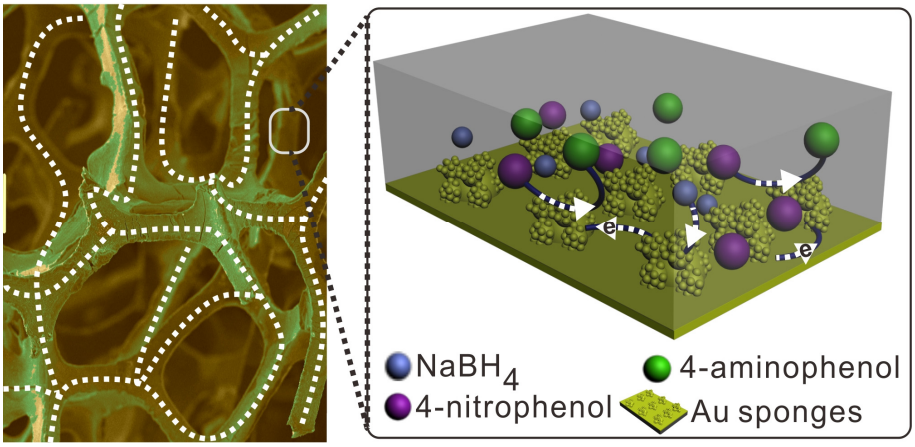

Figure S2. The possible catalytic mechanism of the as-prepared hierarchical Au sponge to the reduction of 4-NP with excess sodium borohydride. White dash lines show the moving pathways of electrons.

1. Y. Yu; J. Zeng; C. Chen; Z. Xie; R. Guo; Z. Liu; X. Zhou; Y. Yang; Z. Zheng, *Adv. Mater.* 2014, **26**, 810.