Electronic Supplementary Information

Freestanding Monolayered Nanoporous Gold Films with High Electrocatalytic Activity via Interfacial Self-Assembly and Overgrowth

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Fig. S1 (a) Optical image of a monolayer of 12 nm gold NCs, obtained via self-assembly at the interfaces between pentanol and the aqueous dispersion of the corresponding citrate-stabilized gold NCs. (b) Optical image of the NPG FSF obtained via overgrowth of gold on the gold NC monolayer shown in Figure 3 (a), floating on the surface of the electroless solution containing the $HAuCl_4$/citrate mixture with the citrate to $HAuCl_4$ molar ratio of 0.3. The amount of $HAuCl_4$ in the aqueous phase (10 mL) is 2.5×10^{-6} mol.

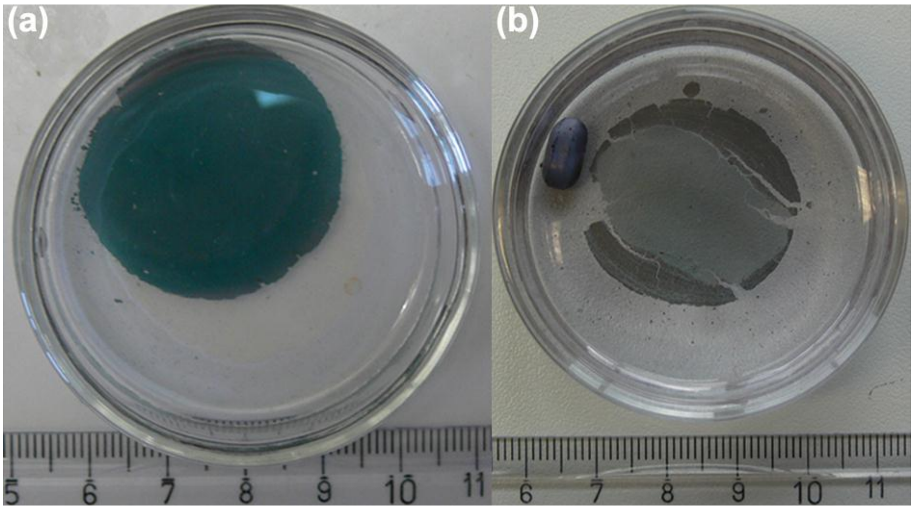

Fig. S2. The high resolution TEM image of NPG FSFs (Fig. 3c in the main text in large size) obtained via overgrowth of gold onto the monolayers of gold NCs with sizes of 12 nm, floating on the surfaces of aqueous electroless plating solutions.

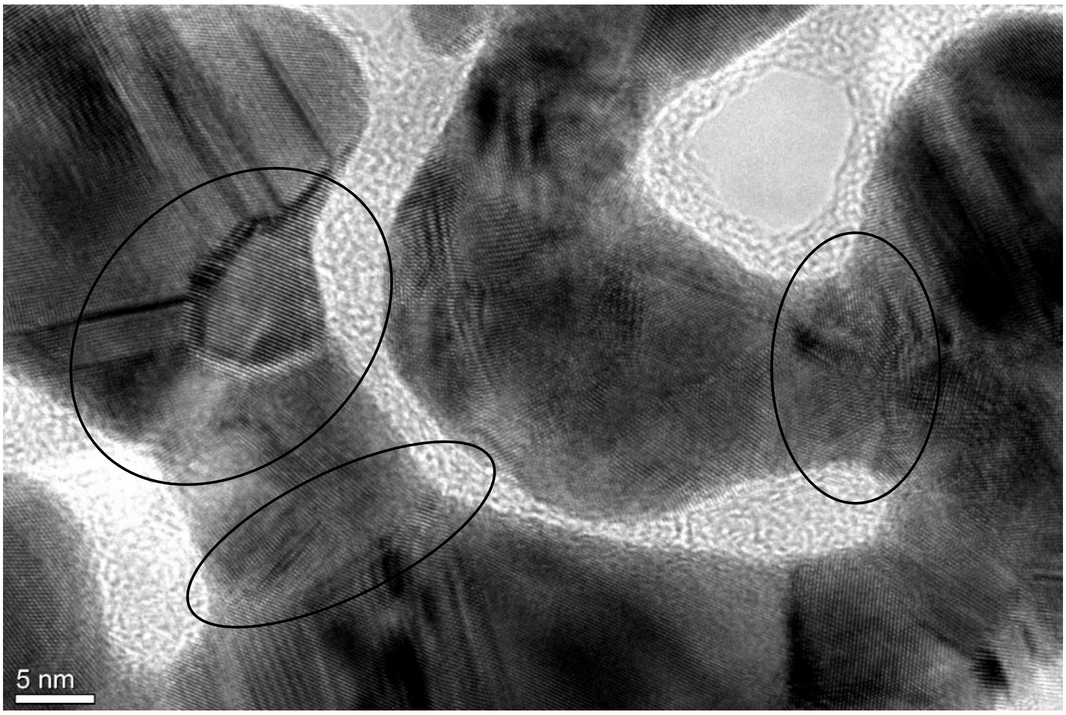

Fig. S3 Low (a) and high (b) magnification TEM images of the NPG FSFs derived from 12 nm gold NCs via conventional electroless plating on the NC monolayers, floating on water. The NC monolayers are obtained via self-assembly of the NCs at the interfaces between pentanol and the aqueous dispersions of the corresponding citrate-stabilized gold NCs. The electroless plating solution contains the mixture of $HAuCl_4$ and $NH_2OH{\cdot}HCl$ (0.1 M, 180 μL) and is dropwise added into the water phase; each drop is 20 μL and added at an interval of 60 sec.

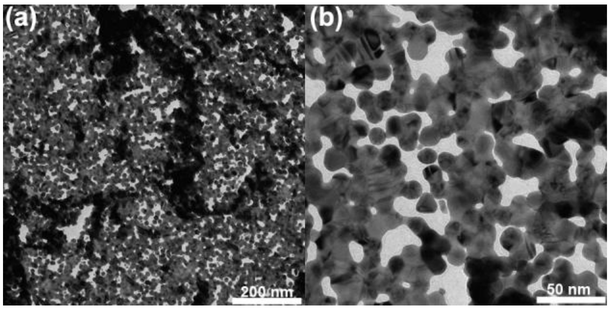

Fig. S4 Typical force-displacement curves of the NPG FSFs derived from 12 nm gold NCs via gold overgrowth of the NC monolayers, floating on the surface of the electroless solution containing the $HAuCl_4$/citrate mixture with the citrate to $HAuCl_4$ molar ratio of 0.3. The amount of $HAuCl_4$ in the aqueous phase (10 mL) is 2.5×10^{-6} mol. The NC monolayer is obtained via self-assembly at the interfaces between pentanol and the aqueous dispersions of the corresponding citrate-stabilized gold NCs. The NPG FSFs are supported on empty copper grids for AFM measurements.

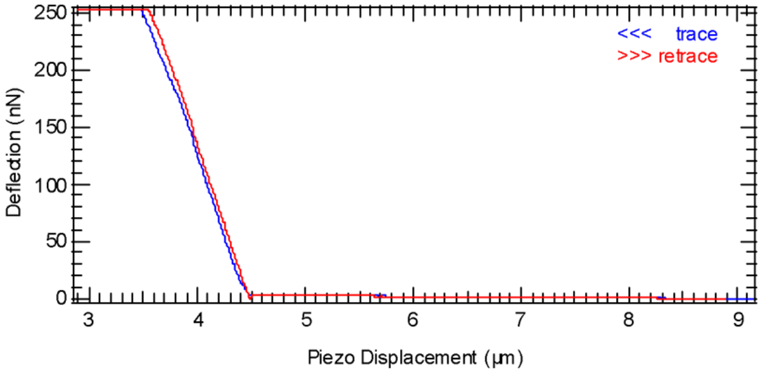

Fig. S5 (a) CV curves of methanol at different concentrations bearing 0.1 M KOH at the electrodes of 12 nm gold NCs. The scan rate is 10 mV s^{-1}. (b) Plot of calibrated oxidation peak current vs. methanol concentration. (c) CV curves of 1.0 M methanol bearing 0.1 M KOH at the electrodes of 12 nm gold NCs at different scan rates. (d) Plot of calibrated oxidation peak current vs. scan rate.

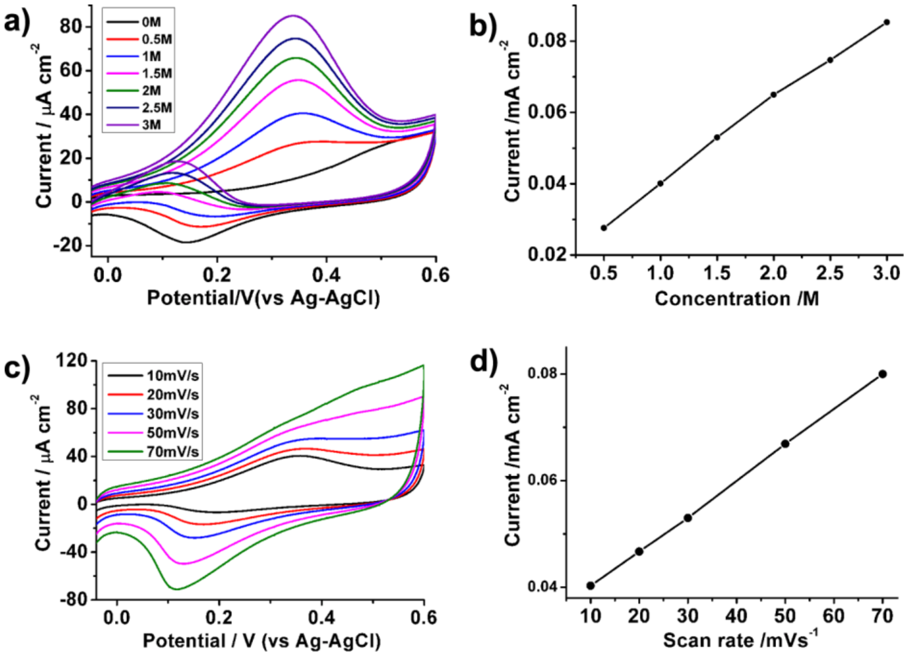

Fig. S6 The variation of oxidation peak current density of NPG FSFs at different scanning cycle numbers. The CV curves are recorded at 1.0 M methanol in 0.1 M KOH solution with electrodes modified by NPG FSFS derived from 12 nm gold NCs. The scanning rate is 10 mV s^{-1}.

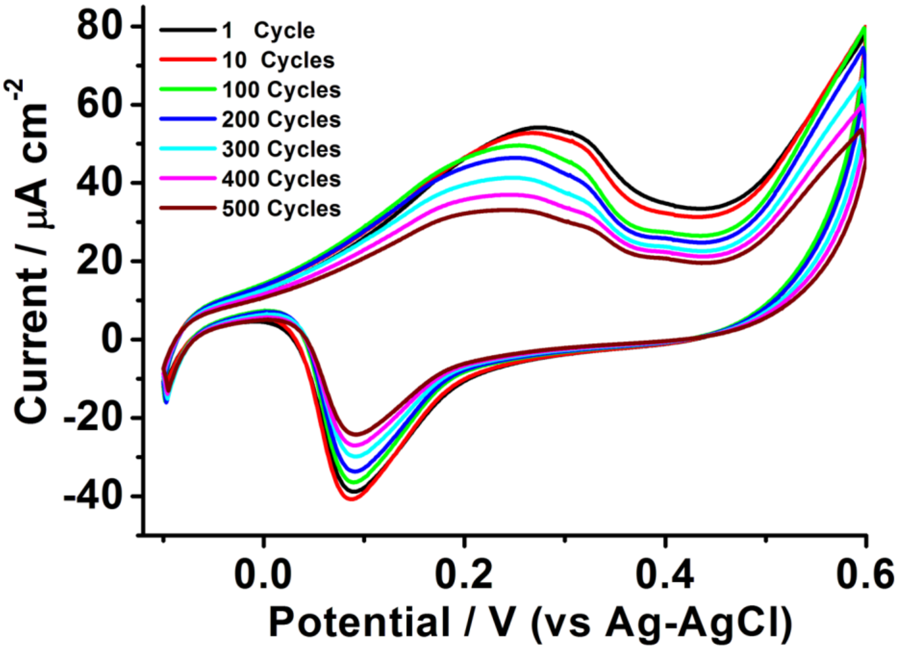

Fig. S7 The variation of oxidation peak current density of 12 nm Au NCs at different scanning cycle numbers (a) and plot of the calibrated CV oxidation peak current density vs. the scanning cycle number (b). The CV curves are recorded at 1.0 M methanol in 0.1 M KOH solution with electrodes modified by NPG FSFS derived from 12 nm gold NCs. The scanning rate is 10 mV s^{-1}.

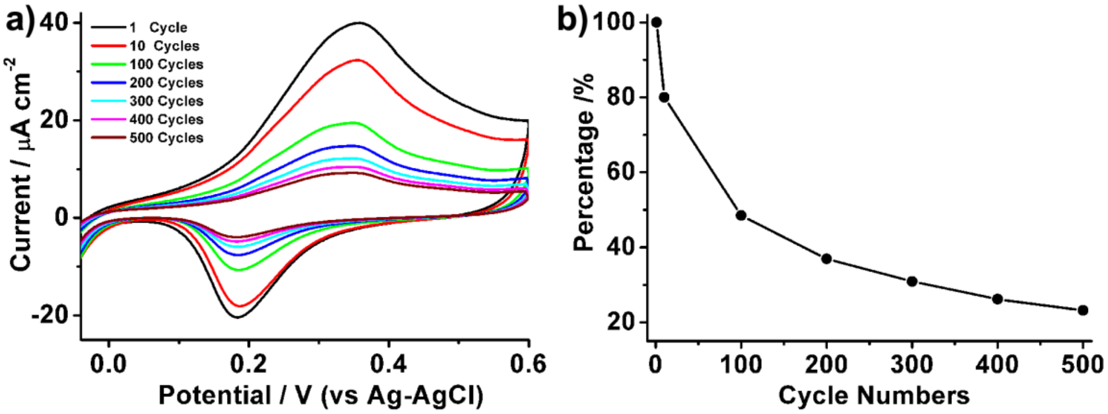

Fig. S8 Cyclic voltammetry for NPG FSFs measured in an alkaline medium (0.1 M KOH). The currents are normalized by physical surface areas of the used electrodes. The peak area is associated with the reduction of Au oxide species and is used for the evaluation of the ECSAs.

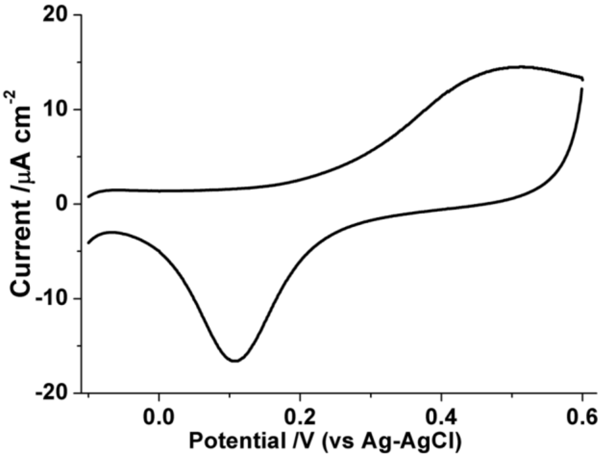

Fig. S9 The current-time curves of the as-prepared NPG FSFs (green line) and 12 nm Au NCs (red line) in 0.1 M KOH solution with 1.0 M methanol, the current-time curve is recorded at 0.2 V and 0.3 V, respectively.