## **Supporting information**

3D nanoporous Ag microstructures fabricated from AgCl microcrystal templates *via* concerted oxidative etching/re-deposition and galvanic

replacement

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**Figure S1**. EDS spectrum and elemental maps of 6pAgCl microcrystals synthesized by the Clinduced precipitation of  $[Ag(NH_3)_2]^+$ .

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**Figure S2.** EDS spectra and elemental maps of np-6pAgMSs galvanized by (A) Sn, (B) Cu, (C) Pb and (D) Al in a solution of 0.5 M NaCl.



**Figure S3.**The morphological evolution of np-6pAgMSs at (A) 0, (B) 1, and (C) 2 mm away from the Zn surface. SEM micrographs were recorded at 30 seconds, 5 minutes, 10 minutes and 3 days after the starting of galvanization.



**Figure S4.** The conversion of AgCl into np-AgMSs (A) without and (B) with NaCl electrolyte using Al as a sacrificial metal. SEM micrographs were recorded at 1, 3 and 10 hours after the galvanization. (C) The proposed galvanization mechanism.

The AgCl microtabular was fabricated *via* the evaporation of  $[Ag(NH_3)_2]^+Cl^-$  under an ambient condition. The AgCl microtabulars were separated, washed several time with DI water and dropped on carbon tape. Then, the immobilized AgCl microtabulars on carbon tape were attached on aluminum foil. Aluminum foil was employed as a sacrificial metal due to it provides a slower galvanization rate compared to Zn. It offers a clear observation on the morphological evolution. However, the galvanic replacement reaction was performed in a boiling solution to accelerate the reaction. DI water or 0.1 M NaCl was employed as media. The morphology of np-AgMSs was investigated at 1, 3 and 10 hours after the dipping of sample into a boiling solution.



Figure S5. SEM micrographs show the gaps between galvanized and non-galvanized AgCl.



**Figure S6.** SEM micrographs of np-AgMSs galvanized from the  $Ag_2SO_4$  microstructures using Zn as a sacrificial metal in a solution of (A) 0.5 M NaCl and (B) 0.5 M NaNO<sub>3</sub> at 0 and 2 mm away from the Zn surface.

The  $Ag_2SO_4$  microstructures were synthesized by an addition of  $AgNO_3$  solution (1 M, 5 mL) into  $Na_2SO_4$  solution (0.25 M, 50 mL) and washed with DI water several times before using as a template.



**Figure S7.**EDS spectrum and elemental maps of np-6pAgMSs during the galvanization with Zn in a solution of 0.5 M NaCl. The tables show the elemental compositions analyzed in the complete (point 1) and incomplete (point 2) galvanized area.



**Figure S8.** Effect of sacrificial metal size on the morphology and grain particle size of np-6pAgMSs galvanized under 0.5 M NaCl using (A) Zn plate and (B) Zn powder.



**Figure S9.** EDS spectra and elemental maps of np-6pAgMSs fabricated by the reduction of 6pAgCl microstructures using (A) 0.2 M NaBH<sub>4</sub> and (B) 0.2 M L-ascorbic acid.



**Figure S10.** Absorption spectra of the catalytic reduction of *p*-nitrophenol by NaBH<sub>4</sub> using np-8pAgMSs (synthesized using 0.5 M NaCl as a galvanization media)



**Figure S11.** Intensity ratio at 400 nm between *p*-nitrophenol in a presence of np-8pAgMSs and *p*-nitrophenol in a presence of NaBH<sub>4</sub>.

The catalytic reduction of nitrobenzene by NaBH<sub>4</sub> on metal surface was revealed in the term of Langmuir-Hinshelwood model. This model described that the metallic nanoparticles reacted with the  $BH_4^-$  to form the metal hydride. Simultaneously, nitrobenzene adsorbs onto the metal surface. The adsorption/desorption of both reagents on the surface is fast and can be modeled in terms of a Langmuir isotherm. The rate-determining step is the reduction of the adsorbed nitrobenzene to aminobenzene, which desorbs afterward.<sup>1</sup>

A solution of *p*-nitrophenol before an addition of catalyst and NaBH<sub>4</sub> has strong absorption band at 317 nm (see Figure S10). The adsorption at 317 nm was decreased with a developing band at 400 nm due to the formation of the *p*-nitrophenolate ion<sup>2, 3</sup> when only catalyst or NaBH<sub>4</sub> was introduced. However, the deprotonation of *p*-nitrophenol was not completed when catalyst was introduced with an absence of NaBH<sub>4</sub>. After catalyst and NaBH<sub>4</sub> were introduced together, the *p*-nitrophenolate ion was reduced to *p*-aminophenol, which has the adsorption at 300 nm. The decreasing in the absorption of the *p*-nitrophenolate ion at 400 nm was not due to the adsorption on catalyst surface. In an absence of NaBH<sub>4</sub>, the intensity at 400 nm was slightly decreased after 6 minutes without any developing of the peak at 300 nm whereas this peak was developed after an addition of NaBH<sub>4</sub> (see Figures S10). Figure S11 presents the intensity ratio at 400 nm between p-nitrophenol in a presence of np-8pAgMSs and p-nitrophenol in a presence of NaBH4. The intensity ratio is nearly constant during mixing process. It implies that the adsorption of *p*-nitrophenolate ion on the Ag surface is not a major factor in a decrease in the intensity at 400 nm.



Figure S12. The effect of grain size in np-6pAgMSs on the catalytic reduction efficiency.



**Figure S13.** SEM micrographs of (A) as-prepared np-8pAgMSs and (B) np-8pAgMSs after 10<sup>th</sup> –cycle of the catalytic reduction.

## References

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