## Formation of nanostructured porous Cu/Au surfaces: the influence of cationic sites on (electro)-catalysis

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## **Supplementary Information**

**Figure S1.** SEM images of Cu/Au electrodeposited at a current density of 3 A cm<sup>-2</sup> from a solution of 0.4 M CuSO<sub>4</sub> containing 5 mM KAuBr<sub>4</sub> in 1.5 M H<sub>2</sub>SO<sub>4</sub> for (a) 5, (b) 10, (c) 15 and (d) 30 sec.



**Figure S2.** SEM images of Cu/Au electrodeposited at a current density of 3 A cm<sup>-2</sup> from a solution of 0.4 M CuSO<sub>4</sub> containing 50 mM KAuBr<sub>4</sub> in 1.5 M H<sub>2</sub>SO<sub>4</sub> for 15 sec.



**Figure S3.** SEM images of Cu/Au electrodeposited at a current density of 3 A cm<sup>-2</sup> from a solution of 0.4 M CuSO<sub>4</sub> containing (a) 5, (b) 10 and (c) 20 mM KAuBr<sub>4</sub> in 1.5 M H<sub>2</sub>SO<sub>4</sub> for 15 sec, (d) corresponding E-time plots recorded during the galvanostatic deposition process for S-0, S-1, S-2 and S-3.



**Figure S4:** SEM images of Cu/Au electrodeposited at a current density of 3 A cm<sup>-2</sup> from a solution of 0.4 M CuSO<sub>4</sub> containing 10 mM KBr in 1.5 M  $H_2SO_4$  for 15 sec.



**Figure S5:** SEM images of Cu/Au electrodeposited at a current density of 3 A cm<sup>-2</sup> from a solution of 0.4 M CuSO<sub>4</sub> containing 10 mM HAuCl<sub>4</sub> in 1.5 M H<sub>2</sub>SO<sub>4</sub> for 15 sec.



**Figure S6-1.** Copper 2p core level X-ray photoemission spectra recorded from the Cu/Au samples S-1(A), S-2(B), S-3 (C) and S-4 (D). Experimental spectra are shown as circles, individual components are shown as lines and solid thick lines represent the best fit curves



**Figure S6-2.** Oxygen 1s core level X-ray photoemission spectra recorded from the Cu/Au samples S-1(A), S-2(B), S-3 (C) and S-4 (D). Experimental spectra are shown as circles, individual components are shown as lines and solid thick lines represent the best fit curves



**Figure S6-3.** Gold 4f core level X-ray photoemission spectra recorded from the Cu/Au samples S-1(A), S-2(B), S-3 (C) and S-4 (D). Experimental spectra are shown as circles, individual components are shown as lines and solid thick lines represent the best fit curves



**Figure S7:** XPS Au 4f spectrum of honeycomb gold electrodeposited on to an evaporated gold surface at a current density of 2 A cm<sup>-2</sup> from a solution of 0.1 M KAuBr<sub>4</sub> in 1.5 M  $H_2SO_4$  for 30 sec.



**Figure S8:** XRD pattern of porous copper electrodeposited at a current density of 3 A cm<sup>-2</sup> from a solution of  $0.4 \text{ M CuSO}_4$  in 1.5 M H<sub>2</sub>SO<sub>4</sub> containing 10 mM KBr for 15 sec.



**Figure S9:** Porous Cu/Au electrodeposited from electrodeposited at a current density of 3 A cm<sup>-2</sup> from a solution of 0.4 M CuSO<sub>4</sub> in 1.5 M H<sub>2</sub>SO<sub>4</sub> containing 10 mM HAuCl<sub>4</sub> for 15 sec. (a) XRD pattern and XPS core level spectra of (b) Au 4f, (c) Cu 2p 7/2 and (d) O1s energy levels.



**Figure S10.** Time dependent UV-vis spectra recorded for the reduction of 4-nitrophenol with NaBH<sub>4</sub> catalysed by (a) honeycomb Cu (S-0) and (b) honeycomb Cu/Au (S-1), (c) plot of  $\ln(A_t/A_0)$  versus time for samples S-0, S-1 and S-3. Note: The electrodeposition time employed here was 5 s.



**Figure S11.** Time dependent UV-vis spectra recorded for the reduction of 4-nitrophenol with NaBH<sub>4</sub> catalysed by honeycomb Cu (S-0) and after the addition of honeycomb Cu/Au (S-1) to the reaction mixture after 10 min.



**Figure S12.** Time dependent UV-vis spectra recorded for the reduction of 4-nitrophenol with NaBH<sub>4</sub> catalysed by honeycomb Cu/Pd. The Cu/Pd sample was prepared by electrodeposition on to a copper foil electrode at a current density of 3 A cm<sup>-2</sup> for 15 s from a solution of 0.4 M CuSO<sub>4</sub> and 1.5 M H<sub>2</sub>SO<sub>4</sub> containing 10 mM Pd(NO<sub>3</sub>)<sub>2</sub>.



Figure S13: XRD pattern of Cu/Au (S-2) after immersion in NaBH<sub>4</sub> for 5 min.