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Monolithic Cu/C hybrid beads with well developed porosity for reduction of 4-nitrophenol to 4-aminophenol

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Materials and methods

Chemicals

Sodium alginate was received from Tianjin GuangFu Chemical Research Institute, China. $Cu(NO_3)_2$ and HNO_3 solution was obtained from Sinopharm Chemical Reagent Corporation, China. 4-NP and $NaBH_4$ were purchased from Aladdin Chemistry Corporation, China. All chemicals were analytical grade and used as received without any further purification.

Preparation of Cu-SA hydrogel beads

2 g of sodium alginate was dissolved in 100 mL of deionized water and stirred until evenly dispersed. The solution was then outgassed for 24 h. $Cu(NO_3)_2$ aqueous solution (0.1 M and 0.3 M) was prepared in 100 mL of deionized water. Cu-SA hydrogel beads with a mean diameter of 4 mm were produced by drop-by-drop addition of sodium alginate into $Cu(NO_3)_2$ aqueous solution under continual magnetic stirring. The as-prepared hydrogel beads were filtered and washed with deionized water and ethanol after completely curing. Finally, the hydrogel beads were dried at 60 ^oC for 24 h.

Preparation of monolithic Cu/C hybrid beads

Cu-SA beads were heated to a preset temperature (500 ^oC, 700 ^oC and 800 ^oC) under the flow of N_2 at a heating rate of 5 ^oC min^{-1}, respectively. After being cooled in N_2, Cu/C hybrid beads were washed with deionized water to thoroughly remove other impurities. Finally, various products, named as Cu/C-500, Cu/C-700 and Cu/C-800, were dried at 60 ^oC in oven for further use. In order to determine the loading of Cu/C beads, the Cu nanoparticles was removed from the beads using 50 mL of 0.5M HNO_3 solution. The resulted sample was filtered and washed with deionized water. Finally, the C beads were dried at 60 ^oC for 24 h.

Catalytic reaction of 4-NP to 4-AP in the presence of Cu/C hybrid beads

The catalytic reaction of 4-NP to 4-AP was carried out in a well-stoppered three flask using Cu/C hybrid beads as a catalyst. 80 mg of the beads was added to 10 mL of 4-NP solution (0.25×10^{-3} M). Then, the above suspension

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was immediately mixed with 10 mg of $NaBH_4$. As the catalytic reaction proceeded, bright yellow solution faded gradually. The catalytic activity was monitored by a UV-vis spectrophotometer at a time interval. After the reaction was completed, the catalyst was obtained from the mixture with filtration and repeatedly washed by deionized water and ethanol. Then, the catalyst was reused in the next cycle.

Materials characterization

Thermogravimetric analyzer (TGA, Q50) was used to measure the remaining weigh of the Cu-SA beads after pyrolysis in N_2. Heating rate is 10 ^oC min^{-1}. The structure of Cu/C hybrid beads was observed by SEM (JSM-7800F, JEOL, Japan) and TEM (JEM-2100, JEOL, Japan). The samples were coated with gold prior to examination. XRD analysis was conducted by Shimadzu XRD-6100 diffractometer using Cu-Kα radiation (λ = 1.54060 Å) for a 2θ range of 10^o to 80^o at a scanning speed of 8^o min^{-1}. BET surface area and porosity of the samples were studied using a N_2 adsorption-desorption instrument (Nova 1200e Surface Area and Pore Size Analyzer).

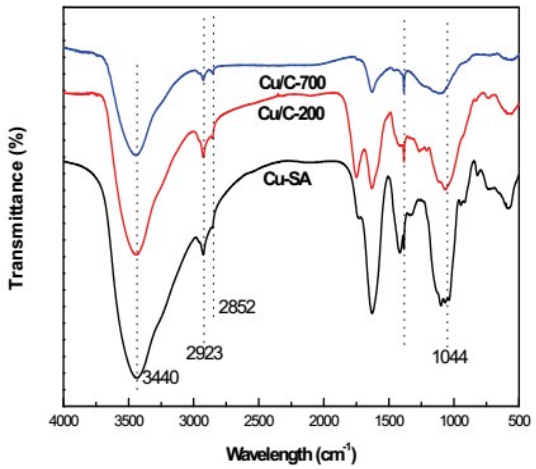

Fig. S1 FTIR spectra of Cu-SA, Cu/C-200 and Cu/C-700 beads.

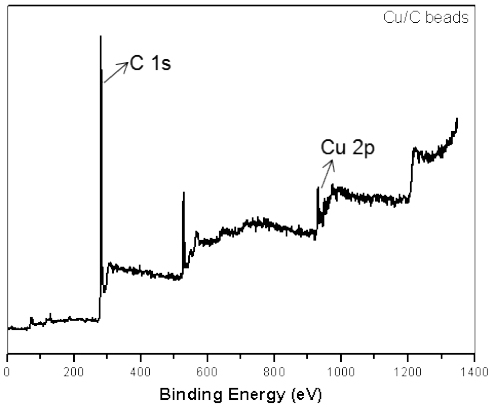

Fig. S2 XPS survey spectra of Cu/C-800 hybrid beads.

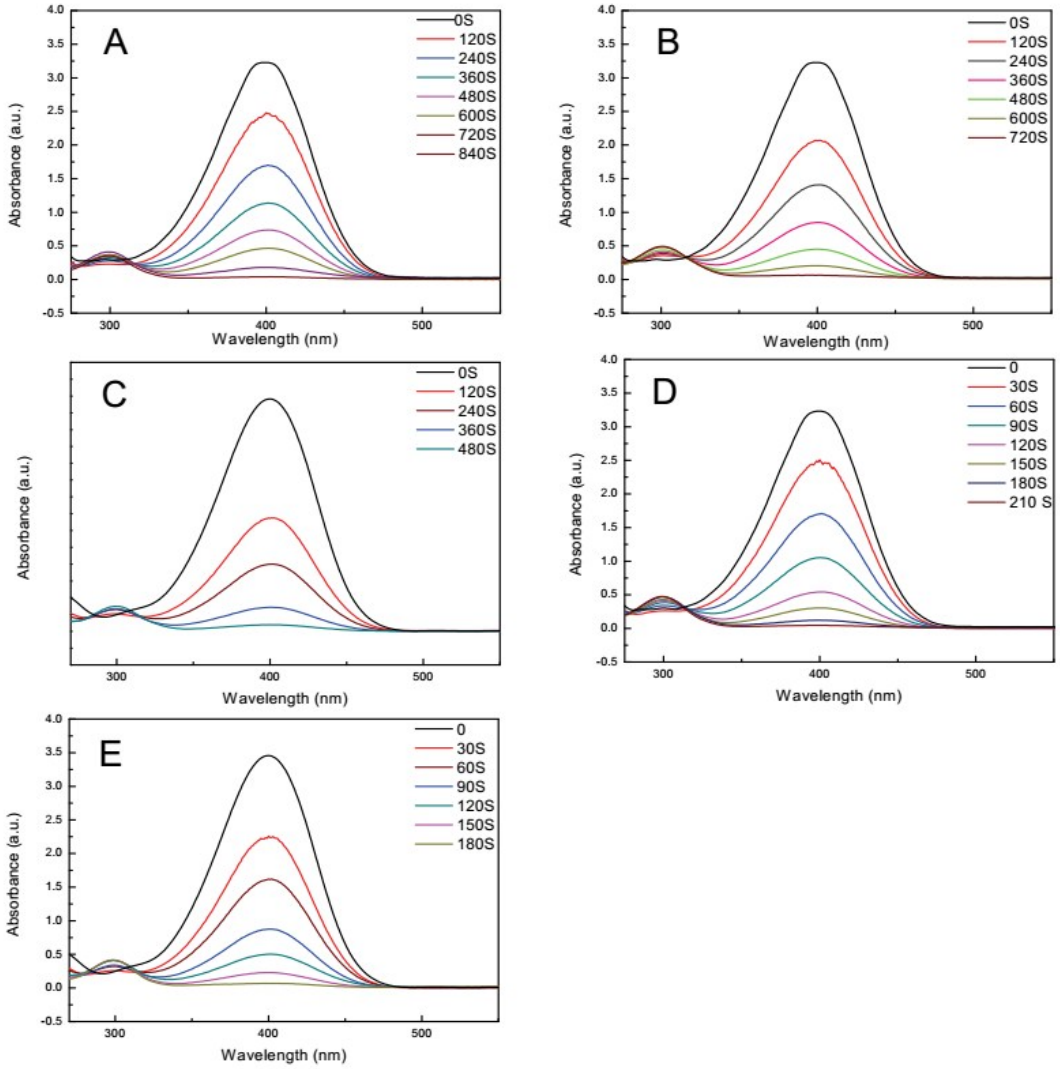

Fig. S3 Time dependant UV-vis absorption spectra of the reduction of 4-NP to 4-AP by $NaBH_4$ in the presence of Cu/C hybrid beads: (A) Cu/C-500, (B) Cu/C-700 and (C) Cu/C-800. The dosage of the catalyst is 10 mg. (D) Cu/C-500 and (E) Cu/C-700. The dosage of the catalyst is 80 mg.

Fig. S4 Video of the catalytic reduction of 4-NP to 4-AP.

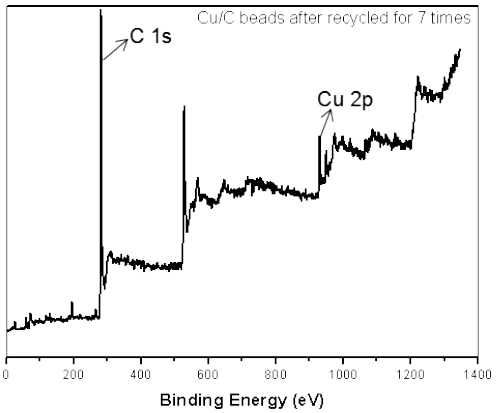

Fig. S5 XPS survey spectra of Cu/C-800 hybrid beads after recycled for 7 times.