

A Gram-Scale Fabrication of Core-Shell Copper nanoparticles for Efficient Hydrogenation of nitroarenes

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2. Experimental

2.1 Materials

Chitosan(CS, deacetylation degree >97%, Shanghai Sinopharmaceutical Group Chemical Reagent Co. Ltd.);Copper nitrate trihydrate (analytical pure, >99.5%);Anhydrous methanol (analytically pure, >99.7%); Nitrobenzene (>99.0%, Sinopharm Chemical Reagents Co. Ltd.); Hydrazine hydrate (85%, Shanghai Aladdin Biochemical Technology Co. Ltd.); Ethyl acetate (analytically pure);Isopropanol (analytically pure);Anhydrous calcium chloride; Ultrapure deionized water; Argon(Ar, >99.99%);4-Nitrophenol(Analytical Pure, >99%, Balinway Technology Co. Ltd.); (The above reagents are uniformly purchased and have not been further purified before use).

2.2 Synthesis of Cu(II)/CS

Add 20 mL isopropyl alcohol into a 50mL three-necked flask, and then add 2.416 g Cs that have been weighed in advance into the flask and swelter at room temperature for 1h.Pour out the redundant and isopropyl alcohol, quickly add 10 mL solvent to 50 °C oil bath pot / min with magnetic stirring at 450 RPM will be 10 ml of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.122 g) of saturated water solution drip slowly, in building the condenser device response 3.5 h, after the reaction, in turn, with deionized water, anhydrous methanol washing three times, the light blue fluid by vacuum suction filter purification from light green sediment, 55 °C after vacuum drying the night get a precursor Cu(II)/CS.

2.3 Synthesis of N-doped copper nanoparticles wrapped in porous carbon

materials (Cu@NC/PC-t-x)

In a typical case, 1.435 g of the above Cu(II)/CS is evenly spread in a quartz boat and the sample is then quickly transferred to a tubular heating furnace. Under the protection of Ar atmosphere, the samples were heated from room temperature to the target temperature for 2 h, in which the flow rate of the tube furnace was 70 mL/min and the heating rate was 5 °C/min. After that, take out the red-brown sample and cool it to room temperature, grind it fine and store it in the centrifuge tube for later use, and label it Cu@NC/PC-t-x, where t represents the final calcination temperature and x for the hours.

2.4 General procedure for the reduction of nitro compounds to amines

In an automated high temperature and high pressure reactor lined with PTFE (with temperature sensor and pressure gauge), 25 uL nitroaromatic compounds were successively added (under the same conditions, change the substituents in different positions (electron-pulling group and electron-donating group)). We discuss the universality of Cu@NC/PC-t-x catalyst for derivatives. Add 10 mg catalyst of Cu@NC/PC-t-x and 10 mL solvent (MeOH : H₂O = 1:4) to it. After fixing the lid of the kettle, use a vacuum pump at the outlet to evacuate it to a vacuum state. Fill one side of the inlet with hydrogen, and whenever the gauge pressure reaches nearly 1 MPa, the gas was quickly released, and the reciprocating is repeated twice, Finally, the pressure in the kettle was maintained at 0.5 MPa. The temperature was programmed for 10 minutes, and the reaction was carried out at 500 rpm/min on 50 °C for 45 minutes. After the reaction is terminated, wait until the kettle is cooled to room temperature and

then slowly vent and release the pressure, 0.5 mL of deionized water was added to quench the reaction, the catalyst was removed by centrifugation and dried for later use, then a small amount of anhydrous CaCl_2 was added to the filtrate to remove the water in the reaction system, and then a small amount of filtrate was placed Extract with 2 mL ethyl acetate in a 5 mL centrifuge tube, and test the supernatant after diluting 3 times with anhydrous methanol. Using n-dodecane as internal standard, product analysis was carried out by Shimadzu gas chromatography-mass spectrometry (GC-MS-2014C). In order to ensure the accuracy of the experiment, each process was carried out three times.

2.5 Catalyst cycle experiment

In cyclic experiments, the catalyst was rapidly precipitated by applied magnetic force centrifugation, the specific method is to take the remaining mixture of the reaction and place it in a 4 mL centrifuge tube at 8000 rpm/min and centrifuge for 1 min, wash the inner wall of the glass vial and the magnet several times with absolute ethanol, and then continue centrifugation. When the catalyst is all collected at the bottom of the centrifuge tube, it is washed twice with absolute ethanol to remove the product attached to the surface of the catalyst. Finally, the obtained solid precipitate was placed in a vacuum drying oven at 65°C overnight to remove unreacted solvents. To ensure that the cycle continues in sequence, the dried catalyst is properly filled after each reaction and the new reactant is filled into the same reaction kettle for the next catalytic process, following the steps above.

2.6 Characterization of catalysts

The synthesized Cu@NC/PC-t-x catalyst was characterized by different techniques. The surface morphology of the samples was investigated by Hitachi 8100 scanning electron microscope (SEM) at 5KV accelerating voltage, which showed the morphology characteristics of the samples at different temperatures. Before observing the sample, spray platinum on the surface of the sample to enhance its conductivity. X-ray energy spectroscopy (EDS) is used to detect the type and content of elements in the sample. The 120KV transmission electron microscope (TEM) uses a carbon support film as a carrier and uses a solvent dispersion method to record the size of Cu-NPS. High resolution projection electron microscopy (HTEM) further revealed the lattice fringes of the sample, in which the electron acceleration energy was 200 kV. Fourier infrared spectroscopy (FIR) confirmed the existence of functional groups in the polymer precursors, and Raman spectroscopy (Raman) re-analyzed the carbonized samples at a laser wavelength of 532nm with an exposure time of 30s and a laser intensity of 5%. The X-ray photoelectron spectrometer (XPS) measurement was performed on a commercial XPS system ULVAC PHI Quantera microscope. Under the conditions of 40KV and 40mA, in the range of 5°~80°, the 2-theta diffraction angle of the synthesized sample was analyzed by powder PXRD using the Bruker D8 X-ray diffractometer with CuK α radiation ($\lambda=1.5418\text{\AA}$). The specific surface area and pore size distribution of the catalyst were estimated and analyzed on the Brunauer-Emmett-Teller specific surface area tester (BET) and Micrometrics ASAP2020 software respectively.

Computational methods

The reaction mechanism of Cu-based catalyst for catalytic reduction of nitrobenzene was further revealed by DFT calculations via the Vienna Ab Initio Simulation Package (VASP)¹. The Perdew-Becke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA) was used to evaluate the exchange correlation energies², while the projector augmented wave (PAW) pseudo-potentials were applied to evaluate ionic cores³. DFT-D3 method of Grimme was used to describe van der Waals interactions⁴. A cut-off energy of 400 eV was employed. The convergence criteria for the energy and force calculations were set to 10^{-5} eV and 0.02 eV/ Å, respectively. $2 \times 2 \times 1$ Gamma-centered k-point grid was utilized to fulfill numerical integration⁵. In order to avoid the interaction between two periodic units, the vacuum space was set to 20 Å.

The adsorption energies of adsorbates were calculated following the definition $E_{\text{ads}} = E_{\text{adsorbate/catalyst}} - E_{\text{adsorbate}} - E_{\text{catalyst}}$, where $E_{\text{adsorbate/catalyst}}$, $E_{\text{adsorbate}}$ and E_{catalyst} represent the total energy of the molecule adsorbed on the surface of catalyst, the energy of the adsorbed molecule, and the energy of the catalyst, respectively.

Table S1. The energy barrier of reaction.

Reactions	ΔE
$\text{PhNO}_2^* + \text{H}^* \rightarrow \text{PhNOOH}^*$	-0.64
$\text{PhNOOH}^* + \text{H}^* \rightarrow \text{PhNO}^* + \text{H}_2\text{O}$	0.43
$\text{PhNO}^* + \text{H}^* \rightarrow \text{PhNOH}^*$	-0.44
$\text{PhNOH}^* + \text{H}^* \rightarrow \text{PhN}^* + \text{H}_2\text{O}$	-3.05
$\text{PhN}^* + \text{H}^* \rightarrow \text{PhNH}^*$	2.32
$\text{PhNH}^* + \text{H}^* \rightarrow \text{PhNH}_2^*$	0.91

Table S2. The calculated adsorption energies of the intermediates

intermediates	E_{ads}
PhNO_2^*	-0.91
PhNOOH^*	-1.55
PhNO^*	-1.12

PhNOH*	-1.56
PhN*	-4.62
PhNH*	-2.30
PhNH ₂ *	-1.39

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2. P.E. Blöchl, Projector augmented-wave method, Phys. Rev. 1994, B50 17953-17979.
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5. Evarestov, R. A.; Smirnov, V. P., Modification of the Monkhorst Pack Special Points Meshes in the Brillouin Zone for DensityFunctional Theory and Hartree-Fock Calculations. Phys. Rev. B: Condens. Matter Mater. Phys. 2004, 70, 233101.

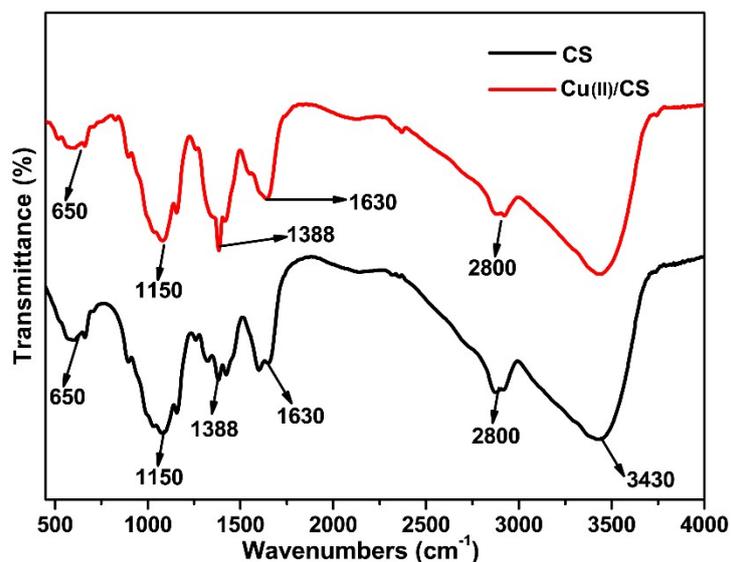


Fig. S1. The IR spectra of CS and Cu (II)/CS

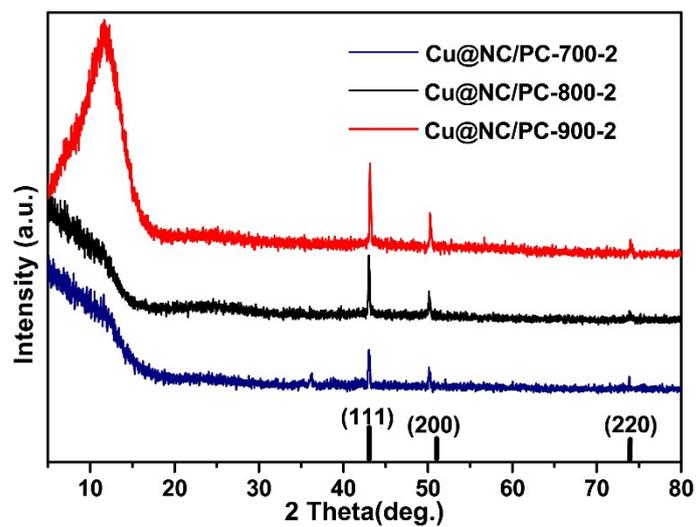


Fig. S2. The PXRD graphic of catalysts with different pyrolysis temperature.

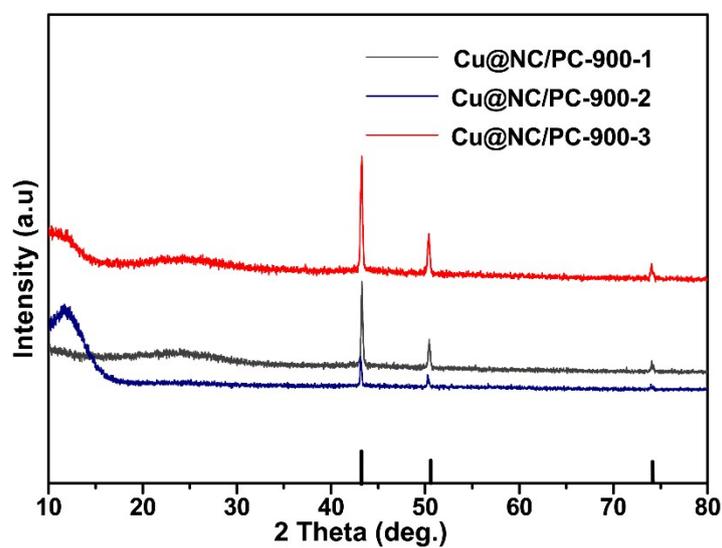


Fig. S3. The PXRD of catalysts with different pyrolysis times.

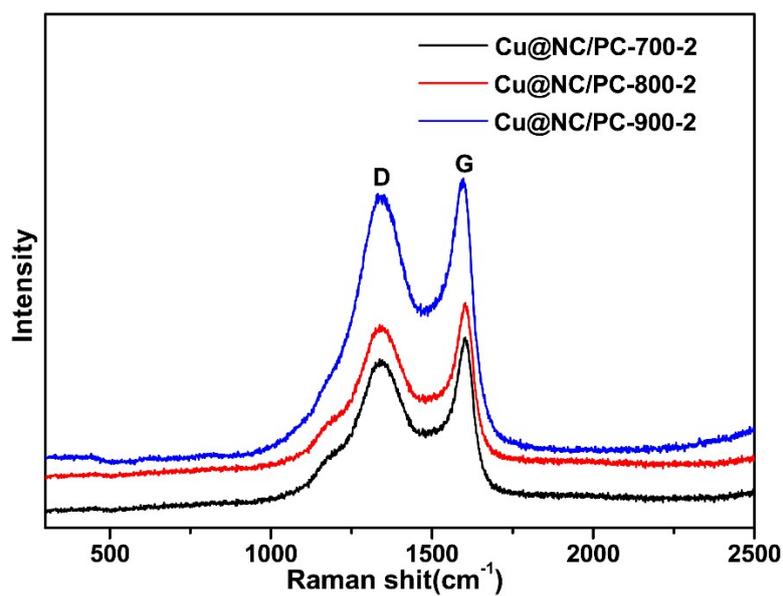


Fig. S4. The Raman spectra of the catalysts.

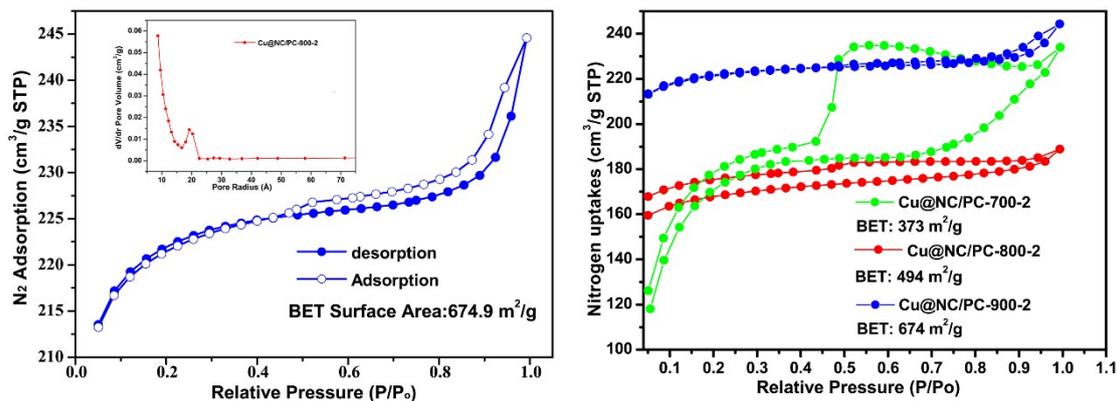


Fig. S5. Left: The nitrogen adsorption of Cu@NC/PC-900-2, the inset graph is pore size

distribution. Right: the nitrogen uptakes of different catalysts.

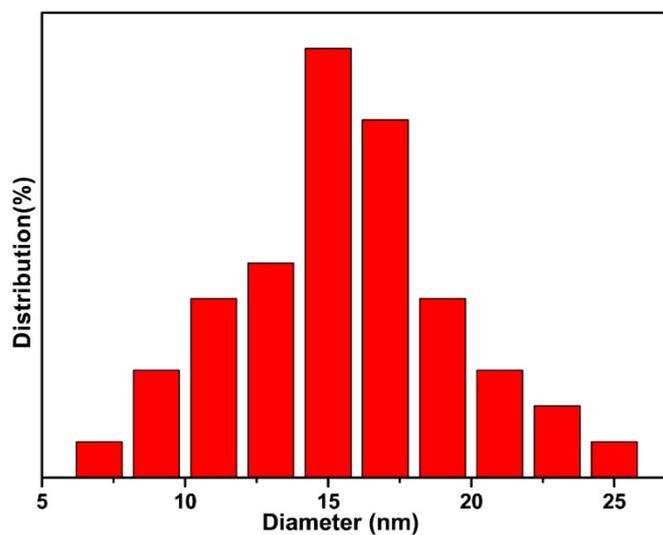


Fig. S6. The particle size distribution of Cu@NC/PC-900-2.

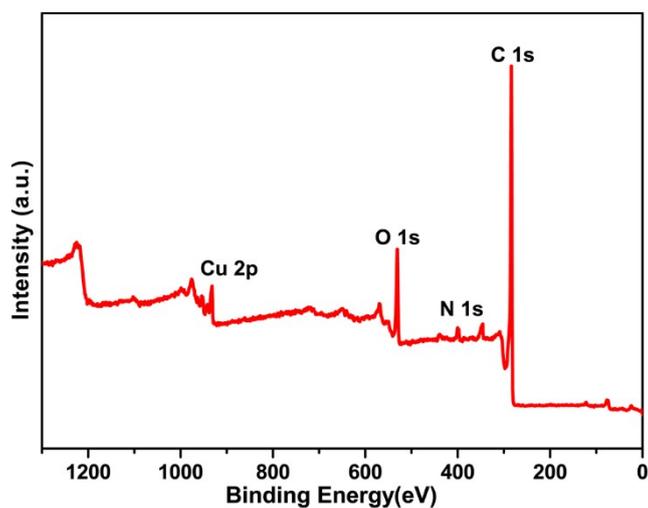


Fig. S7. The overall XPS spectra of Cu@NC/PC-900-2.

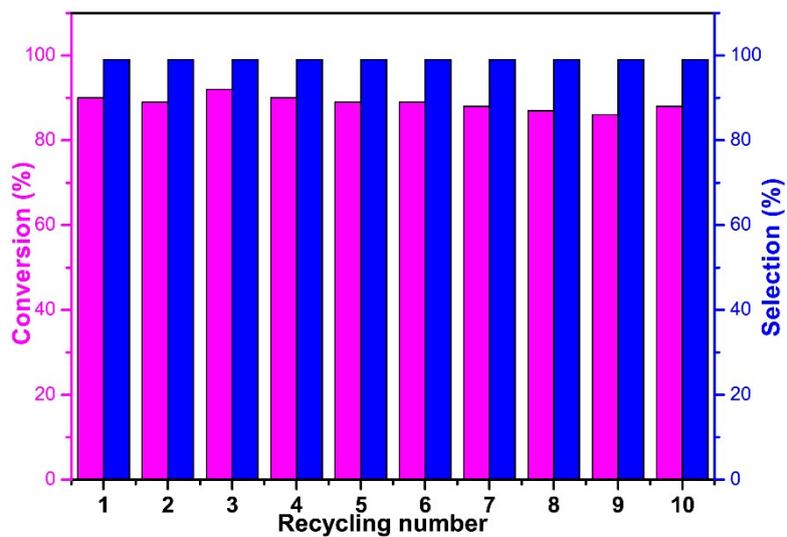


Fig. S8. The cyclic tests of Cu@NC/PC-900-2.

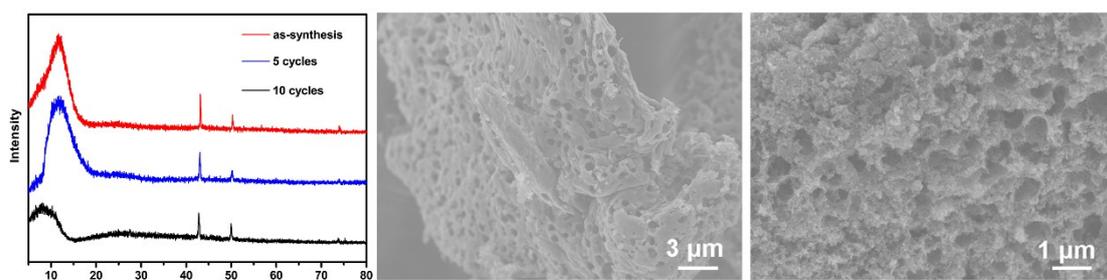


Fig. S9. (a) XRD and SEM graphics of Cu@NC/PC-900-2 after cyclic reaction.

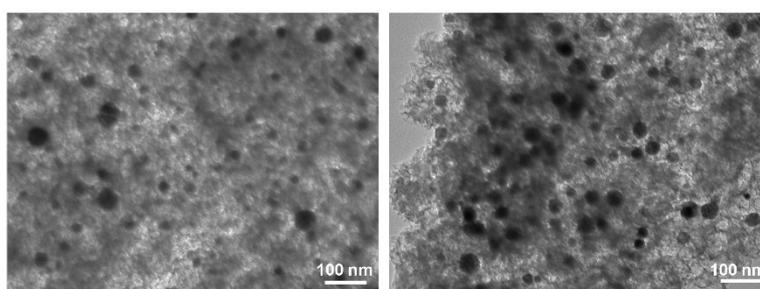


Fig. S10. Left: TEM image of as-synthesized and right is the TME image of Cu@NC/PC-900-2

after cyclic reaction.