Supporting information

Cu_2O mesoporous spheres with high internal diffusion capacity and improved catalytic ability for aza-Henry reaction driven by visible light

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1. EXPERIMENTAL SECTION

1.1 Materials and instruments

Unless otherwise stated, all chemical materials ware purchased from commercial sources and used without further purification. X-ray power diffraction (XRD) analysis was conducted on a Bruker advance-D8 power diffractometer with Cu Kα radiation (λ=0.154178 nm). Field-emission scanning electron microscopic (FESEM) images were performed on a Hitachi S-4800 microscope operating at 5 kV. Transmission electron microscopic (TEM) images and high-resolution transmission electron microscopic (HRTEM) images were obtained on a JEM-2011F microscope with accerating voltage of 200 kV and a JEOL JEM-3010 microscope operated at 200 kV, respectively. The nitrogen adsorption-desorption isotherms were collected on an ASAP2010 apparatus at 77 K. The surface areas were caculated by the Brunauer-Emmett-Teller (BET) method, and the pore-size distributions was derived from the adsorption using the Barrett-Joyner-Halenda (BJH) theory.

1.2 **Synthesis of Cu_2O spheres**

The porous Cu_2O nanospheres with small pore size (SP-Cu_2O) were prepared according to template synthetic process with some modification.[1] Typically, 0.5 g triblock copolymer pluronic P123 (MW 5800) was firstly dissolved in 40 ml deionized water at 293 K under constant stirring for at least 5 h. Then, 3 mL of 0.2 M Cu $(NH_3)_4^{2+}$ solution (10:1, NH_3:Cu^{2+}) was poured into the solution of P123 solution under constant stirring. After 40 min, 6 mL of 0.6 M ascobic acid solution was added dropwise into the above mixture, during this procedure, the reaction underwent a series of color changes from deepblue, lightblue, limpid, white turbid, and finally to yellow turbid. After stirring for 40 min, the resulting precipitate was collected by centrifuging,

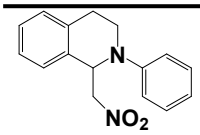
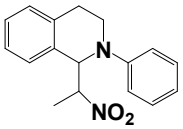
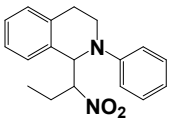
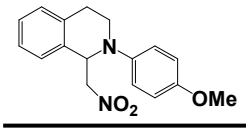
washed with ethanol at 333 K overnight to remove the P123 and finally dried in vacuum at 333 K for 4 h.

The porous Cu_2O nanospheres with large pore size (LP-Cu_2O) were prepared using the etching method. Typically, 5 mg of the as prepared SP-Cu_2O was added into 10 mL of the ethanol solution containing 1.2 mg/mL of L-proline under constant stirring. After 8 h, the precipitate was collected by centrifuging, washed several times with distilled water and ethanol, and finally dried in vacuum at 333 k for 4 h.

1.3 Representative procedure for aza-Henry reaction.[2]

Table. S1 Parameters of products.

20.9 mg 1,2,3,4-Tetrahydroisoquinoline derivative (0.1 mM), 2.0 mg porous Cu_2O spheres and 1 ml nitromethane were added in a Schlenk tube and mixed by ultrosonic cleaner for 3 minutes. The vial was stirred under high power LEDs (460 nm, 4 V) for the indicated time in an oxygen atmosphere provided by balloon. After the reaction was completed, the catalyst was removed by filtration. The filtrate was dried in vacuo and the crude product was purified by column chromatography using hexanes/ethyl acetate (5/1, v/v) to afford the desired product (Table S1).

Product	R_f	
	0.5	Yellow solid
	0.6	Yellow oil
	0.6	Yellow oil
	0.4	Yellow solid

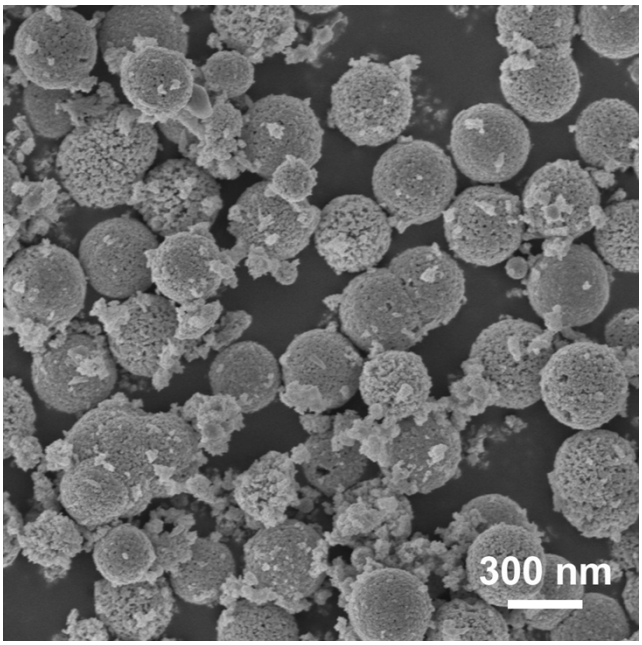


Fig. S1 SEM image of LP-Cu_2O with longer etching time.

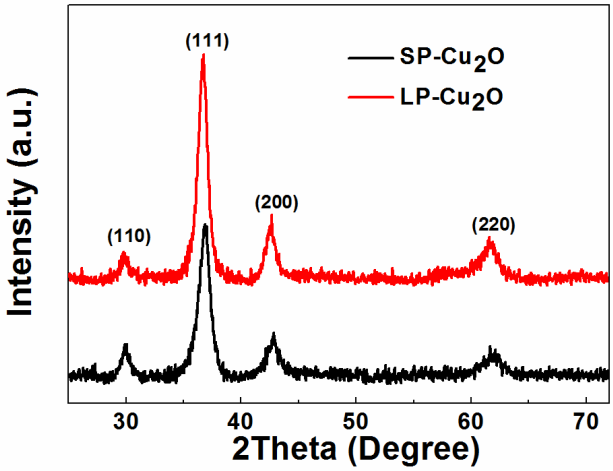


Fig. S2 XRD patterns of the as prepared SP-Cu_2O and LP-Cu_2O.

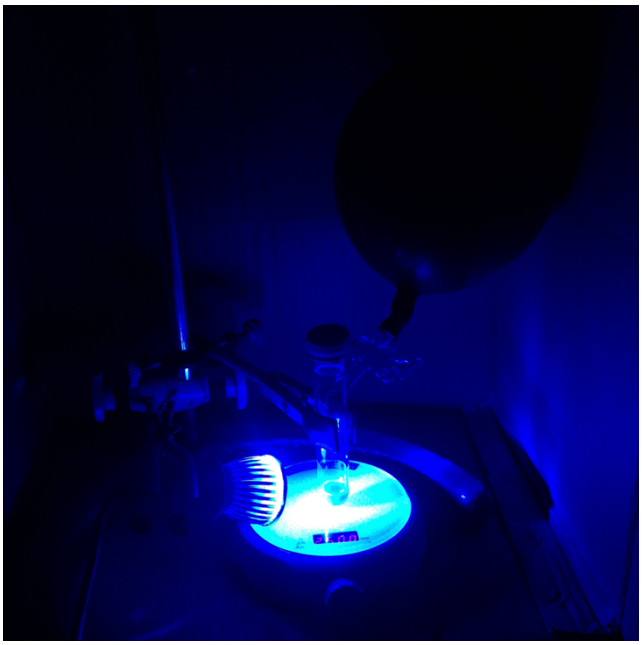


Fig. S3 The apparatus of photocatalytic aza-Henry reaction.

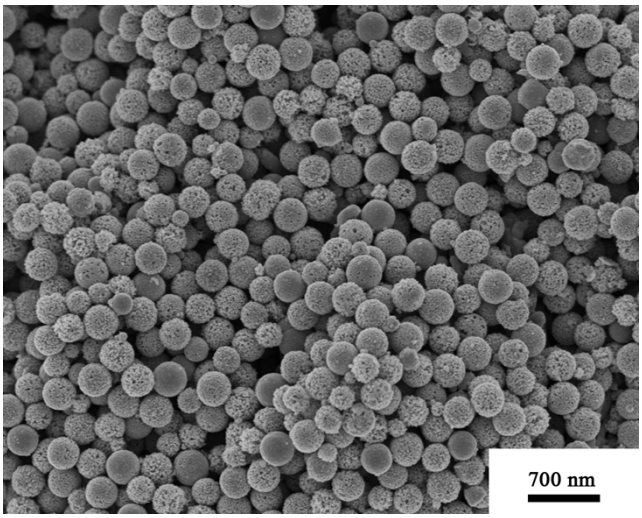


Fig. S4 SEM image of LP-Cu_2O after 5 cycles.

1 Y. Shang, D. F. Zhang and L. Guo, *J. Mater. Chem.,* 2012, **22**, 856.

2 (a) Y. Pan, S. Wang, C. W. Kee, E. Dubuisson, Y. Yang, K. P. Loh and C. Tan, *Green Chem.,* 2011, **13**, 3341; (b) D. P. Hari and B. Konig, *Org. Lett.,* 2011, **13**, 3852.