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## COMMUNICATION

# Cu<sub>2</sub>O mesoporous spheres with high internal diffusion capacity and improved catalytic ability for aza-Henry reaction driven by visible light

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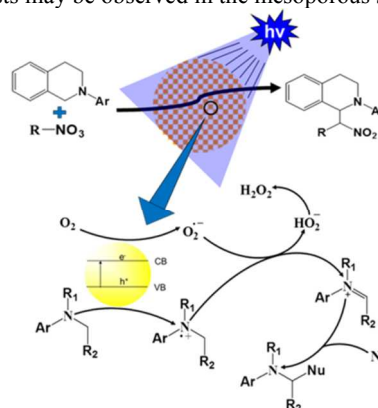
Jun Wang, Jingwen Ma, Xiaojie Li, Yang Li, Guoliang Zhang, Fengbao Zhang, and Xiaobin Fan\*

**Mesoporous Cu<sub>2</sub>O spheres with large pore size (LP-Cu<sub>2</sub>O) bring out the better performance towards photocatalytic aza-Henry reaction than Cu<sub>2</sub>O spheres with small pore size (SP-Cu<sub>2</sub>O). This work highlights the internal diffusion coefficient as a critical parameter for fabrication of porous catalysts.**

Organic synthesis driven by visible light has become one of the fastest growing fields in organic chemistry, because the visible light accounts for the major part of the sun light which is a clean, abundant, and reproducible energy resource.<sup>1</sup> Photocatalysts are often indispensable in organic reaction driven by visible light since the majority of organic substrates do not absorb the photons in the visible region.<sup>1f,2</sup> Recently, photo-induced organic catalytic reactions have been conducted by using the homogeneous organic dyes (Eosin Y or Rose Bengal) and photo redox inorganic (Ir (III) or Ru (II)) complexes as photocatalysts.<sup>3</sup> However, the practical applications of these photocatalysts are hampered because of their high costs and the difficulty of separating them from the mixture. The ability to recover and reuse heterogeneous photocatalysts can not only eliminate the contamination of the organic products but also reduce the waste disposal cost in large scale reactions.<sup>2b,4</sup> As an important type of heterogeneous catalysts, the inorganic semiconductor with suitable band-gap can absorb the visible light and use the photo generated electrons/hole to catalyze a lot of reactions.<sup>5</sup> Being a p-type oxide semiconductor with a direct band gap of 2.17 eV, the Cu<sub>2</sub>O has been widely used for the visible light driven photocatalytic degradation of organic pollutants and photon-activated water splitting.<sup>6</sup> In addition, Cu<sub>2</sub>O porous materials have been successfully synthesized and applied in dye adsorption and catalysis.<sup>7</sup> However, the example in which they photocatalyze bond formation in organic synthesis has not been reported currently. Therefore, their practical efficiency for catalyzing the bond formation is still a mystery.

The photocatalytic process always contains three procedures as follow: the hole-electron separation, electron/hole transfer and surface reaction. Hole-electron separation and electron/hole transfer are conducted quite fast, while the surface reaction is a relatively slow process. Therefore surface reaction process is the rate determining step, which takes the major impact on the reaction rate. Since the reaction catalyzed by heterogenetic catalysts occurs when

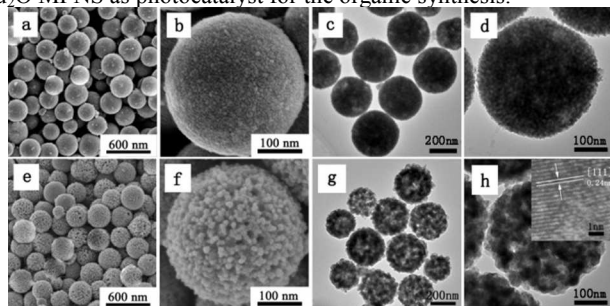
the reactant molecules come in contact with the active surface, mass transfer limitations play an important role on the surface reaction.<sup>8</sup> As an important type of heterogeneous catalysts, the porous materials with tunable pore architecture are getting considerable attention, because of their ability to interact with atoms, ions and molecules not only at their surfaces, but interior of the material.<sup>9</sup> The mass transfer limitations of the porous catalysts contain both external mass transfer and internal mass transfer. In a reaction with the porous solid as catalysts, the mass transfer of the reactants first proceed from the bulk fluid to the external surface of the solid, then into and through the pores within the pellet to the catalytic surface of the pores, where the reaction occurs.<sup>8</sup> With sufficient stirring of the reaction system, the influence of external diffusion can be ignored, whereas the internal diffusion will play an important role on the catalytic performance.<sup>10</sup> As the internal diffusion rate is proportional to the pore size, the internal diffusion rate can be adjusted via controlling the pore size of the material, and maximum performance of these catalysts may be observed in the mesoporous systems.



**Scheme 1.** Illustration for the process and proposed mechanism of aza-Henry reaction catalysed by porous Cu<sub>2</sub>O spheres under blue LED illumination.

In this work, we report the fabrication of the porous Cu<sub>2</sub>O spheres with different pore sizes by using an etching strategy. Different from common mineral acids, L-proline in organic solvent can readily etch Cu<sub>2</sub>O spheres with a controllable manner, resulted in the mesoporous Cu<sub>2</sub>O spheres. Then, we studied their performance on the aza-Henry reaction. Comparing studies show that the Cu<sub>2</sub>O spheres with larger

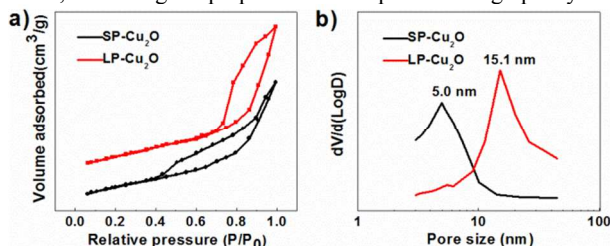
pore size takes the higher reactive activity and can be readily reused in catalyzing visible light promoted aza-Henry reactions of N-aryl-tetrahydroisoquinoline and nitromethane, nitroethane via intermolecular C–H functionalization (Scheme 1). The results prove that internal diffusion takes a profound effect on the performances of Cu<sub>2</sub>O MPNS as photocatalyst for the organic synthesis.



**Fig. 1** SEM (a, b, e, f) and TEM (c, d, g, h) images of SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O. Inset in (h) shows the HRTEM of LP-Cu<sub>2</sub>O.

The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Fig. 1a and 1e show FESEM images of SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O. They illustrate that both the SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O spheres are dispersed uniformly and with average diameter estimated to be about 320 nm. Fig. 1c and 1g are the corresponding TEM images, which further prove that the obtained Cu<sub>2</sub>O spheres have the uniform size and porous structure. The magnified SEM (1b, 1f) and TEM (1d, 1h) images of typical sphere illustrate both samples have the short-range-ordered porous network features and the pore size of LP-Cu<sub>2</sub>O is larger than the SP-Cu<sub>2</sub>O, after the etching treatment. Noting that extending the etching time will destroy the mesoporous structure, as shown in Fig. S1, a great portion of spheres are broken when the etching time is increased to 10 h. From HRTEM shown in the inset of image (1h), the clear lattice fringes reveal the high crystallinity of the product. The lattice spacing of the LP-sphere is measured to be 0.24 nm, which corresponds to the lattice spacing of the (111) crystal plane of the cubic Cu<sub>2</sub>O.

X-ray diffraction (XRD) was employed to characterize the crystal structure of the samples. Fig. S2 shows the X-ray patterns of the samples of SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O, the strong diffraction peaks exhibit the high crystallinity of the samples and all the peaks can be well indexed to the 110, 111, 200 and 220 peaks of cubic Cu<sub>2</sub>O according to the JCDPS card (No.05-0667). The average crystal sizes of the SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O were calculated to be 7.62 nm and 6.35 nm, respectively, using the Debye-Scherrer formula based on the broader peaks in XRD patterns. The reduced grain size may be caused by the etching treatment. Moreover, no other diffraction peaks belonging to possible impurities such as Cu and CuO could be detected, indicating the prepared two samples with high purity.



**Fig. 2** (a) Nitrogen adsorption-desorption isotherm. (b) The corresponding BJH pore size distribution curve of the SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O.

Nitrogen sorption measurement, which was conducted at 77 K, was used to study the porosity of the Cu<sub>2</sub>O spheres. Fig. 2a shows the N<sub>2</sub> adsorption-desorption isotherms of SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O. It

is obvious that these two isotherms belong to type IV hysteresis loops at relative pressures of  $P/P_0 = 0.42\text{--}0.97$ , providing the evidence for the mesoporous structure. The BET surface area for SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O are measured to be 61.2 and 63.4 m<sup>2</sup>g<sup>−1</sup>, respectively, which suggests that the surface area do not change significantly after the etching treatment. BJH pore size distribution in Fig. 2b displays the pore size distribution is narrow. The mean pore size of LP-Cu<sub>2</sub>O increases from 5.0 to 15.1 nm after etching process. In addition, we could see a little peak appeared at about 5 nm from BJH curve of LP-Cu<sub>2</sub>O in Fig. 3b due to a small part of unetched pores.

According to the mass transfer theory, the diffusion of liquid within the pore of the porous solid is generally consistent with Fick-Diffusion.<sup>11</sup> When the liquid diffuses in the pore with large pore diameter, the collision occurs mainly between the fluid molecules rather than with the pore wall. The effective diffusion coefficient can be defined as follow:

$$D_{ABP} = \frac{\varepsilon D_{AB}}{\tau}$$

$\varepsilon$ : The void fraction of the porous catalyst

$\tau$ : The twist factor

$D_{AB}$ : The diffusion coefficient of the component A in the solvent

$D_{ABP}$ : The effective diffusion coefficient

The void fraction  $\varepsilon$  is proportional to the pore size and pore volume. The twist factor  $\tau$  is inversely proportional to the crystal size and pore size.  $D_A$  is a constant in a certain solution system. According to the above data, the LP-Cu<sub>2</sub>O has a larger pore diameter and pore volume, while a smaller crystal size than SP-Cu<sub>2</sub>O. It can draw that the LP-Cu<sub>2</sub>O has a larger value of  $\varepsilon$  and a smaller value of  $\tau$  than SP-Cu<sub>2</sub>O. Therefore,  $D_{ABP}$  value of the LP-Cu<sub>2</sub>O is larger than SP-Cu<sub>2</sub>O. In other words, the component A diffuse faster in the pore of LP-Cu<sub>2</sub>O than in the SP-Cu<sub>2</sub>O.

**Table 1.** Oxidative coupling reaction of N-aryl-tetrahydroisoquinolines with nitroalkanes.

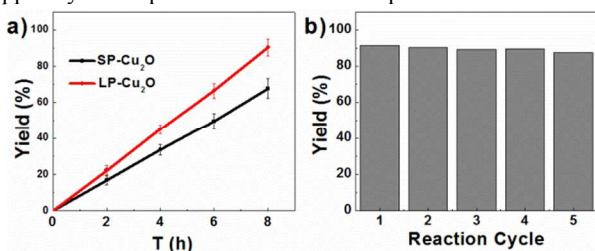
Catalyst	Ar	R	Yield [%]
SP-Cu <sub>2</sub> O	[C6H5]	[H]	67.7
LP-Cu <sub>2</sub> O <sup>a</sup>	[C6H5]	[H]	90.3
LP-Cu <sub>2</sub> O <sup>b</sup>	[C6H5]	[Me]	86.2
LP-Cu <sub>2</sub> O <sup>c</sup>	[C6H5]	[Et]	88.4
LP-Cu <sub>2</sub> O <sup>d</sup>	[4-MeO-C6H5]	[H]	82.7
Blank	[C6H5]	[H]	4.8

All experiments were performed with 2 mg of photocatalysts, 0.1 mmol of N-aryl-tetrahydroisoquinoline derivative in 1 mL of neat nitroalkanes. Reactions were run in Schlenk tubes with an attached oxygen balloon and irradiated with 4 W of blue LEDs for 8 h. The footnotes a, b, c, d represent the reactions between corresponding N-aryl-tetrahydroisoquinoline derivatives and nitroalkanes with LP-Cu<sub>2</sub>O as catalysts.

Catalytic activities of the SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O towards photocatalytic aza-Henry reaction were evaluated with N-aryl-tetrahydroisoquinoline as the amine substrate and nitro-alkanes as solvent. The reaction was carried out in a Schlenk tubes with oxygen as oxidizing agent and blue Light Emitting Diodes (LEDs, hv 460 nm, 4 W) as light source (Fig. S3). The reaction results were shown in table 1. Compared with SP-Cu<sub>2</sub>O, the LP-Cu<sub>2</sub>O showed a better reactivity after 8 h of irradiation (SP-Cu<sub>2</sub>O, LP-Cu<sub>2</sub>O<sup>a</sup>), which indicated LP-Cu<sub>2</sub>O takes a higher catalytic activity than SP-Cu<sub>2</sub>O under the same reaction conditions. Various N-aryl-tetrahydroisoquinoline derivatives were reacted with nitromethane, nitroethane, or 1-nitro-propane and gave the desired coupling



product in good yields of 86.2–90.3% (LP-Cu<sub>2</sub>O<sup>a, b, c</sup>). Nitromethane always gave better results than other nitroalkanes and the reaction was insensitive to electronic effects on the aromatic rings (LP-Cu<sub>2</sub>O<sup>d</sup>). A low yield of product was observed in the absence of the catalyst (Blank). The mechanism of the Cu<sub>2</sub>O photocatalytic aza-Henry reaction is not clear at this stage. However, according to our results and literature report, the mechanism can be proposed as follow (Scheme 1). The VB, generated under Blue LED irradiation, is able to abstract an electron from the tertiary via a single electron transfer process. The aminyl cation radical then lost a hydrogen atom by a radical anion to generate iminium ion. The iminium can be trapped by nucleophiles to obtain the final product.



**Fig. 3** (a) The yield of product as function of reaction time in the LP-Cu<sub>2</sub>O catalysed aza-Henry reaction between tetrahydroisoquinoline and nitromethane. (b) Recycling experiments for LP-Cu<sub>2</sub>O catalysed aza-Henry reaction between N-aryl-tetrahydroisoquinoline and nitromethane.

Furthermore, we explored the photocatalytic reaction rates of SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O. As shown in Fig. 3a, the photo-oxidation aza-Henry reaction was fitted as zero order reaction, which meant that the concentration of reagents in solution did not affect the reaction rate. Theoretically, in addition to the internal diffusion, the performances of the mesoporous Cu<sub>2</sub>O spheres may be also affected by the intrinsic catalytic activity, catalyst dosage, light intensity and etc. In order to study the effect of internal diffusion to the performance of the mesoporous Cu<sub>2</sub>O spheres, other factors should be excluded. The influencing of intrinsic catalytic activity to the reaction could be neglected owing to the similar crystallinity and crystal size properties of the SP-Cu<sub>2</sub>O and LP-Cu<sub>2</sub>O. The impact of catalyst dosage to the reaction can also be ignored. Considering we took the same amount of LP-Cu<sub>2</sub>O and SP-Cu<sub>2</sub>O for this reaction, due to the nearly same specific surface area value of the two catalysts, the total catalytic surface area will be the same. In this reaction system, the light intensity doesn't take an effect on the catalytic activity of catalyst, because the reaction was conducted under the same light resource, the impact of light intensity on the reaction rate can be ignored. Compared with SP-Cu<sub>2</sub>O, the LP-Cu<sub>2</sub>O showed an increase in reaction rate and overall yield of the reactions, which meant that the LP-Cu<sub>2</sub>O spheres had a higher actual catalytic activity. The actual catalytic activity was proportional to its effective surface area where the reagent can attach. Since the LP-Cu<sub>2</sub>O and SP-Cu<sub>2</sub>O possess the similar BET surface area, when we used the same amount of the catalysts the total catalytic surface area will be the same. Therefore, the actual catalytic activity was defined by the concentration gradient inside the pores, which was determined by mass transfer. Since the reaction was conducted at the sufficient stirring condition, the effect of the external diffusion to the reaction rate can be ignored, thereby the internal diffusion played an important role on the reaction rate. The results demonstrated that the reaction catalysed by the porous Cu<sub>2</sub>O sphere with the large effective diffusion coefficient has the higher catalytic activity. The results also gave us a proposal that the fabrication of porous catalyst should be not only to increase the surface area, but also to improve the efficiency of mass transfer.

The reusability of LP-Cu<sub>2</sub>O was evaluated by repeating the same reaction procedure using the recovered catalyst. The solid catalyst

was recycled by centrifuging the residue mixture, washing with ethanol repeatedly and drying in vacuum at 50 °C for 2 h. As shown in Fig. 3b, LP-Cu<sub>2</sub>O could be reused for at least 5 cycles without distinct loss of its catalytic activity. The morphology and crystal structure showed no obvious change after 5 cycles of photocatalytic reaction (Fig. S4). All these results showed the high photocatalytic activity and good stability of the LP-Cu<sub>2</sub>O.

## Conclusions

In summary, the porous Cu<sub>2</sub>O spheres with different pore size were successfully fabricated by template method and etching treatment. The obtained porous Cu<sub>2</sub>O spheres have high specific surface area, high crystallinity and well-defined morphology. In the light driven aza-Henry reactions, the LP-Cu<sub>2</sub>O exhibited better catalytic activity compared with SP-Cu<sub>2</sub>O. The results show the internal diffusion takes the great impact on the reaction catalysed by porous catalysts and the reaction rate can be effectively improved by accelerating the internal diffusion rate, which can be attained by using the catalysts with large effective diffusion coefficient.

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## Notes and references

State Key Laboratory of Chemical Engineering, School of Chemical Engineering and Technology, Collaborative Innovation Center of Chemical Science and Engineering, Tianjin University, Tianjin 300072, China. Tel: (+86) 22-27408778, Fax: (+86) 22-27408778, E-mail: xiaobinfan@tju.edu.cn.

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