ChemComm

COMMUNICATION



Cite this: Chem. Commun., 2014, 50, 14237

Received 1st September 2014, Accepted 24th September 2014

DOI: 10.1039/c4cc06869f

www.rsc.org/chemcomm

Cu₂O mesoporous spheres with a high internal diffusion capacity and improved catalytic ability for the aza-Henry reaction driven by visible light⁺

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Mesoporous Cu_2O spheres with a large pore size (LP- Cu_2O) bring out a better performance towards the photocatalytic aza-Henry reaction than Cu_2O spheres with a small pore size (SP- Cu_2O). This work highlights the internal diffusion coefficient as a critical parameter for the fabrication of porous photocatalysts.

Organic synthesis driven by visible light has become one of the fastest growing fields in organic chemistry, because visible light accounts for the major part of the sun's light which is a clean, abundant, and reproducible energy resource.¹ Photocatalysts are often indispensable in organic reactions driven by visible light since the majority of the organic substrates do not absorb the photons in the visible region.^{1f,2} Recently, photo-induced organic catalytic reactions have been conducted by using the homogeneous organic dyes (Eosin Y or Rose Bengal) and photoredox inorganic (Ir(III) or Ru(II)) complexes as photocatalysts.3 However, the practical applications of these photocatalysts are hampered because of their high costs and the difficulty in 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.^{2b,4} As an important type of heterogeneous catalysts, an inorganic semiconductor with a suitable band-gap can absorb visible light and use the photogenerated electrons/hole to catalyze a lot of reactions.⁵ Being a p-type oxide semiconductor with a direct band gap of 2.17 eV, Cu₂O has been widely used for the visible light driven photocatalytic degradation of organic pollutants and photon-activated water splitting.⁶ In addition, Cu₂O porous materials have been successfully synthesized and applied in dye adsorption and catalysis.7 However, an example in which they photocatalyze bond formation in organic synthesis has not been reported to date. Therefore, their practical efficiency for catalyzing the bond formation is still a mystery.

A photocatalytic process always comprises three procedures as follows: the hole-electron separation, electron/hole transfer and surface reaction. Hole-electron separation and electron/hole transfer occur quite fast, while surface reaction is a relatively slow process. Therefore the surface reaction process is the ratedetermining step, which has a 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 in the surface reaction.⁸ As an important type of heterogeneous catalysts, porous materials with tunable pore architectures are getting considerable attention because of their ability to interact with atoms, ions and molecules not only at their surfaces, but also in the interior of the material.9 The mass transfer limitations of the porous catalysts include both external mass transfer and internal mass transfer. In a reaction with porous solids as catalysts, the mass transfer of the reactants first proceed from the bulk fluid to the external surface of the solid, and then into and through the pores within the pellet to the catalytic surface of the pores, where the reaction occurs.8 With sufficient stirring of the reaction system, the influence of external diffusion can be ignored, whereas the internal diffusion plays an important role in the catalytic performance.¹⁰ 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 the maximum performance of these catalysts may be observed in the mesoporous systems.

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In this work, we reported the fabrication of the porous Cu₂O spheres with different pore sizes by using an etching strategy. Differently from common mineral acids, L-proline in organic solvents can readily etch Cu₂O spheres in a controllable manner, resulting in the formation of mesoporous Cu₂O spheres. Then, we studied their performance on the aza-Henry reaction. Comparative studies show that the Cu₂O spheres with a larger pore size have a higher reactivity and can be readily reused in catalyzing visible light promoted aza-Henry reactions of *N*-aryl-tetrahydro-isoquinoline and nitromethane, nitroethane *via* intermolecular C-H functionalization (Scheme 1). The results prove that

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[†] Electronic supplementary information (ESI) available: Experimental details, Fig. S1–S4. See DOI: 10.1039/c4cc06869f



 $\label{eq:scheme1} \begin{array}{l} \mbox{Illustration of the process and proposed mechanism of aza-} \\ \mbox{Henry reaction catalysed by porous Cu_2O spheres under blue LED illustration.} \end{array}$

internal diffusion has a profound effect on the performance of Cu_2O MPNS as a photocatalyst in the organic synthesis.

The morphologies of the samples were characterized by field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM). Fig. 1a and e show FESEM images of SP-Cu₂O and LP-Cu₂O. They illustrate that both the SP-Cu₂O and LP-Cu₂O spheres are dispersed uniformly and have an average diameter estimated to be about 320 nm. Fig. 1c and g are the corresponding TEM images, which further prove that the obtained Cu₂O spheres have a uniform size and porous structure. The magnified SEM (Fig. 1b and f) and TEM (Fig. 1d and h) images of typical spheres illustrate that both samples have short-range-ordered porous network features and the pore size of LP-Cu₂O is larger than that of SP-Cu₂O, after the etching treatment. Noting that extending the etching time will destroy the mesoporous structure, as shown in Fig. S1 (ESI[†]), a great portion of spheres is broken when the etching time is increased to 10 h. As seen in the inset of the HRTEM image (Fig. 1h), the clear lattice fringes reveal the high crystallinity of the product. The lattice spacing of the LP-spheres is measured to be 0.24 nm, which corresponds to the lattice spacing of the (111) crystal plane of the cubic Cu₂O.

X-ray diffraction (XRD) was employed to characterize the crystal structure of the samples. Fig. S2 (ESI[†]) shows the X-ray patterns of the samples of SP-Cu₂O and LP-Cu₂O, the strong diffraction peaks exhibit a high crystallinity of the samples and all the peaks can be



Fig. 1 SEM (a, b, e and f) and TEM (c, d, g and h) images of SP-Cu₂O and LP-Cu₂O. Inset in (h) shows the HRTEM of LP-Cu₂O.

well indexed to the 110, 111, 200 and 220 peaks of cubic Cu₂O according to the JCDPS card (No. 05-0667). The average crystal sizes of the SP-Cu₂O and LP-Cu₂O were calculated to be 7.62 nm and 6.35 nm, respectively, using the Debye–Scherrer formula based on the broader peaks in the 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 that the two samples prepared have high purity.

Nitrogen sorption measurements, which were conducted at 77 K, were used to study the porosity of the Cu₂O spheres. Fig. 2a shows the N₂ adsorption–desorption isotherms of SP-Cu₂O and LP-Cu₂O. It is obvious that these two isotherms belong to type IV hysteresis loops at relative pressures of $P/P_0 = 0.42$ to 0.97, providing evidence for the mesoporous structure. The BET surface area for SP-Cu₂O and LP-Cu₂O and LP-Cu₂O are measured to be 61.2 and 63.4 m² g⁻¹, respectively, which suggests that the surface area does not change significantly after the etching treatment. The BJH pore size distribution in Fig. 2b shows that the pore size distribution is narrow. The mean pore size of LP-Cu₂O increases from 5.0 to 15.1 nm after the etching process. In addition, we could see a small peak appeared at about 5 nm from the BJH curve of LP-Cu₂O in Fig. 3b due to a small amount 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.¹¹ When the liquid diffuses into the pore with a 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 follows:

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



Fig. 2 (a) Nitrogen adsorption–desorption isotherm. (b) The corresponding BJH pore size distribution curve of SP-Cu₂O and LP-Cu₂O.



Fig. 3 (a) The yield of product as function of reaction time in the LP-Cu₂O catalysed aza-Henry reaction between tetrahydroisoquinoline and nitromethane. (b) Recycling experiments for the LP-Cu₂O catalysed aza-Henry reaction between *N*-aryl-tetrahydroisoquinoline and nitromethane.

 ε : the void fraction of the porous catalyst; τ : the twist factor; D_{AB} : the diffusion coefficient of the component A in the solvent; D_{ABP} : the effective diffusion coefficient.

The void fraction ε is proportional to the pore size and pore volume. The twist factor τ 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-Cu₂O has a larger pore diameter and pore volume, but a smaller crystal size than SP-Cu₂O. It can be inferred that LP-Cu₂O has a larger value of ε and a smaller value of τ than SP-Cu₂O. Therefore, the D_{ABP} value of the LP-Cu₂O is larger than SP-Cu₂O. In other words, component A diffuses faster into the pores of LP-Cu₂O than in SP-Cu₂O.

The catalytic activities of the SP-Cu₂O and LP-Cu₂O towards the photocatalytic aza-Henry reaction were evaluated using N-aryl-tetrahydroisoquinoline as the amine substrate and nitro-alkanes as the solvent. The reaction was carried out in a Schlenk tube with oxygen as the oxidizing agent and blue Light Emitting Diodes (LEDs, $h\nu$ 460 nm, 4 W) as the light source (Fig. S3, ESI[†]). The reaction results are shown in Table 1. Compared with SP-Cu₂O, LP-Cu₂O showed a better reactivity after 8 h of irradiation (SP-Cu₂O, LP-Cu₂O^a), which indicates that LP-Cu₂O has a higher catalytic activity than SP-Cu₂O 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-Cu₂O^{a,b,c}). Nitromethane always gave better results than other nitroalkanes and the reaction was insensitive to electronic effects on the aromatic rings (LP-Cu₂O^d). A low yield of the product was observed in the absence of the catalyst (Blank). The mechanism of the Cu₂O photocatalytic aza-Henry reaction is not clear at this stage. However, according to our results and literature reports, the mechanism can be proposed as follows (Scheme 1). The VB, generated under Blue LED irradiation,

Catalyst	Ar	R	Yield [%]
SP-Cu ₂ O	$[C_6H_5]$	[H]	67.7
$LP-Cu_2O^a$	$\left[C_{6}H_{5}\right]$	ĨΗĴ	90.3
$LP-Cu_2O^b$	C ₆ H ₅	[Me]	86.2
$LP-Cu_2O^c$	$[C_6H_5]$	[Et]	88.4
$LP-Cu_2O^d$	$[4-MeO-C_6H_5]$	ĨΗĨ	82.7
Blank	[C ₆ H ₅]	[Ħ]	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 ballon and irradiated with 4 W of blue LEDs for 8 h. ^{*a*} The reactions between corresponding *N*-aryl-tetrahydroisoquinoline derivatives and nitroalkanes with LP-Cu₂O as catalysts. ^{*b*} The reactions between corresponding *N*-aryl-tetrahydroisoquinoline derivatives and nitroalkanes with LP-Cu₂O as catalysts. ^{*c*} The reactions between corresponding *N*-aryl-tetrahydroisoquinoline derivatives and nitroalkanes with LP-Cu₂O as catalysts. ^{*c*} The reactions between corresponding *N*-aryl-tetrahydroisoquinoline derivatives and nitroalkanes with LP-Cu₂O as catalysts. ^{*d*} The reactions between corresponding *N*-aryl-tetrahydroisoquinoline derivatives and nitroalkanes with LP-Cu₂O as catalysts.

is able to abstract an electron from the tertiary *via* a single electron transfer process. The aminyl cation radical then loses a hydrogen atom by a radical anion to generate the iminium ion. The iminium ion can be trapped by nucleophiles to obtain the final product.

Furthermore, we explored the photocatalytic reaction rates of SP-Cu₂O and LP-Cu₂O. As shown in Fig. 3a, the photooxidation aza-Henry reaction was fitted as a 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 Cu₂O spheres may be also affected by the intrinsic catalytic activity, catalyst dosage, light intensity, etc. In order to study the effect of internal diffusion on the performance of the mesoporous Cu₂O spheres, other factors should be excluded. The influence of intrinsic catalytic activity on the reaction could be neglected owing to the similar crystallinity and crystal size properties of SP-Cu₂O and LP-Cu₂O. The impact of catalyst dosage on the reaction can also be ignored. Taking the above into consideration we took the same amount of LP-Cu₂O and SP-Cu₂O for this reaction, as 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 does not have an effect on the catalytic activity of the catalyst, because the reaction was conducted under the same light resource; hence the impact of light intensity on the reaction rate can be ignored. Compared with SP-Cu₂O, LP-Cu₂O showed an increase in the reaction rate and overall yield of the reactions, which meant that the LP-Cu₂O 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-Cu₂O and SP-Cu₂O possess similar BET surface areas, when we used the same amount of the catalysts the total catalytic surface area would be the similar. 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 under sufficient stirring conditions, the effect of the external diffusion to the reaction rate can be ignored; thereby the internal diffusion played an important role in the reaction rate. The results demonstrated that the reaction catalysed by porous Cu₂O spheres with a large effective diffusion coefficient has a higher catalytic activity. The results also gave us a suggestion that the fabrication of the porous photocatalysts should be not only to increase the surface area, but also to improve the efficiency of mass transfer.

The reusability of LP-Cu₂O 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-Cu₂O could be reused for at least 5 cycles without a distinct loss of its catalytic activity. The morphology and crystal structure showed no obvious change after 5 cycles of photocatalytic reaction (Fig. S4, ESI†). All these results showed the high photocatalytic activity and good stability of the LP-Cu₂O.

In summary, the porous Cu₂O spheres with different pore sizes were successfully fabricated using the template method and etching treatment. The obtained porous Cu₂O spheres have a high specific surface area, high crystallinity and well-defined morphology. In the light driven aza-Henry reactions, the LP-Cu₂O exhibited better catalytic activity compared with SP-Cu₂O. The results show the internal diffusion has a great impact on the reaction catalysed by porous photocatalysts 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.

This study was supported by the National Natural Science Funds for Excellent Young Scholars (no. 21222608), Research Fund of the National Natural Science Foundation of China (no. 21106099), Foundation for the Author of National Excellent Doctoral Dissertation of China (no. 201251), the Tianjin Natural Science Foundation (no. 11JCYBJC01700) and the Program of Introducing Talents of Discipline to Universities (no. B06006).

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