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Original article Cu₂O nanocrystals with various morphology: Synthesis, characterization and catalytic properties

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ABSTRACT

Cu₂O nanocubes, octahedra, spheres and truncated rhombic dodecahedral were prepared and their structural, morphological, and electronic properties were investigated by X-ray diffraction analysis, X-ray absorption near edge structure, scanning electron microscope and transmission electron microscope and X-ray absorption near edge structure. Cu₂O nanocrystals were successfully employed to catalyze the 1,3-dipolar cycloaddition reaction for the synthesis of 1,4-disubstituted triazoles. Cu₂O nanocubes and octahedral showed the superior catalytic performance in the cycloaddition reaction. These results reveal that crystal-plane engineering of oxide catalysts is a useful strategy for developing efficient catalysts for organic reaction.

Keywords: Nanocrystal Morphology Cu₂O

Azide-alkyne cycloaddition

1. Introduction

In recent years, there is a growing interest to the controlled synthesis of Cu_2O nanocrystals with uniform morphology not only for the development of synthetic strategies, but also for the comprehensive study of the effect of the crystal plane on the surface chemistry and catalytic properties of Cu_2O catalysts [1-6]. Furthermore, Cu_2O nanocrystals are relatively easy to make, inexpensive, readily available, safe, and has low toxicity and good environmental acceptability, which favors the investigation of their properties and applications in catalysis [6-10].

Huang *et al.* reported the correlation between the morphology and catalytic activity of Cu₂O nanocrystals in propylene oxidation, CO oxidation and the photocatalytic degradation of dyes [11-18]. These and many other examples clearly illustrate the importance of shape and morphology control to the efficient application of Cu₂O nanocrystals [19-21].

The Cu(I)-catalyzed azide-alkyne cycloaddition (CuAAC) as most famous click reaction are efficient method for the synthesis of 1,4-disubstituted 1,2,3-triazoles that have tremendous applications in many areas such as polymers, drug discovery, and advanced material science, *etc.* [22-28]. In recent years, our group have reported some work on catalytic application of copper-based catalysts for azide-alkyne cycloaddition and achieved some meaningful results [29-31]. However, due to the complicated interaction between Cu species with ligands or supports, the Cu-based catalysts are not ideal model catalysts to study the relationships between structures and activities. Therefore, in this work, uniform Cu₂O nanocrystals, including rhombic dodecahedrons, spheres, octahedrons and cubes were synthesized according to well-established procedures with some modification [13, 32]. We also report detailed structural characterization and the crystal-plane effects on the catalytic properties in the 1,3-dipolar cycloaddition of organic azides and alkynes. The catalytic performances of Cu₂O nanocrystals normalized to the percentage of the exposed Cu atom were followed the order d-Cu₂O> o-Cu₂O> s-Cu₂O.

2. Results and discussion

The Cu₂O nanocubes, octahedra, spheres and truncated rhombic dodecahedra were synthesized in aqueous solutions following previously reported procedures [13, 32]. Exact amounts of CuCl₂ solution, SDS surfactant, NaOH solution, and NH₂OHHCl as a reducing reagent were added in the sequence listed, and the mixture was aged for 1 h at 40 $^{\circ}$ C for growth the Cu₂O nanocrystals.

X-ray diffraction (XRD) was used to investigate the structures and phase purities of Cu_2O nanocrystals. Fig. 1 shows typical diffraction patterns of the Cu_2O nanopowders with no other crystalline impurities of CuO or metallic Cu, which fairly match with that of cubic bulk Cu_2O (JC-PDS file No. 78–2076) [33].

In order to probe the 3d character of Cu in the Cu₂O samples, the Cu L-edge XANES spectra were collected from all Cu₂O nanocrystals with cubic, octahedral, spheres and truncated rhombic dodecahedral structures. According to Fig. 2, it is clear that all samples shows two distinct peaks at ~935.6 eV and ~955.6 eV which are assigned to the transitions of $Cu2p_{3/2}$ (L₃) and $2p_{1/2}$ (L₂) electrons into the empty d-states, respectively. The difference among L_3 and L_2 , which is determined by the spin-orbit coupling, has value of ~20 eV. The post- L₃-edge structures at ~938.6, 944.5 and 951.6 eV are the characteristics of Cu₂O and relevant with previous reports [34]. Similarly, post L₂-edge structure at 958.0 eV in Cu₂O is reported in previous published reports [34]. It is seen that shape and intensity of various spectral features of o-Cu₂O and c-Cu₂O resembles to that of reported Cu₂O [34]. Thus, it appears that only c-Cu₂O represents Cu⁺¹ states. Drastic changes for these parameters for s-Cu₂O and d-Cu₂O reflect the possibility of different oxidation state of Cu. It is reported that Cu₂ p_{3/2} peak appear at 1 eV and 2.5 eV lower photon energy for Cu metal and CuO than that of Cu₂O except the significant change of energy [34]. In this case, no energy shift is observed for this edge, hence, copper ions has +1 oxidation state in s-Cu₂O and d-Cu₂O samples too. It is shown that intensity of $Cu_2p_{3/2}$ peak is associated with density of states of d-character at the bottom of conduction band, distorted by strong core-hole potential [34]. Thus modifications of d-character seem to be associated with low intense Cu2p_{3/2} peaks of s-Cu₂O and d-Cu₂O. The structures at 938.6 and 958.0 eV also exhibit intensity variations. To study the intensity variation of these structures, XANES spectra is de-convoluted in Fig. S1 in Supporting information as shown in Fig. 2b. The intensity of spectral feature at 938.6 eV is almost thrice for c-Cu₂O, s-Cu₂O and d-Cu₂O to that of o-Cu₂O. The intensity for c-Cu₂O is maximum for structure appearing at 958.0 eV and almost same for rest of the samples.

Fig. 3 and Fig. 4 show the SEM and TEM images of typically synthesized Cu_2O nanocubes with sizes of 500–600 nm, octahedral with sizes of 250–350 nm, rhombic dodecahedra with sizes of 0.7–1.1 μ m and spheres with sizes of 0.8–1.3 μ m respectively. Cubes and octahedral are more uniformly-sized, whereas rhombic dodecahedra and spheres have larger size distributions.

To compare the catalytic performance of all Cu₂O nanocrystals, cycloaddition reaction of benzyl chloride, phenyl acetylene and NaN₃ to synthesize 1-benzyl-4-phenyl-1,2,3-traizole were investigated in present of water as the standard "green" solvent without any additive under air at 70 °C. The specific cycloaddition reaction rate of benzyl chloride, phenyl acetylene and NaN₃ normalized to the percentage of the exposed Cu atoms for various Cu₂O nanocrystals followed the order d-Cu₂O > o-Cu₂O > c-Cu₂O > s-Cu₂O (Table 1). It took 120 min of reaction for the Cu₂O spheres to attain a product yield of 91%, but when Cu₂O nanocubes and octahedra were used, the product yield was improved to an excellent yield of 97% at 120 min. Remarkably, the use of Cu₂O rhombic dodecahedra rhombic dodecahedra as a catalyst significantly reduced the time of reaction to just 90 min with a yield of 97%. The above results clearly confirm that the morphology of Cu₂O nanocrystals controls their catalytic activity.

The morphology effect of Cu_2O nanocrystals on the product yield was also studied (Fig. 5). Results clearly demonstrated that on the basis of per unit mass of catalyst, the crystal-plane-controlled catalytic performance of Cu_2O nanocrystals in the 1,3-dipolar cycloaddition follows the order octahedral> cubes> rhombic dodecahedra~ spheres. The above results clearly confirm that the morphology of Cu_2O nanocrystals controls their catalytic activity.

To illustrate the scope of this method, we extended the cycloaddition reaction of a wide variety of terminal alkynes and organic halides in presence of d-Cu₂O, o-Cu₂O and c-Cu₂O. In most cases similar results were obtained (Table 2). First, various benzyl chlorides/bromides and phenyl acetylenes with the substitution of electron withdrawing and electron donating groups on the phenyl ring were investigated and did not have any appreciable influence on the outcome of the reaction (entries 1–17). Furthermore, steric hindrance of the ortho substituents on the benzyl chloride had little effect on the reaction yields (entries 2 and 3). As can be seen from the Table 1, in case of deactivated alkynes such as propargyl alcohol and 2-methyl-3-butyn-2-ol, when benzyl bromide was used under the similar reaction conditions, the corresponding products were obtained in higher yields than the case of benzyl chloride (entries 7, 8 and 17, 18). On the other hand, *t*-butyl bromide as a deactivated halide reacted nicely with various alkynes to obtain the corresponding 1,4-disubstituted triazoles in excellent yields (entries 13-15).

The recyclability of catalyst is an important and critical topic in the field of heterogeneous catalysis. Therefore the recyclability of the d-Cu₂O, c-Cu₂O and o- Cu₂O as catalysts was also surveyed (Fig. 6). After completing one run of reaction, the reaction mixture was centrifuged and another cycle of the reaction was carried out using the same particles. The results revealed that catalysts could be reused at least four times without appreciable dramatic yield loss.

Expectedly, in presence of the recovered d-Cu₂O, the reaction rate slightly decreased as compared to fresh d-Cu₂O (Fig. 7).

The SEM images of the recycled catalysts after the fourth cycle show some morphological and surface changes and therefore these changes and also small losses of catalyst mass (10%–15% of the total mass of catalyst) during washing procedure may be caused in the low diminution in the activity from the first to the fourth cycle (Fig. 8).

To further confirm the structures and phase purities of recycled Cu_2O nanocrystals, XRD patterns of the recycled nanocrystals were recorded (Fig. 9). The XRD patterns of the recycled d-Cu₂O and c- Cu₂O showed only peaks of the Cu₂O nanopowders with no impurities, but recycled o-Cu₂O indicated mixed phases of Cu₂O and CuO, probably arising from slight oxidation of Cu¹ during cycloaddition reaction. To investigate heterogeneous nature of the d-Cu₂O, c-Cu₂O and o- Cu₂O nanocrystals, the cycloaddition of benzyl chloride, NaN_3 and phenylacetylene after hot filtration was done and it was observed that no product is formed after separation of nanocrystals and therefore they act heterogeneously in the reaction. Also, ICP analysis was employed to be sure that no leaching of copper took place during cycloaddition reaction.

3. Conclusion

For the first time, Cu_2O nanocubes, octahedra, rhombic dodecahedra and icosahedra have been used as catalysts in the 1,3-dipolar cycloaddition reaction of benzyl chloride, phenyl acetylene and NaN₃ for the generation of 1,4-disubstituted triazoles. The catalytic performance of Cu_2O nanocrystals on the basis of the exposed Cu atoms followed the order d- Cu_2O > o- Cu_2O -c- Cu_2O > s- Cu_2O . A wide variety of triazoles with excellent yields have been synthesized, demonstrating that o- Cu_2O and c- Cu_2O are broadly useful and highly efficient catalysts for the azide-alkyne cycloaddition reaction. Also these nanocrystals are recyclable catalysts at least four times.

4. Experimental

Chemicals: Anhydrous copper(II) chloride, sodium hydroxide, SDS, and hydroxylamine hydrochloride were purchased from Aldrich and Merck. All chemicals were used as received without further purification.

Cu₂O nanocrystal synthesis: For the synthesis of Cu₂O nanocrystals with cubic, octahedral, spheres and truncated rhombic dodecahedral structures, 5 mL of 0.1 mol/L CuCl₂ solution and 0.87 g of SDS powder were respectively added to four beakers containing 89.2, 83.2, 78.2, and 69.2 mL of deionized water with vigorous stirring. After complete dissolution of SDS powder, 1.8 mL of 1.0 mol/L NaOH solution was added. Finally, 4.0, 10.0, 15.0 and 24.0 mL of 0.1 mol/L NH₂OH.HCl were quickly injected into beakers respectively. The solutions were kept in the water bath for 1 h at 40 °C to growth of nanocrystals. The product was collected by centrifugation, washed by excessive water and ethanol for several times to remove unreacted chemicals and SDS surfactant, and finally dried in vacuum at 50 °C.

General procedure for azide–alkyne cycloaddition: To a solution of Cu₂O (1 mg) in H₂O (2 mL) were added alkyne (0.5mmol), the organic halide (0.55 mmol) and NaN₃ (0.55 mmol). The reaction mixture was warmed to 70 °C continuing stirring with monitoring by TLC until total conversion of the starting materials. After addition of water (3 mL), the resulting mixture was extracted with EtOAc (2× 10 mL). The collected organic phases were dried with anhydrous CaCl₂ and the solvent was removed in vaccum to give the corresponding triazoles, which did not require any further purification.

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Fig. 1. XRD patterns of the Cu₂O nanocrystals synthesized with various morphologies



Fig. 2. (a) The Copper L-edge XANES spectra of the Cu₂O nanocrystals synthesized with various morphologies; (b) reflects the intensity variations of structures appearing at 938.6 and 958 eV.



Fig. 3. SEM images of different morphologies of c-Cu₂O (a), o-Cu₂O (b), s-Cu₂O (c), d-Cu₂O (d).



Fig. 4. TEM images of different morphologies of c-Cu₂O (a), o-Cu₂O (b), s-Cu₂O (c), d-Cu₂O (d).



Fig. 5. The morphology effect of Cu_2O nanocrystals for the synthesis of 1-benzyl-4-phenyl-1,2,3-traizole



Run number

Fig. 6. Recycling studies of d-Cu₂O, c-Cu₂O and o- Cu₂O catalysts in azide-alkyne cycloaddition



Fig. 7. Reaction kinetic plots by using the fresh and recovered d-Cu₂O catalyst, respectively.



Fig. 8. SEM images of a) d-Cu₂O; b) o- Cu₂O and c) c- Cu₂O after azide-alkyne cycloaddition



Fig. 9. XRD patterns of the recycled Cu₂O nanocrystals

Entry	Catalyst	Exposed Cu atoms (%)	Amount used (mg)	Time (min)	Yield (%)
1	c-Cu ₂ O	28.49	1.2	120	97
2	o-Cu ₂ O	33.45	1	120	97
3	s-Cu ₂ O	14.08	2.4	120	91
4	d-Cu ₂ O	18.60	1.8	90	97

Table 1. Comparison of catalytic potential of different Cu₂O nanocrystals for the synthesis of 1-benzyl-4-phenyl-1,2,3-traizole

Table 2. Cycloaddition of benzyl halides with terminal alkynes in the presence of d-Cu₂O, o-Cu₂O and c-Cu₂O

 \mathbf{R}^1

$X + NaN_3 + R^3$	$- = \frac{Cu_2O}{H_2O, 70}$	R ²					
Entry	\mathbb{R}^1	R ²	Х	R ³			
					d-Cu ₂ O ^b	o-Cu ₂ O ^c	c-Cu ₂ O ^d
1	Ph	Н	Cl	Ph	97	97	97
2	4-Me-Ph	Н	Cl	Ph	97	96	95
3	2-Me-Ph	Н	Cl	Ph	93	90	88
4	4-NO ₂ -Ph	Н	Cl	Ph	95	94	94
5	Ph	Н	Cl	4-MeO-Ph	97	96	95
6	Ph	Н	Cl	4-Me-Ph	96	96	92
7	Ph	Н	Cl	(HO)CH ₂	88	81	83
8	Ph	Н	Cl	HOCH(CH ₃)(CH ₂) ₂	85	79	76
9	Ph	Н	Br	Ph	97	97	97
10	Ph	Н	Br	4-MeO-Ph	97	96	97
11	Ph	Н	Br	4-Me-Ph	97	97	97
12	Ph	Ph	Br	Ph	91	87	85
13	CH3(CH2)3	Н	Br	Ph	96	94	93
14	CH3(CH2)3	Н	Br	4-MeO-Ph	93	92	94
15	CH3(CH2)3	Н	Br	4-Me-Ph	95	90	88
16	Ph	Н	Br	(HO)CH ₂	93	91	92
17	Ph	Н	Br	HOCH(CH ₃)(CH ₂) ₂	90	88	85

^a Isolated yield; ^bReaction time= 90 min; ^cReaction time = 120 min