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Selective Synthesis of Cu₂O Nanocrystals as Shape-Dependent Catalysts for **Oxidative Arylation of Phenylacetylene**

Lingling Li, Caiyun Nan, Qing Peng,* and Yadong Li^[a]

Copper(I) oxide is a typical p-type semiconductor with a band-gap energy of 2.17 eV. In recent years, great effort has been put into the synthesis of Cu₂O nanocrystals (NCs) and their applications such as photocatalysis,^[1] CO oxidation,^[2] and gas sensing.^[3] In particular, Cu₂O (bulk or in NC form) was reported as an efficient catalyst for C-C, C-N, and C-O bond-formation cross-coupling reactions.^[4] Lately, internal alkynes have been produced by cross-coupling of alkynes with arylboronic acids, which are less toxic and more temperature- and air-stable.^[5] However, most of these studies involved noble palladium salts or copper halides as catalysts and/or the addition of ligands and additives. Cu₂O was also demonstrated to have highly efficient catalytic activity for the synthesis of internal alkynes via aerobic oxidative arylation of terminal alkynes using pyridine as additive.^[5d] However, several problems arise by the addition of ligands and additives: 1) it is difficult to recycle the catalysts, 2) cost and waste are greatly increased, and 3) research into their shape-dependent catalytic properties is limited owing to coordination of the catalysts with ligands or additives in the reaction system.

The advantages of nanoparticles have been extensively recognized in organic catalysis.^[6] Cu₂O nanoparticles can have enhanced activity even in the absence of ligands or additives thanks to their large surface-to-volume ratio and good dispersion in catalytic reaction systems; this provides an opportunity to solve the above-mentioned problems and to serve as a complement to traditional reaction conditions. Moreover, the catalytic properties of nanoparticles depend on the type and distribution of crystal planes, edges, corners, and individual chemicals in the reaction system.^[7] Therefore, control over nanoparticle size and morphology may in turn allow control in the specific activity and selectivity for organic catalysis. That is, ligand- and additive-free synthesis of internal alkynes may be realized with arylboronic acids as one of the substrates catalyzed by Cu₂O NCs of various shapes and sizes.

Over the past decades, much progress has been made in the controlled synthesis of Cu₂O.^[1-3,8] Fine-tuning of Cu₂O NCs provides an ideal model catalyst with well-defined size and geometric structures for organic reactions. Herein, we report the selective synthesis of monodisperse Cu₂O cubes, rhombic dodecahedra, and octadecahedra in an octadecylamine (ODA) system as well as their catalytic properties in our designed aerobic oxidative coupling of arylboronic acids and phenylacetylene (Scheme 1).

$$ArB(OH)_2 + Ph \longrightarrow O_2 \\ Cu_2O NCs Ar \longrightarrow Ph$$

Scheme 1. The designed aerobic oxidative coupling reaction.

Cu₂O NCs were prepared by using a modified protocol for alkylamine systems.^[3c,9] Scanning electron microscopy (SEM) investigation revealed three types of NCs: cubes, rhombic dodecahedra, and octadecahedra, all of which were obtained with narrow size distribution (Figure 1 a-c). Their X-ray diffraction (XRD) patterns were all indexed to pure cubic-phase Cu₂O (JCPDS No. 78-2076, Pn3m, a =0.4267 nm; Figure 1 d). Notably, the intense ratio of (110) and (200) varied among the three samples. Rhombic dodecahedra and cubes are unifaceted with {110} and {100}, respectively, as previously reported.^[3c] Cu₂O octadecahedra were single crystalline, each composed of six {100} and twelve {110} facets as demonstrated by high-resolution transmission electron microscopy (HRTEM; Supporting Information, Figure S1a), which is in accordance with the moderate intense ratio of (110) and (200) in the above XRD patterns. The Cu₂O octadecahedron is essentially a truncated rhombic dodecahedron with six of its fourteen vertices truncated by {100} planes.^[8c,10] This is the first report on the synthesis of Cu₂O octadecahedra with such a narrow size distribution, and sizes could be easily tuned from 125 to 500 nm by controlling formation times at 200°C (Figure S2).

To understand the synthetic mechanism of Cu₂O NC formation, we carried out two proof experiments without the addition of ODA. Polydisperse microcrystals of 1.5-2 µm and nanoparticles were obtained in n-hexadecane and 1-octadecene (ODE), respectively (Figures S3a and S3b). XRD patterns confirmed them to be cubic-phase Cu₂O (Figure S3c). It is well known that thermal decomposition of Cu-(CH₃COO)₂·H₂O (Cu(OAc)₂·H₂O) produces cuprous salt above a certain temperature (170°C, for instance), depending on the atmosphere, heating rate, etc.^[11] Therefore Cu₂O

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Figure 1. Typical SEM images of Cu₂O NCs with various morphologies: a) cubes, b) rhombic dodecahedra, and c) octadecahedra. d) XRD patterns of as-obtained Cu₂O NCs.

NCs were actually obtained by thermal decomposition of $Cu(OAc)_2 H_2O$ in the present work. Herein, ODA served as an intermediate for electron transfer while facilitating the nucleation and growth kinetics of Cu_2O NCs.^[9] In addition, the shapes of Cu_2O NCs were inherently sensitive to the molar ratio of cupric precursor to ODA. Cubes, octadecahedra, and rhombic dodecahedra were successively obtained upon decreasing the above-mentioned molar ratio. In other words, {100} facets are more stable than {110} in high concentrations of ODA. This could be ascribed to the anisotropic adsorption capacity of ODA on different facets of Cu_2O NCs.

As shown in Figure S1b, 2D arrays of Cu₂O octadecahedra with 100% morphology yield had a tendency to lie on {110} facets when doped on the silicon wafer. Viewed in the direction of <110>, subunits of the building blocks adopted a quasi-hexagonal configuration (labeled by a white square in Figure S1b). It should be noted that Cu₂O octadecahedra tend to disassemble when dispersed in n-hexane (Figure S1d). In the context of self-assembly, it was reported that van der Waals (vdW) interaction among the surface alkylamine molecules give rise to the formation of Cu₂O nanocrystal superlattices.^[3c] However, the size of Cu₂O octadecahedra is much larger than the length scale of vdW forces (<100 nm) in our work, which made it rather difficult to form large areas of Cu₂O superlattice self-assembly by vdW forces. At present, a wide variety of interparticle interactions (vdW, hydrogen bonds, electrostatic and molecular surface forces) have been studied extensively, among which



cross-linking interactions are commonly used.^[12] ODA has good solubility in ethanol, yet is hardly soluble in n-hexane at room temperature. Cross-linking interactions between the dissolved ODA molecules and those tethered to the surfaces of Cu₂O octadecahedra caused their ordered self-assembly. The magnitude of cross-linking depends on the concentration of linkers in solution and the bond energies.^[12] As a result, self-assembly was difficult in nhexane due to the poor solubilitv of ODA.

Having established that, we tested the catalytic properties of Cu_2O octadecahedra. Cu_2O octadecahedra with size ~125 nm were chosen as the model catalyst. The reaction shown in Scheme 1 was carried out without the addition of ligands (see the Experimental Section below for details). Phenylboronic acid (**1a**) and phe-

nylacetylene (2) were chosen as model substrates to optimize reaction conditions by altering the bases (Table 1). N,N'-Dimethylethylenediamine (DMEDA) and Cs₂CO₃ gave disappointing results (entries 1 and 2), whereas product 1,2-diphenylethyne (**3a**) was obtained in 89% yield with *t*BuOK as the base (Table 1, entry 3). Two additional substrates of arylboronic acids **1b** and **1c** were tested under the optimized reaction conditions, and both provided excellent yields (Table 1, entries 4 and 5).

Table 1. $\rm Cu_2O$ octade cahedra-catalyzed oxidative arylation of arylboronic acid and phenylace tylene. $^{[a]}$

	ArB(OH) ₂ + Ph \longrightarrow $\frac{Cu_2O NCs, air}{tBuOK, 60°C}$ Ar \longrightarrow Ph				
Entry	Ar (1)	Base	Product	Yield [%] ^[b]	
1	$C_{6}H_{5}(1a)$	DMEDA	3a	13	
2	$C_{6}H_{5}(1a)$	Cs_2CO_3	3a	trace	
3	$C_{6}H_{5}(1a)$	tBuOK	3a	89	
4	$4-CH_{3}OC_{6}H_{5}(1b)$	tBuOK	3 b	92 ^[c]	
5	$4-ClC_{6}H_{5}(1c)$	tBuOK	3c	92 ^[c]	

[a] Reactions were carried out at 60 °C under ambient conditions for 18 h; catalyst: 0.02 mmol Cu₂O, solvent: 2 mL dioxane and 0.5 mL *i*PrOH. [b] GC yield using *n*-hexadecane as the internal standard. [c] ¹H NMR yield using trichloroethylene as the internal standard.

Thereafter we studied the catalytic properties of the three differently shaped Cu_2O NCs (~125 nm) upon recycling (Figure S4). As shown in Table 2, all showed excellent yields

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Table 2. Cu₂O NC-catalyzed oxidative arylation of phenylboronic acid and phenylacetylene upon recycling.[a]

	$PhB(OH)_{2} + Ph \longrightarrow \frac{Cu_2O \text{ NCs, air}}{fBuOK, 60^{\circ}C} Ph \longrightarrow Ph$				
Entry	Catalyst	Cycle No.	Yield [%] ^[b]		
1	cubes	1	94		
2	cubes	2	47		
3	cubes	3	32		
4	rhombic dodecahedra	1	84		
5	rhombic dodecahedra	2	87		
6	rhombic dodecahedra	3	96		
7	rhombic dodecahedra	4	90		
8	octadecahedra	1	89		
9	octadecahedra	2	93		
10	octadecahedra	3	92		
11	octadecahedra	4	97		
12	commercial Cu ₂ O	1	47		
13	no catalyst	1	-		
14	CuO nanoleaves	1	-		



in the first run (entries 1, 4, and 8), but there was considerable distinction in their activities in the following cycles (entries 2, 3, 5, 6, 7, 9, 10, and 11). Cu₂O octadecahedra and rhombic dodecahedra could be reused at least four times without appreciable loss of activity, whereas Cu₂O cubes had very poor recyclability, with half of the activity lost in the second run (entry 2). Compound 3a was obtained in $47\,\%$ yield by using commercial $\mathrm{Cu_2O}$ microcrystals as the catalyst (Table 2, entry 12). Importantly, no product could be detected in the absence of catalyst (entry 13) by GC. In view of the above results, Cu₂O octadecahedra were the most robust catalysts with the highest activity and could remain consistently active in the recycled runs of the ligandfree oxidative arylation reaction.

The present Cu₂O NC-catalyzed aerobic oxidative coupling reaction could be defined as semi-homogeneous, given the good dispersion of Cu₂O NCs in the reaction system (insets at top right of Figure 2). The three different Cu_2O NC shapes showed similar catalytic activity in the first run, despite their variations in morphologies and exposed facets. Their specific surface area was preliminarily calculated on the assumption that they all have symmetrical geometries (Figure S5). The reaction appeared not to be sensitive to nanocatalyst morphology, as previously reported.^[13] However, the activity of Cu₂O NCs upon recycling (or stability) depends heavily on their morphology. It is expected that surface reconstruction or dissolution of active atoms at corners or edges by the reactants or even the solvent occurs during catalysis.^[14] After each cycle, Cu₂O NCs were examined by SEM (Figure 2 and Figure S6). Cu₂O cubes had the lowest stability, with their surfaces etched rough after the first cycle of oxidative arylation (Figure 2b). During the second run, severe aggregation was caused by close linking of smaller Cu₂O fragments. The decreased activity of Cu₂O cubes could be due to the loss of active atoms into the reaction system and their difficulty in being recycled. In the case of COMMUNICATION

Cu₂O rhombic dodecahedra, no change was observed in either size or morphology during the reaction (Figure 2e,f and Figures S6a and S6b). Considering the above SEM images, {100} facets of Cu₂O cubes are speculated to be vulnerable to perturbation of the organic reaction, whereas {110} planes of Cu₂O rhombic dodecahedra were quite stable. SEM images of Cu₂O octadecahedra during recycling further confirmed this speculation. As shown in Figure 2h, a large portion of Cu2O octadecahedra were distorted slightly concave on certain facets after the first run (marked with white squares in Figure 2h); 0.012 mmol of Cu₂O octadecahedra remained, as confirmed by inductively coupled plasma (ICP) mass spectrometry, and were nearly etched to nanocages after the fourth cycle (Figure 2i). Cu₂O octadecahedra were carefully examined after the third run, to address detailed shape evolution of the catalyst during recycling. Under closer observation of a single Cu₂O octadecahedron, all the concave surfaces could be ascribed to {100} facets (Figure 3a,b).

In previous reports, Cu₂O nanoframes could be prepared by particle aggregation and acidic etching or selective oxidative etching.^[1b,8c] To understand the formation of Cu₂O octadecahedral nanoframes in our catalytic reaction, X-ray photoelectron spectroscopy (XPS) was performed to detect the valence of catalysts. XPS results show only two peaks at 932.2 and 951.9 eV in the Cu 2p photoelectron spectrum of Cu₂O octadecahedra before being subjected to the catalytic reaction, indicating their surfaces remained Cu^I. However, after the third catalytic cycle for Cu₂O octadecahedra, two additional peaks at 933.5 and 953.9 eV appeared, and could be indexed to Cu 2p3/2 and 2p1/2 of CuO, respectively. This means that partial Cu₂O octadecahedra were oxidized to CuO during aerobic oxidative arylation. The three different Cu₂O NC shapes naturally displayed distinct shape evolution (or stability) during the catalytic reaction, as illustrated in Figure 3d. Accordingly, a primary consideration was taken into the formation mechanism of Cu2O octadecahedral nanoframes. Active copper atoms are thought to be more readily "pulled" from {100} facets than {110} and oxidized to CuO in the present reaction environment (namely, leaching). It should be noted that partial oxidative etching of Cu₂O octadecahedra did not elicit loss of activity for the catalytic reaction. We prepared CuO nanoleaves of 100 nm length and 50 nm width (Figure S7). They did not show activity in the arylation of phenylacetylene, as detected by GC. As shown in Figure 3c, only partial Cu₂O octadecahedra were oxidized to CuO in the catalytic reaction, which may decrease the amount of Cu₂O catalyst. However, the exposure of more active facets (the concave counterparts) after being etched could finally improve their catalytic activity. For Cu₂O rhombic dodecahedra, no loss of activity was caused, as their size and morphology did not change during recycling. The slight improvement might be attributed to the removal of surfactant on Cu₂O NCs in the recycled runs.^[15] However, nanoframes could not be formed, as they are unifaceted with {100} for Cu₂O cubes; the severe leaching of active atoms brought about a significant loss of activity

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Figure 2. Typical SEM images of Cu_2O NCs before and after the catalytic reaction: cubes a) before and after the b) first and c) second cycles. Rhombic dodecahedra d) before and after the e) first and f) fourth cycles. Octadecahedra g) before and after the h) first and i) fourth cycles. The catalytic reaction systems are shown in the insets.

during recycling. We are currently working on further mechanistic investigations.

In conclusion, cubic, rhombic dodecahedral, and octadecahedral Cu₂O NCs were selectively synthesized in the ODA system assisted by ODE, among which Cu₂O octadecahedra with such a narrow size distribution are reported herein for the first time. The 2D self-assembly and disassembly of Cu₂O octadecahedra can be easily controlled by their dissolution in ethanol and *n*-hexane, respectively. Meanwhile, we designed a ligand-free arylation of phenylacetylene with arylboronic acids catalyzed by as-obtained Cu₂O NCs. They all show good to excellent yields, while displaying distinct shape evolution (or stability) during the catalytic reaction. Cu₂O octadecahedra have the best catalytic activity upon recycling, although they were etched on {100} facets in the formation of nanoframes, possibly through oxidative etching. This work provides not only a facile and selective synthesis of Cu₂O NCs, but also offers a better understanding of their

catalytic performance in practical organic reactions, which could aid in the selection of suitable nanocatalysts with high activity upon recycling for idiographic reactions.

Experimental Section

Typical procedure for the synthesis of Cu₂O octadecahedra: ODE (2 mL, 90%; Alfa Aesar) was introduced to molten ODA (4.04 g, AR; Sinopharm Chemical Reagent Co. Ltd.) at 80°C in a capped vial. After stirring for 10 min, Cu(OAc)₂·H₂O (0.1 g, \geq 98%; Alfa Aesar) was added to the mixture; stirring was continued at 100°C for 15 min to ensure complete dissolution. The mixture was then heated at 200°C for 25 min.

General procedure for the oxidative arylation of phenylacetylene: Substrates 1 (0.3 mmol) and 2 (0.2 mmol), base (1 mmol), catalyst (Cu₂O NCs, 0.02 mmol), and solvent (2.5 mL) were added to a 10 mL two-necked flask. The reaction mixture was stirred at 60°C for the indicated time. After reaction, EtOAc (10 mL) was added to the flask, and the resulting mixture was centrifuged at 6000 rpm (room temperature, 5 min). The supernatant was collected, and EtOAc (5 mL) was then added to the

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Figure 3. a) A typical TEM image of Cu_2O octadecahedra after the third cycle of the catalytic reaction and b) their corresponding SEM image. c) XPS of Cu_2O octadecahedra before the catalytic reaction and after the third cycle; the inset shows a model of a Cu_2O octadecahedral nanoframe. d) Evolution of the three different Cu_2O NC shapes during the catalytic reaction; molecular O_2 is displayed as ball-and-stick models.

precipitate for the next centrifugation; after three further cycles of centrifugation (same conditions as above), the combined supernatant was concentrated under reduced pressure, and later dissolved in EtOAc (2 mL) for further analysis. Thin-layer chromatography (TLC) was used to monitor all reactions. GC was operated on an SP-6890 instrument. Yields were measured by the internal standard method; for GC *n*-hexadecane (GCS, >99.5%; Aladdin) was the internal standard. ¹H NMR and ¹³C NMR spectra were recorded in CDCl₃ on a JEOL JNM-ECA 300 instrument. The yields of **3b** and **3c** were measured with trichloroethylene (GCS, >99.5%; Aladdin) as the internal standard.

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Keywords: catalysis \cdot copper(I) oxide \cdot oxidative arylation \cdot shape-dependent stability \cdot nanocrystals

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Nanocrystals

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Selective Synthesis of Cu₂O Nanocrys-



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