



Short communication

# Ordered mesoporous copper oxide nanostructures as highly active and stable catalysts for aqueous click reactions

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## ABSTRACT

We demonstrate that ordered mesoporous CuO with gyroid mesostructures can be used as highly efficient, stable, and recyclable self-supported catalysts for click reactions in aqueous media.

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## 1. Introduction

Click chemistry introduced by the work of Sharpless [1] and Meldal [2] is one of most efficient cycloaddition methods. This approach has attracted tremendous interests in various fields including material chemistry [3–5], combinatorial chemistry [6], and drug discovery [7]. The copper(I)-catalyzed azide-alkyne cycloaddition (ACC) reaction, one of the primary examples of click chemistry, proceeds in different solvents and yields stable triazoles with possible applications in DNA modification, as well as pharmaceutical and organic synthesis [8]. However, the instability of the Cu(I) species as manifested by the easy aerial oxidation of Cu(I) to Cu(II) has limited the application of Cu-catalyzed ACC reaction in other fields.

In the past years, many researches about AAC reactions catalyzed by Cu(II) catalyst have been investigated. In 2002, Sharpless and co-workers used CuSO<sub>4</sub> as catalyst for the ACC reaction with reductant [9]. In 2009, Zhu and co-workers used Cu(OAc)<sub>2</sub> catalyst in alcoholic solvent without reductants [10]; these authors also proved the

reduction of Cu(II) to Cu(I) by alkynes during homocoupling reactions [11]. To improve catalytic activity of Cu(II) in ACC reactions, Kaboudin and co-workers reported Cu(II)-β-cyclodextrin complex and this complex exhibited similar activity with previously reported Cu(I) catalyst in optimized condition [12].

To overcome the limitations of homogeneous catalytic systems, such as difficult catalyst recovery and low thermal stability, heterogeneous systems have been investigated as alternative catalysts [13–21]. The fabrication of porous nanostructures represents a promising approach to increase the catalytically active surface area and enhance the accessibility of the surface sites to the reactants, thereby enhancing the performance of heterogeneous systems [22,23]. Nanocasting represents one of the most successful strategies for fabricating ordered nanoporous materials. The nanoporous materials fabricated by this method show good thermal stability, high crystallinity, and highly ordered pore structures [24–26]. Particularly, the nanoporous materials templated from mesoporous silica with cubic gyroid structure such as KIT-6 are highly appealing, as their 3D-interconnected pore structure can provide highly accessible catalytically active surfaces, as well as structural stability during catalytic reactions. However, to our knowledge, no previous studies have investigated the use of copper(II) oxide nanoporous structures for click reactions.

Here we report for the first time high-performance heterogeneous catalysts for click reactions, based on ordered mesoporous copper(II) oxide (m-CuO) with 3D double gyroid mesostructure. The m-CuO

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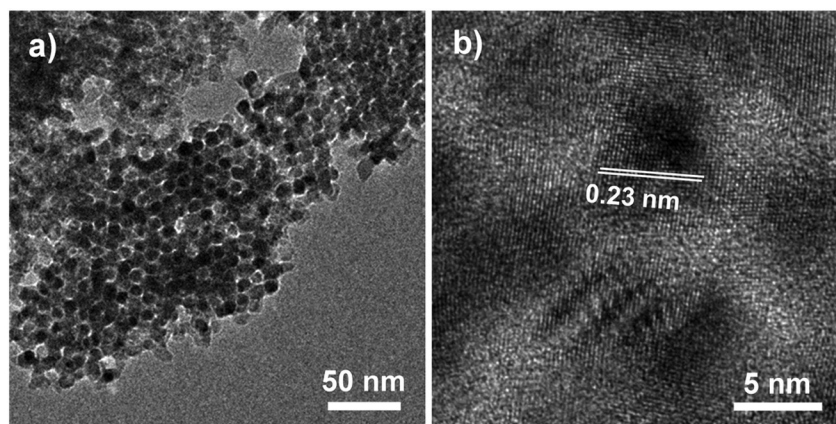


Fig. 1. (a) TEM and (b) HRTEM images of m-CuO nanostructures.

catalysts showed high activity, recyclability, and excellent stability in the azide-alkyne cycloaddition reactions in aqueous media.

## 2. Experimental

### 2.1. Synthesis of ordered mesoporous copper(II) oxide nanostructures

Ordered mesoporous copper(II) oxide replica was synthesized by nitrate combustion method [27]. 1.9 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (Aldrich) was dissolved into 2.0 g of DI water, and 1.0 g of KIT-6 was added to the blue-coloured solution. The slurry was dried at 100 °C for 1 h. The silica-copper nitrate composite was placed with ammonia solution (28%, Samchun chemical) in a separate container, with a cover to prevent ammonia solution vapour dispersed through the atmosphere. Colour change was observed during this combustion step. After 1 h, the ammonia-treated composite was dried at 100 °C for 1 h, and subsequently added into a solution composed of 1.9 g of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and 3.0 g of DI water, and dried. Then, ammonia vapour treatment and drying were conducted. The dried powder was calcined at 400 °C for 6 h. (Caution: This calcination process explosively occurs, so using a wide crucible is highly recommendEd.) The resulting dark-grey compound was mixed with 0.1 M NaOH aqueous solution, and kept at 90 °C for 1 h to remove the silica template, then centrifuged at 4000 rpm for 10 min. These etching-centrifuging processes were repeated twice more, and the product was filtered, washed with DI water and ethanol, then dried at 60 °C.

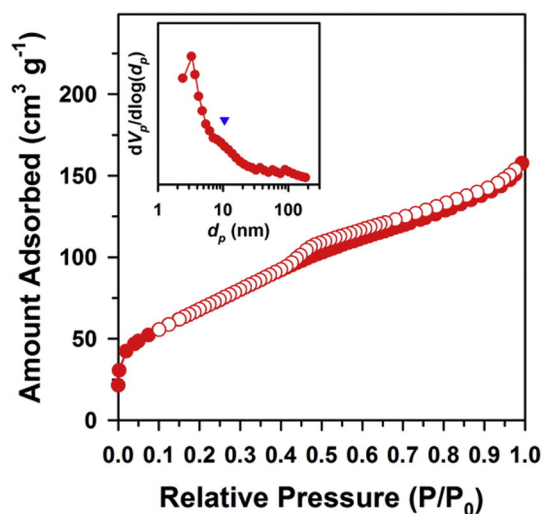


Fig. 2.  $\text{N}_2$  adsorption-desorption isotherms of m-CuO and the corresponding pore size distribution (inset).

### 2.2. General procedure for click reactions

1.0 mg of m-CuO NPs (0.013 mmol, 1 mol%), benzylazide (0.15 mL, 1.26 mmol), phenylacetylene (0.195 mL, 1.77 mmol), and 3.6 mL  $\text{H}_2\text{O}$  were placed in a 10 mL pressure schlenk tube. The reaction mixture was stirred at 50 °C. After 9 h, the reaction product analyzed by  $^1\text{H}$  NMR using Varian Mercury Plus (300 MHz).

### 2.3. Recyclability test

After the reaction, the catalyst particles were precipitated by centrifugation and washed with dichloromethane and ethanol. The particles were vacuum dried at room temperature and were used as a catalyst for another cycle of the reaction.

### 2.4. Catalyst characterization

X-ray diffraction (XRD) patterns of the samples were obtained by using a high-power X-ray diffractometer (D/Max 2500 V/PC, Rigaku) with a  $\text{Cu K}\alpha$  source at 40 kV and 200 mA. Crystallite size of the framework particle of m-CuO was calculated by Scherrer equation.

$$D_{hkl} = \frac{0.9\lambda}{(FWHM) \cos(\theta)}$$

$D_{hkl}$  and  $\lambda$ , FWHM, and  $\theta$  indicate crystallite size, wavelength of X-ray, full-width-half-maximum of a peak in radian, and Bragg angle respectively.

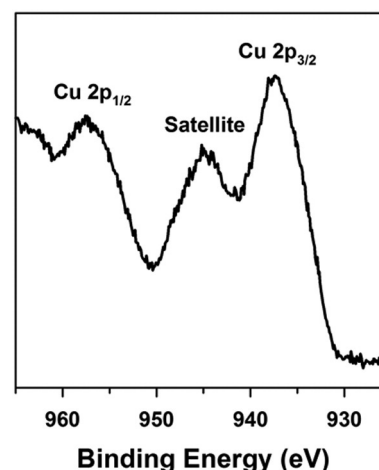


Fig. 3. Cu 2p XPS spectrum of m-CuO sample.

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