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Surfactant-assisted hydrothermal synthesis and characterization of copper nano/microstructures and their application as catalysts in click chemistry

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ABSTRACT

A facile solution-phase process was developed for the selective preparation of single-crystalline copper (Cu) nanohexagons, nanospindles, and microflowers by the reduction of cuprous iodide with sodium ascorbate in the presence of surfactants such as cetyltrimethylammonium chloride and Pluronic F-127 or cetyltrimethylammonium bromide. The Cu nanoparticle samples obtained at different stages of growth were studied by X-ray diffraction (XRD). The final products were characterized by XRD, scanning electron microscopy, and UV–vis spectroscopy. The UV–vis spectra of the as-synthesized Cu nanostructures exhibited morphology-dependant optical property. The Cu microflowers showed significant catalytic activity in click chemistry.

1. Introduction

In the past years, much effort has been devoted to the controlled synthesis of metal nanostructures because of their unique chemical and physical properties than the bulk materials [1,2]. Nano-copper catalysts have attracted increasing attention from organic chemists because of their high catalytic activity, diverse application, low cost, and good stability [3]. Therefore, the synthesis of Cu micro/nanostructures has been extensively investigated during the past several years. Many synthetic methods, including polyol process, templated synthesis, reverse micelles, microemulsion, electrochemical deposition, chemical solution process, chemical vapor deposition, and irradiation have been used to synthesize Cu micro/nanostructures with different shapes [4–9]. However, in contrast to many reports on the synthesis of wire and plate-like nanostructures of face-centered-cubic metals (Ag, Pt, and Au) [10–16], Cu nanostructures have not been reported. Successful synthetic strategies for the preparation of low-dimensional Cu micro/nanostructures are still a challenge, and a slow reduction process may favor their formation. In this study, a facile hydrothermal process for the selective synthesis of anisotropic Cu nanocrystals is described, and three different morphologies such as nanohexagons, nanospindles, and microflowers were obtained by utilizing different surfactants. Hexagon and spindle-like Cu nanocrystals were synthesized using CTAC and F-127, respectively, as the surfactants, whereas flower-like microcrystals were synthesized using CTAB. Herein, we report that Cu microflowers show excellent catalytic activity for the click reactions.

2. Experimental

Materials: Pluronic F-127 (F-127) was obtained from Sigma chemical company. Cuprous iodide (CuI), and sodium ascorbate (VCNa) were supplied by Aladdin chemical company. Polyethylene glycol (PEG-200), cetyltrimethylammonium chloride (CTAC), cetyltrimethylammonium bromide (CTAB), acetone, and ethanol were supplied by Sinopharm chemical reagent factory. All of the chemical reagents in the experiment were of analytical grade, and used as received without further purification.

Synthesis of Cu nanoparticles: In a typical procedure for the synthesis of Cu nanohexagons, 0.015 mmol of CuI was added into 20 mL of PEG-200 under magnetic stirring, and then 0.5 mmol of VCNa was dissolved into the solution. Finally, 0.075 mmol of CTAC and 0.5 mL of NaOH (1 M) were sequentially added into the above mixture. After being vigorously stirred for 15 min, the mixture was put into a Teflon-lined autoclave of 25 mL capacity and maintained at 140 °C for 24 h, then cooled to room temperature. The products were collected, and washed thoroughly with deionized water and absolute ethanol. Finally, the products were dried in a vacuum oven before further characterization. When 0.075 mmol CTAC was substituted by 0.075 mmol F-127, and maintained at 140 °C for 24 h while other

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reaction conditions were kept constant, Cu nanospindles were obtained. Similarly, when 0.075 mmol CTAC was substituted by 0.075 mmol CTAB, Cu microflowers were obtained.

Characterization: The phase purity and crystal structure of the products were analyzed by X-ray diffraction (XRD) using D8 advance X-ray diffraction (Bruker AXS company, Germany) equipped with Cu Kα radiation ($\lambda = 1.5406$ Å), employing a scanning rate of 0.02 s^{-1} in the 2θ range from 10° to 80°. Field emission scanning electron micrographs (FESEMs) were used to determine the morphologies of the products. The FESEM images were obtained using a field emission scanning electron microscope (Hitachi S-4800 II, Japan). UV–vis absorption spectra of the samples were measured by a spectrophotometer (UV-2450, Shimadzu, Japan) equipped with a 10 mm quartz cell.

Representative procedure for Cu microflowers – Catalyzed click reaction: In a V-shaped reactor vial, phenylacetylene 1a (2 mmol, 224 μL) and benzyl azide 2a (2 mmol, 250 μL) were added to a solution of Cu microflowers (2 mol%, 2.6 mg) in toluene (1 mL). The reaction mixture was magnetically stirred at 65 °C for 2 h. The progress of the reaction was monitored by thin layer chromatography (TLC). After consumption of 1a and 2a, the reaction mixture was cooled to room temperature, filtered and washed with dichloromethane. After concentration of the filtrate, the white solid was purified by short silica gel chromatography using a 3:1 mixture of hexane and ethyl acetate as the eluent, to afford 1-benzyl-4-phenyl-1H-1, 2, 3-triazole 3a as a white solid; yield: 433 mg (92%).

3. Results and discussion

The phase and purity of the Cu nanohexagons, nanospindles, and microflowers were confirmed by the XRD pattern shown in Fig. 1 (1a–1c). All the diffraction peaks can be indexed to Cu (111), (200), and (220) planes of the face-centered-cubic structure of Cu (PDF Card no. 04-0836). No characteristic peak from impurity was detected.

In order to understand the formation of the Cu nanoparticles, the samples obtained at various stages of growth were studied using XRD. Fig. 1(2a–2d) shows XRD patterns of the products obtained at 140 °C for 2, 6, 12, and 18 h, respectively. From the pattern in Fig. 1(2a), only CuI (PDF Card no. 06-0246) was observed, after 2 h reaction. Fig. 1(2b) shows the XRD pattern of the products collected after 6 h reaction. Herein, both CuI and Cu coexisted in the products, indicating that CuI was partially reduced by VCNa under the reaction conditions. After the reaction for 12 h, the intensity of CuI peaks weakened, whereas that of Cu peaks intensified, because CuI gradually transformed into Cu, as shown in Fig. 1(2c). After 18 h reaction, the peak of CuI disappeared and only the Cu peaks remained, as shown in Fig. 1(2d).

The morphologies of Cu nanoparticles were analyzed using SEM. Fig. 2(b) and (d) shows the typical SEM image of Cu nanohexagons and nanospindles. As shown in Fig. 2(b), the hexagon structure has a length of ~0.6–0.9 μm. As shown in Fig. 2(d), the spindle-like structure has a length and width of ~200–300 and ~80–100 nm, respectively. As shown in Fig. 2(a) and (c), irregular Cu hexagons and spindles were obtained when the amount of CTAC and F-127 was 0.015 mmol. When the amount of CTAC and F-127 was increased to 0.075 mmol, Cu nanohexagons and nanospindles were obtained, as shown in Fig. 2(b) and (d). As shown in Fig. 2(f), the flower-like structure have a diameter of ~2–3 μm. CTAB facilitated the formation of the microflowers. In order to clearly show the effect of CTAB on the morphology of the Cu nanoparticles, the experiments were carried out with different amounts of CTAB while the other experimental conditions remained constant. As shown in Fig. 2(e), the Cu pompons were obtained when the amount of CTAB was 0.015 mmol. Further, when the amount of CTAB was increased to 0.075 mmol, many Cu microflowers were obtained, as shown in Fig. 2(f). The results indicate that the morphology of final products could be controlled by varying the amounts of CTAB. Moreover, when the amount of three types of surfactants was increased, the morphologies of the corresponding products became like regular crystals without any change.

The above experimental results show that Cu nanohexagons, nanospindles, and microflowers can be selectively synthesized by utilizing different surfactants. The Cu nanohexagons, nanospindles, and microflowers are intrinsically higher in energy than the thermodynamically favored shapes, and their formation is favored only during a slow reduction process. It is well known that CuI has a low solubility in aqueous solutions; therefore, it could not be completely dissolved under the current conditions. The free cuprous (Cu^+) ions were maintained at a low level in the solution, and the Cu atoms were formed by a slow reduction process.

Fig. 3 shows the UV–vis spectra of as-synthesized Cu nanoparticles. Fig. 3(a) and (b) shows the absorption maxima of the Cu nanohexagons and nanospindles at a wavelength of 608 and 598 nm, respectively. For the Cu microflowers, the absorption maximum shows a slight red shift to 645 nm (Fig. 3c). Although the reason of this red shift is not understood, the results indicate that the as-synthesized Cu nanostructures exhibited morphology-dependent optical property.

The catalytic activities of various fabricated Cu nano/microstructure materials were examined in the click reaction of phenylacetylene (1a) and benzyl azide (2a) in toluene at 65 °C for 2 h in the absence of any supports and bases (Table 1). The click reactions using Cu nanohexagons and nanospindles as the catalysts afforded the corresponding triazole 3a in moderate yields (38–42%, entries 2 and 3). Surprisingly, the use of Cu microflowers afforded 3a in a very high yield (92%, entry 4).

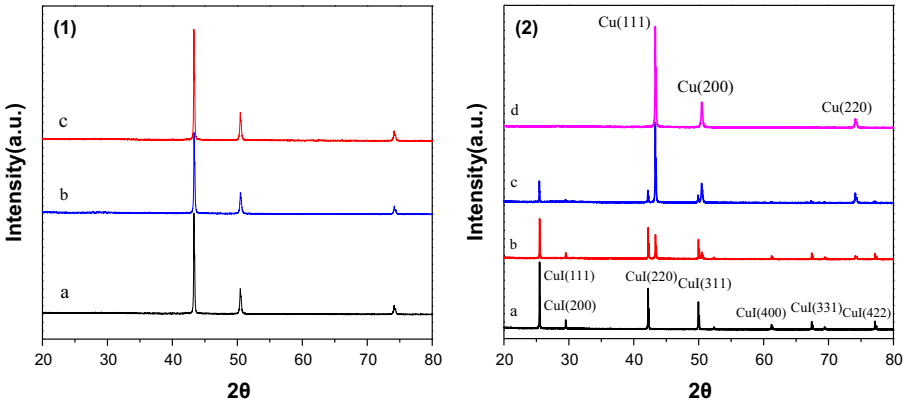

Fig. 1. (1) XRD patterns of Cu nanohexagons, nanospindles, and microflowers, (2) XRD patterns of Cu nanoparticles at various stages of growth: (a) 2 h; (b) 6 h; (c) 12 h; (d) 18 h.