



Size-controllable synthesis of hierarchical copper carbodiimide microcrystals and their pronounced photoelectric response under visible light



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ABSTRACT

Similar to cupric oxides and sulfides, the nitrogen-containing analogue copper carbodiimide (CuNCN) is considered as a potentially promising photoelectric material. However, there is lack of fundamental investigations on controllable synthesis and photoelectric properties of CuNCN nano/microcrystals. Herein, a facile method was developed to synthesize high-quality CuNCN semiconductor microcrystals with different sizes and hierarchical nanostructures at room temperature. This reaction was carried out in aqueous solutions, avoiding the involvement of non-aqueous solutions and high temperature solid phase reaction during the synthesis of CuNCN microcrystals. Photoelectric response of as-prepared CuNCN microcrystals was first observed under the irradiation of visible light at room temperature. The aqueous synthetic route can also provide an inspiration to acquire other metal carbodiimides nano/microcrystals.

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1. Introduction

Metal carbodiimides/cyanamides are a type of unique compounds, which have attracted great interest of researchers for a few decades. They are potentially functional materials deriving from the two negative charges of carbodiimide/cyanamide anion and the large electron negativity of the terminal nitrogen atoms [1–6]. The $[\text{NCN}]^{2-}$ anions in these compounds possesses two forms, namely the symmetrical carbodiimide $[\text{N}=\text{C}=\text{N}]^{2-}$ form and the lower symmetrical cyanamide $[\text{N}-\text{C}\equiv\text{N}]^{2-}$ form [5–8]. Unlike high localized $\text{O } 2p^6$ states in metal oxides, the electronic states of the $[\text{NCN}]^{2-}$ group are delocalized at valence band maximum and conduction band minimum. The electronic states act as a bridge to form the electron interaction between the central metal cation and the chelated $[\text{NCN}]^{2-}$ anion, which results in nontrivial physical or chemical properties just like the typical semiconductors of pnictides or chalcogenides [9–11]. Therefore, substituting O^{2-} or S^{2-} ion in metal oxides or sulfides semiconductor with $[\text{NCN}]^{2-}$ anion may induce new type of semiconductor materials [10–13].

Copper carbodiimide (CuNCN) is a nitrogen-containing analogue of cupric oxide and sulfide [9]. Excellent photoelectric properties are anticipated by substituting O^{2-} or S^{2-} ion in copper oxides or sulfides (e.g., Cu_2O , CuO , and Cu_2S) with $[\text{NCN}]^{2-}$ anion. Moreover, the carrier concentration in CuNCN is controllable because it is stoichiometric, which is important for photoelectric materials. The crystal structure of CuNCN is shown in Fig. 1. Each Cu atom in the NCN^{2-} unit is coordinated with six N atoms and forms linear Cu–Cu chains with alternative Cu–Cu distances of 2.992 Å and 3.432 Å. The loosely packed structure and unique N–C–N species are expected to be an excellent photoelectric material. However, there is no study on the photoelectric properties of these metal carbodiimides yet.

In recent years, a large number of metal carbodiimides/cyanamides have been synthesized *via* different synthetic routes [14–18]. However, the synthetic procedures on metal carbodiimides/cyanamides are generally based on complicated non-aqueous methods with heating or high temperature solid state reaction [16–22]. The synthesis of these compounds *via* aqueous methods at room temperature was rarely reported [23,24]. Moreover, the major attention on these compounds is primarily focused on their crystal structures and electronic properties in these works [25–32]. Therefore, morphology and size-controllable synthesis of

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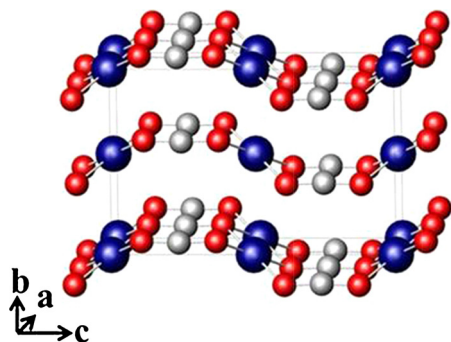


Fig. 1. Crystal structure of CuNCN with Cu in blue, N in red and C in grey. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

nano/micrometer scale metal carbodiimides *via* aqueous solution method at room temperature is still a challenge. The studies on metal carbodiimides, especially for those of nano/microstructured metal carbodiimides are seldom reported in the past years.

In this paper, a controllable aqueous method was presented to synthesize two types of CuNCN microcrystals (MCs) at room temperature. The size and nanostructure can be tuned *via* controlling the ratio of $[\text{NH}_3]/[\text{Cu}^+]$. At low ratio of $[\text{NH}_3]/[\text{Cu}^+]$, leaf-like nuclei are assembled to form small MCs with coarse surface. While, irregular monocrystalline CuNCN nanosheets are formed and assembled into large MCs with smooth surface because the nucleation of CuNCN MCs is seriously suppressed to grow up at high $[\text{NH}_3]/[\text{Cu}^+]$ ratio. The photoelectric response of these as-prepared CuNCN was observed for the first time under the irradiation of visible light at room temperature. The synthetic route can also be applied to acquire other metal carbodiimides MC/NCs with controllable morphology and sizes.

2. Experimental

2.1. Synthesis of CuNCN MCs

In a typical synthesis of small CuNCN MCs, 0.5 mmol of CuCl, 1 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ ($[\text{Cu}^+]/[\text{NH}_3] = 1:32$) and 10 mL of deionized water were in turn added into a 20 mL vial under stirring to form a blue solution. Then 1 mmol (0.1 M) of H_2NCN solution was added into the vial under stirring for 5 min. Finally, a black product was obtained. The products were taken out, and centrifuged to collect at 10,000 rpm for 3 min.

In a typical synthesis of large CuNCN MCs, 0.5 mmol of CuCl, 5 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ ($[\text{Cu}^+]/[\text{NH}_3] = 1:160$) and 5 mL of deionized water were in turn added into a 20 mL vial under stirring to form a blue solution. Then 1 mmol (0.1 M) of H_2NCN solution was added into the vial under stirring for 5 min. Finally, a black product was obtained. The products were taken out, and centrifuged to collect at 8000 rpm for 3 min.

2.2. Characterization

Field emission scanning electron microscopy (FESEM) images were acquired using FEI Sirion 200 with an energy dispersive X-ray (EDS) analysis. Low and high resolution transmission electron microscopy (TEM) images and selected area electron diffraction (SAED) were taken on JEOL JEM-2100F at an accelerating voltage of 200 kV. TEM samples were prepared by dip-casting CuNCN MCs dispersed in ethanol onto carbon-coated copper TEM grids. X-ray diffraction (XRD) patterns were collected on a Bruker D8 Focus X-ray diffractometer equipped with a monochromatized source of CuK α radiation ($\lambda = 0.15406$ nm) at 1.6 kW (40 kV, 40 mA). The

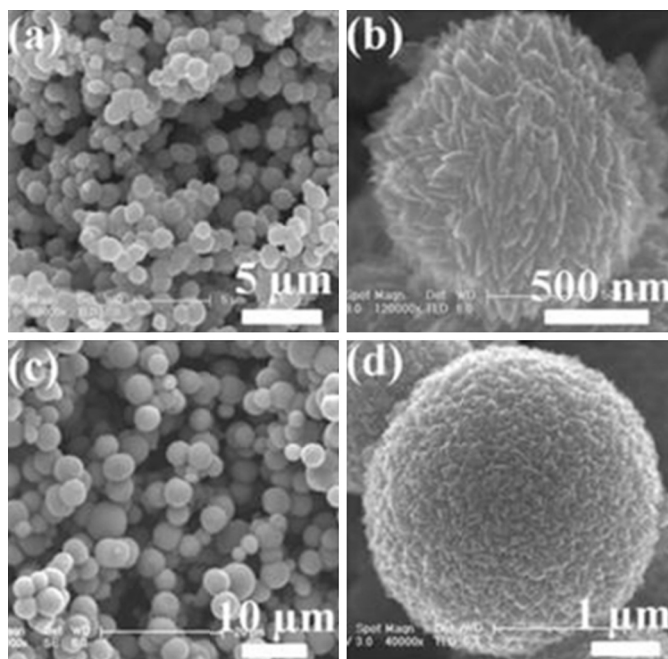


Fig. 2. (a and c) FESEM images of small and large CuNCN MCs with the average diameters of $1.33 \pm 0.15 \mu\text{m}$ and $4.12 \pm 0.64 \mu\text{m}$ respectively. (b and d) The morphology of an individual small and large CuNCN MC respectively.

pattern was recorded in a slow-scanning mode with 2θ from 10° to 65° with a scan-rate of $2^\circ/\text{min}$. UV-vis-NIR absorbance spectrum was recorded on a Hitachi U-4100 spectrophotometer with a scanning velocity of 240 nm/min. X-ray photoelectron spectroscopy (XPS) data were obtained using ESCALAB250 X-ray Photoelectron Spectroscopy for surface analysis. Raman spectroscopy was performed on a RenishawinVia Raman microscope using green laser ($\lambda = 532$ nm) excitation. Fourier transform infrared spectroscopy (FTIR) measurements were carried out in a Shimadzu FTIR Prestige-21. Current–voltage characteristics were measured under a visible light with a 300 W xenon lamp (filter: $\lambda = 420$ nm). Magnetic properties were studied using a Quantum Design physical properties measurement system (PPMS). DC susceptibility was measured under field-cooling (FC) conditions in a 1×10^4 Oe magnetic field from 10 to 290 K.

3. Results and discussion

Two types of CuNCN products with different sizes and nanostructures were obtained controllably *via* controlling the ratio of $[\text{NH}_3]/[\text{Cu}^+]$ at room temperature. The morphology of two types of CuNCN MCs were characterized by TEM and FESEM images. As shown in Fig. 2(a), S1(a) and S2, monodisperse CuNCN MCs have uniform size with an average diameter of $1.33 \pm 0.15 \mu\text{m}$ at low ratio of $[\text{NH}_3]/[\text{Cu}^+]$ (32:1). Moreover, the MCs have particular secondary nanostructure as shown in FESEM images of an individual CuNCN MC inner (Fig. 2(b) and S1(b)). There were numerous leaf-like CuNCN NCs with an average size of 164×52 nm, which were assembled to form one CuNCN MC. However, large MCs with different nanostructures were obtained *via* similar synthetic method at high ratio of $[\text{NH}_3]/[\text{Cu}^+]$ (160:1) (Fig. 2(c) and S3(a)). The large MCs were made of a lot of irregular nanoflakes, which form a smooth surface as shown in Fig. 2(d) and S3(b). The average diameter of the CuNCN MCs is $4.12 \pm 0.64 \mu\text{m}$, which is larger than that of MCs assembled by leaf-like nanostructure. Therefore, the ratio of $[\text{NH}_3]/[\text{Cu}^+]$ plays an important role in the CuNCN MCs' formation process.

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