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.

Keywords: Metal carbodiimides; CuNCN; Microcrystal; Hierarchical nanostructures

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 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 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 minutes. Finally, a black product was obtained. The products were taken out, and centrifuged to collect at 10000 rpm for 3 minutes.

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 minutes. Finally, a black product was obtained. The products were taken out, and centrifuged to collect at 8000 rpm for 3 minutes.

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 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 ESCA-lab250 X-ray Photoelectron Spectroscopy for surface analysis. Raman spectroscopy was performed on a Renishaw inVia 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 $164 \text{ nm} \times 52 \text{ nm}$, 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.

The formation process of the two types of CuNCN MCs with different nanostructures is illustrated in Fig. 3. Firstly, a transparent blue copper ammonia precursor solution was obtained via solving CuCl into different amounts of ammonia water. An intermediate product, $\text{Cu}_4(\text{NCN})_2\text{NH}_3$, precipitated after H_2NCN solution was rapidly injected into the precursor at room temperature [23,24]. Finally, a deep black precipitation (CuNCN) formed due to the oxidation of $\text{Cu}_4(\text{NCN})_2\text{NH}_3$ in the air.

The morphology of CuNCN products was controlled *via* changing $[\text{NH}_3]/[\text{Cu}^+]$ ratio in the precursor solution. The leaf-like CuNCN

monocrystalline nuclei were formed rapidly at low $[\text{NH}_3]/[\text{Cu}^+]$ (32:1) ratio. Then the CuNCN nuclei grew and assembled into small spherical CuNCN MCs with an average diameter of $1.33 \pm 0.15 \mu\text{m}$ as shown in Fig. 2(a). However, at high $[\text{NH}_3]/[\text{Cu}^+]$ (160:1) ratio, the CuNCN nuclei were depressed to grow along a preferable crystal direction, forming irregular flake-like CuNCN nuclei because of the inhibition of more masking agents in the reaction. Finally, the flake-like CuNCN nuclei were assembled into large MCs with a different hierarchical nanostructure.

In the synthetic process, CuCl was difficult to dissolve completely when the ratio of $[\text{NH}_3]/[\text{Cu}^+]$ is lower than 32:1. However, the reaction was very slow when the ratio of $[\text{NH}_3]/[\text{Cu}^+]$ is higher than 160:1 because of the inhibition of more masking agent. In this process, the production of CuNCN MCs reduced gradually. In addition, CuNCN MCs can be synthesized via substituting CuCl with CuCl_2 as copper precursor. It is obvious that morphology of the product is different when CuCl was used as the precursor because the different cohesive abilities between CuCl and CuCl_2 with $\text{NH}_3 \cdot \text{H}_2\text{O}$. The CuNCN MCs is irregular, especially for higher ratio of $[\text{NH}_3]/[\text{Cu}^{2+}]$ (160:1) as shown in Fig. S4. Moreover, a lot of flake-like CuNCN MCs formed in the wall of vial at high $[\text{NH}_3]/[\text{Cu}^{2+}]$ (160:1) ratio (Fig. S5).

To further investigate the formation process of CuNCN MCs with different hierarchical nanostructures, TEM images of CuNCN MCs with leaf-like secondary nanostructure were obtained as shown in Fig. 4(a) and 4(b). The diameter of the individual CuNCN MC is $1.23 \mu\text{m}$, which is consisted with the average diameter calculated from FESEM image. One MC consists of a lot of leaf-like NCs, which can be obviously observed in the edge of the MC. However, there is indistinct in the middle of the MC because of larger thickness of the MC. The SEAD of the leaf-like part in the MC indicates that it is single-crystalline (Fig. 4(d)). The leaf-like single crystal nucleates along (120) crystalline plane as shown in Fig. 4(c). All of the results from TEM images further prove the formation mechanism as mentioned in Fig. 3.

The crystal structures of two CuNCN MCs were confirmed by XRD patterns. The typical XRD patterns of the two CuNCN MCs can be indexed with the calculated diffraction pattern of CuNCN (ICSD#161461) as shown in Fig. S6 [22]. Diffraction peaks of large size CuNCN MCs at 2θ degrees of 18.7° , 28.6° , 30.2° , 33.2° , 34.5° , 38.4° , 48.3° , 51.4° , 53.7° , 57.5° and 62.2° correspond to (110), (120), (-110), (211), (-111), (103), (030), (0-31), (-122), (2-13) and (-2-32) planes of CuNCN MCs respectively (Fig. 5(a)). Diffraction peaks of small CuNCN MCs are similar to those of large MCs except for the disappearance of diffraction peaks at 2θ degrees of 27.0° , 44.6° and 52.8° corresponding to (-111), (103) and (-122) planes due to their worse crystallinity comparing to large MCs. In addition, the diffraction peaks of small MCs display a little right shift and wider full width at half maximum compared with that of large CuNCN MCs because of their smaller size of crystalline grains and worse crystallinity.

The UV-vis-NIR absorbance spectroscopy of CuNCN MCs is shown in Fig. 5(b). The result indicates the absorption of CuNCN MCs range from ultraviolet to near-infrared region of 1200 nm. CuNCN MCs present a deep black color as indicated in Fig. 3. It is estimated that the band gap of CuNCN MCs is ~ 0.92 eV by plotting $(\alpha h\nu)^2$ (the square of the absorption coefficient (α) multiplied by the photon energy ($h\nu$)) versus $h\nu$ as shown in Fig. 5(b). The band gap locates in the range of optimal band (0.8-1.8 eV) for photovoltaic materials, which expands the family of Cu compounds (cupric oxides and sulfides) for solar applications. However, copper oxides mainly refer to Cu_2O and CuO , with the band gaps of 2.0-2.2 eV and 1.2-1.9 eV, respectively. The carrier concentration of Cu_xS ($x=0.5-2$) are different, depending on their composition. However, CuNCN is stoichiometric, which makes it with the steady carrier concentration. This is good for its further applications in the photoelectric devices.

Raman spectrum of CuNCN MCs was performed to confirm molecular structure of the materials. The raman peak of CuNCN MCs locates in 1091

cm^{-1} , which is corresponding to the typical molecular vibration of CuNCN. However, the peak intensity is low and the full width at half maximum is wide due to the worse crystallinity of MCs compared to the bulk materials. In addition, FTIR spectra of MCs shows strong absorption peak located at 2028 cm^{-1} , which ascribes to the asymmetric stretching vibration of NCN group ($\nu_{\text{as(NCN)}}$) (Fig. 5(d)). This value is consistent with the reported result (2010 cm^{-1}) in the references [11,22]. NCN deformation vibration ($\delta_{\text{(NCN)}}$: 688 cm^{-1} and $2\delta_{\text{(NCN)}}$: 1176 cm^{-1}) are weaker, which was also found in the references as depicted in Fig. 5(d). Magnetic properties were measured under field-cooling condition in a 1×10^4 Oe magnetic field from 10 to 290 K. The temperature dependence of the magnetic susceptibility indicates that the material is paramagnetic as shown in Fig. S7, in agreement with the reported results [33,34].

To confirm the compositions and chemical states of elements in CuNCN samples, XPS test was performed as shown in Fig. 6(a, b, c and d), corresponding to XPS survey of all elements, Cu 2p, C 1s, and N 1s, respectively. There are two narrow and symmetric peaks at the binding energy of 933.1 eV and 953.2 eV in Fig. 6(b), corresponding to Cu $2p_{3/2}$ and Cu $2p_{1/2}$ with a peak splitting of 20.1 eV. There are several satellite peaks at the 943.0 eV, 944.6 eV, 956.2 eV and 963.2 eV corresponding to Cu (II), which indicates the Cu (I) in the reactant of CuCl transform to Cu (II) in the reaction. In addition, the peaks at the 934.5 eV and 937 eV might arise from a little CuCl_2 due to the oxidized Cu (I) in the process of the reaction. There is a pronounced peak of C 1s at binding energy of 285.0 eV resulting from carbon in the environment (Fig. 6(c)). The other two weaker peak at 285.3 eV and 286.4 eV arising from C-O and C=N bonds respectively [35-37]. Fig. 6(d) is the XPS of N 1s located at the bonding energy of 397.9 eV and 400.3 eV, corresponding to N-O and N=C bonds stemming from environment [37-39]. The peak at 398.9 eV belongs to remained NH_3 at the surface of CuNCN. All these confirm that the products are composed of CuNCN.

Photoelectric properties were performed under the irradiation of visible light at room temperature (Fig. 7). The CuNCN MCs with small sizes were pressed into ~ 1 mm thick film, on which silver paste was dropped to form a sandwich structure (inset in Fig. 7). Current-voltage (I-V) curve of CuNCN MCs film reveals pronounced photoelectric response comparing to the non-irradiated curve. The photocurrent density increased more than 8 times of dark current density from $1.39 \mu\text{A}/\text{cm}^2$ to $11.6 \mu\text{A}/\text{cm}^2$ at bias voltage of 1 V, which indicates that CuNCN MCs own good photoelectric properties originating from intense absorption for visible light region as shown in the UV-vis absorbance spectroscopy of CuNCN MCs (Fig. 5b). In addition, photoelectric properties of CuNCN MCs with large sizes were also measured. The measured results indicate that the photoelectric properties of CuNCN MCs don't obviously depend on the size of MCs.

4. Conclusions

In summary, a controllably synthetic method was presented to fabricate two types of CuNCN MCs with different sizes and hierarchical nanostructures at room temperature. The stoichiometric CuNCN MCs have a band gap of ~ 0.92 eV, which is similar with the bandgap of copper oxide and sulfide. The result indicates that CuNCN might be potential as a good photoelectric material. The synthetic route can be exploited to acquire size- and morphology-controllable metal carbodiimides NC/MCs.

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Figure captions

Fig. 1. Crystal structure of CuNCN with Cu in blue, N in red and C in grey.

Fig. 2. (a,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,d) The morphology of an individual small and large CuNCN MC respectively.

Fig. 3. Schematic illustration of two CuNCN MCs' formation process.

Fig. 4. (a) TEM image of a small CuNCN MC. (b) The morphology of the CuNCN MC's edge. (c) HRTEM image of the leaf-like nucleus in the CuNCN MC. (d) SAED of the leaf-like nucleus in the CuNCN MC.

Fig. 5. (a) XRD of the two CuNCN MCs. Curves a and b correspond to XRD of small and large CuNCN MCs respectively. (b) UV-vis absorbance spectroscopy of CuNCN MCs, the inset is plotting $(\alpha h\nu)^2$ (the square of the absorption coefficient (α) multiplied by the photon energy ($h\nu$)) versus $h\nu$. (c) Raman spectrum of CuNCN MCs. (d) FTIR of CuNCN MCs.

Fig. 6. (a) Overview XPS of the several elements in CuNCN MCs. (b,c,d) Cu 2p, C 1s and N 1s of the three elements in CuNCN MCs.

Fig. 7. Photoelectric responses of CuNCN MCs: J-V curves in the dark (black) and under visible light (red) illumination at room temperature. The inset is the measurement setup schematically.

Fig.1

Fig.2

Fig.3

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Fig.6

Fig.7

Graphic Abstract