Applied Surface Science 453 (2018) 173–181

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Cuprous oxide nanostructures tuned by histidine-containing peptides and their photocatalytic activities

Chengdong Wang [a,b], Liyan Zhang [a], Jingge Yang [a], Dong Wang [a], Yawei Sun [a], Jiqian Wang [a,*]

[a] State Key Laboratory of Heavy Oil Processing, Centre for Bioengineering and Biotechnology, China University of Petroleum (East China), 66 Changjiang West Road, Qingdao 266580, China
[b] Qingdao Industrial Energy Storage Research Institute, Qingdao Institute of Bioenergy and Bioprocess Technology, Chinese Academy of Sciences, Qingdao 266101, China

ARTICLE INFO

Article history:
Received 24 October 2017
Revised 22 April 2018
Accepted 27 April 2018

Keywords:
Cuprous oxide
Peptides
Photocatalytic activities

ABSTRACT

Peptides have been used as modifiers and templates in the fabrication of a variety of inorganic nanostructures including noble metals, silica oxide, and metal oxides. In this work, three peptides, including HGGGHGHGGGHG (HG12), HGGGHG (HG6) and RHTDGLRRIAAR (CN225), were used to tune the morphologies of cuprous oxide (Cu_2O) nanoparticles. Unlike the morphologies of modified octahedron with polyvinylpyrrolidone (PVP) and truncated cube with cetyltrimethyl ammonium bromide (CTAB), the Cu_2O nanoparticles regulated by peptides showed completely different shapes and size. In the presence of HG12, the nanoparticles still showed octahedral morphology with the edge length of 84 nm, but there were distinct defects on the (1 1 1) facets. The Cu_2O nanoparticles were sphere-like with the diameter of ~86 nm under the regulation of HG6. In the presence of CN225, the Cu_2O sample was spherical aggregates of smaller nanoparticles, and the diameter of the aggregates was about 128 nm. The interactions between Cu^{2+} and peptides have been investigated through UV–Vis spectrometer, circular dichroism spectrometer (CD) and isothermal titration calorimetry (ITC). The different coordinating structures of peptide molecules to Cu^{2+} ions dominated the nucleation and succedent crystal growth. The cuprous oxide synthesized with CN225 showed the best photocatalytic activity among the synthesized Cu_2O particles, and about 67% methyl orange could be removed within 2 h under UV–Vis irradiation. The high photocatalytic activity of Cu_2O-CN225 was attributed to the relatively small size and the (1 1 1) crystal planes on the primary particles.

1. Introduction

Cuprous oxide (Cu_2O) is a promising material in the fields of solar energy utilization [1–5], water splitting [6–10], gas sensors [11,12], non-enzyme glucose sensor [13,14], Li-ion battery [15,16], photocatalysis [17–19], and organic catalysis [20–24]. In the past decade, many researches have been focused on the shape and size-control of Cu_2O. The cubic, spherical, and octahedral Cu_2O nanopartcicles have been synthesized through the surfactant-assisted or solvothermal route. Cu_2O nanoparticles could be synthesized at relative low temperature with surfactant assistance. For example, monodispersed cubic Cu_2O were synthesized in the presence of cetyltrimethylammonium at 55 °C [25]. Cu_2O with different morphologies [26–29] and heterostructures with noble metal and mesoporous carbon have been prepared through wet chemical methods [30,31]. It has been proved that the photocatalytic activity of Cu_2O nanoparticles is not only related with their morphologies and particle size but also their exposed crystal facets [28].

The biomimetic synthesis of inorganic materials has attracted much interest in the past few decades. The inorganic oxides such as SiO_2 and iron oxide were prepared under the regulation of peptides or proteins in vitro or in vivo [32–35]. Many biomolecules can induce the formation of unique nanostructures at relatively mild condition. Complexes of copper ion and proteins or peptides have been reported by several research groups [36–40]. The copper-coordinating peptide HG12 has been used to prepare Cu nanocrystals [41] and semiconductors Cu_2S with controllable size through reduction route in aqueous solution [42]. The peptides or proteins utilized to synthesize copper-based nanoparticles are usually histidine-rich molecules. For example, the peptide AHHAHHAAD originated from a histidine-rich protein II of Plasmodium falciparum [43] and protein apoferritin [44] are used in copper nanoparticle preparation. The copper nanotubes have also been synthesized with bioengineered histidine loop flagella scaffolds

* Corresponding author.
E-mail address: jqwang@upc.edu.cn (J. Wang).

https://doi.org/10.1016/j.apsusc.2018.04.240
0169-4332/

[45]. The copper(II)-peptide complexes may play an important role during nucleation of copper nanoparticles and then the nanoparticle growth continually [43,45]. Moreover, Cu_2O nanoparticles could also be synthesized through an electrodeposition method in the presence of proteins [46] or peptides [47].

Other copper containing nanostructures have also been fabricated through Cu^{2+} ion and protein complexes. As apoferritin provides special cavities in which copper ions are captured and reduced, Cu and CuFe Prussian Blue nanoparticles have been prepared in the presence of apoferritin [44]. The copper-protein quantum clusters with 5 or 13 copper atoms per protein molecule have been synthesized with bovine serum albumin (BSA) protein, and the luminescence of this kind of complex is high sensitive to very low Pb^{2+} or H_2O_2 concentration [48]. Although the Cu^{2+}/peptide and Cu^{2+}/protein complexes have already been used to synthesize nanoparticles, the regulation of Cu_2O nanoparticle morphologies and structures by peptide is seldom reported and the related mechanism is still unclear by so far.

Herein we synthesized the cuprous oxide nanostructures at room temperature with three histidine-containing peptides, HG12, HG6 and CN225. The shapes and photocatalytic activities of Cu_2O nanoparticles were compared with those synthesized with PVP and CTAB. We also tried to elucidate the role of peptides in crystal growth through UV–Vis, circular dichroism and ITC measurement. Besides the effects of Cu^{2+}/peptide complexes in nucleation stage, these peptides also performed as capping reagents or modifiers in Cu_2O crystal growth stage just like PVP and CTAB. Due to the interaction between Cu^{2+} and amide and imidazolyl groups on peptides, the peptide molecules induced the Cu_2O crystals to grow along the ⟨1 1 1⟩ orientation. The polycrystalline Cu_2O-CN225 nanoparticles showed the best photocatalytic activities in methyl orange degradation.

2. Experimental section

2.1. Materials

Polyvinylpyrrolidone (PVP, product code K-30, MW = 58,000) and cupric sulfate pentahydrate were purchased from Alfa Aesar. Ascorbic acid and cetyltrimethyl ammonium bromide (CTAB) were purchased from Sinopharm Chemical Reagent Co. Ltd. All these chemicals were used as received without further purification. Peptides HG12 and CN225 were purchased from ChinaPeptides Co., Ltd. And the peptide HG6 was synthesized on a Liberty peptide synthesizer (CEM) through a standard solid-phase synthesis method as described in our previous paper [49]. The purity of these peptides was above 98% according to the HPLC results (Fig. S1).

2.2. Synthesis of Cu_2O nanoparticles

In the typical Cu_2O synthesis procedure, HG12 (0.0059 g) and $CuSO_4$ (0.016 g) were dissolved in 10 ml deionized water. Then 1 ml of 2 M NaOH solution was slowly added into the reaction vial. 1 ml of 0.6 M ascorbic acid solution was dropped into reaction mixture after 30 min. The mixture was kept in a water bath of 25 °C for another 3 h. The reaction solution was stirred vigorously during all the above procedures. After aging for 3 h, the solution was centrifuged at 8000 rpm for 10 min to collect the nanoparticles. The precipitates were washed three times with water and alcohol sequentially. And then the orange precipitates were dried at 60 °C in a vacuum oven for 5 h. The cuprous oxide was redispersed into ethanol for further analysis. The procedures of Cu_2O synthesis in presence of other peptides was the same as that in presence of HG12.

2.3. Characterization of Cu_2O nanoparticles

A volume of 20 μL Cu_2O nanoparticle ethanol suspension was dropped onto a copper grid with Formvar/carbon support film and then the extra solution was blotted with filter-paper. The samples were observed with a JEOL JEM-2100 UHR transmission electron microscope (TEM) operated at the acceleration voltage of 200 kV. Scanning electron microscopy (SEM) of the Cu_2O nanostructures was characterized on a Hitachi S-4800 SEM operated at 5 kV. The X-ray diffraction (XRD) analysis was carried out on a PANalytical X'Pert Pro MPD diffractometer (Netherlands) using operated voltage 40 kV and current 40 mA with Cu Kα (λ = 1.5406 Å) at a scan rate (2θ) of 5°/min. The FTIR spectra were collected using a Nicolet 6700 spectrometer with a DTGS detector. UV–Vis absorption spectra were obtained using a Shimadzu UV-2450 spectrophotometer.

2.4. Visible circular dichroism spectroscopy

The peptide solutions with Cu^{2+} were characterized using a Bio-Logic MOS-450 spectrometer. The visible circular dichroism was carried out using a 1 cm path length cell. The data were recorded between 250 and 800 nm. The spectra were expressed in Δε (M^{-1} cm^{-1}).

2.5. Isothermal titration calorimetry

ITC measurements were carried out on a MicroCal ITC200 calorimeter (Malvern, UK) at 25 °C. The ligand and receptor solutions were prepared with 20 mM tri(hydroxymethyl)aminome thane (Tris) at pH 8.0. All solutions were centrifuged at 9000 rpm before using. 19 injections of 1.5 μL of 2.5 mM cupric sulfate solution were titrated into reaction cell containing receptor (peptide) solution with a spacing of 150 s between two injections. The mixtures were stirred at 400 rpm. The control titrations were carried out by injecting copper solution into buffer without peptide molecules. The ITC data were fitted by Origin 7.0 software supplied by Microcal using the one-site model.

2.6. Photocatalytic activity of Cu_2O nanoparticles

Cu_2O nanoparticles were dispersed into methyl orange solution (40 mg/L) at the concentration of 0.05 g/L. The reaction solution was kept in dark for 5 h in order to make the organic molecules to adsorb onto the crystal surface. The photocatalytic reaction was carried out under Xe light irradiation with constant stirring. The luminous power of Xe light was 50 W and the visible output was 4500 Lumens. The distance between reaction cell and light source was 25 cm. The light intensity reaching the reaction cell was measured with a power meter to be 500 mW/cm^2. The aliquots were sampled every 10 min and centrifuged at 8000 rpm for 5 min. And then the supernatant was examined via UV–Vis spectroscopy to determine the methyl orange concentration. The total irradiation time was up to 120 min. The reusability of the photo catalyst was studied with the most active Cu_2O-CN225. The Cu_2O particles were separated through centrifugation at the rate of 10,000 rpm after 2 h reaction, and fresh methyl orange solution was added and a new cycle was started.

3. Results and discussion

The molecular structures of the additive reagents are shown in Scheme 1. It has been reported that the additives in crystal growth solution can affect the relative stabilities of different crystal planes for pre-grown crystals and result in different morphologies [50].