SYNTHESIS OF NOVEL HIGHLY POROUS CuS GOLF BALLS BY HYDROTHERMAL METHOD AND THEIR APPLICATION IN AMMONIA GAS SENSING

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ABSTRACT

A novel kind of porous CuS golf balls with an average diameter of 2 μm have been successfully synthesized by using CuCl powders as source PVP as soft template based on a template-directed approach. This process involves the conversion of CuCl to CuS via reaction with H_2S , which is produced by hydrolyzing thiourea. The transformation of oxidation state of Cu^+ to Cu^{2+} can proceed smoothly due to the larger lattice energy of CuS in comparison with that of CuCl. The as-prepared samples have been characterized by X-ray diffraction, scanning electron microscopy and photoluminescence analysis. NH_3 sensing properties of CuS golf balls with arrays of dimples and indentations have been investigated at room temperature with a simply adapted photoluminescence-type gas sensor. The results reveal that the porous CuS golf balls sensor exhibited excellent performances with a short respond time about 33 s and a short recovery time 44 s respectively.

Keywords: CuS golf balls; gas sensing; template-directed approach

INTRODUCTION

Recently various methods have been reported on the synthesis of chalcogenide materials due to their excellent chemical and physical properties^[1]. CuS, one of the important semiconductor transition metal chalcogenides has been extensively studied in recent years for their potential applications in numerous fields, such as in photothermal conversion, as p-type semiconductors in solar cell devices, as coatings for microwave shields in the form of thin films, as super ionic materials, optical filters, room temperature ammonia gas sensors, cathode material in lithium rechargeable batteries, and as thermoelectric cooling material^[2-6]. Many recent efforts have been devoted to the synthesis of CuS micro- and nanocrystals with various morphologies, such as hollow spheres^[6], nanotubes^[7,8], nanorods^[1,9,10], nanoplates^[11], nanodisks^[12], nanofibers^[13], and concaved cuboctahedrons^[14]. However, up to now, the morphology of CuS golf balls with thick-walled microbeads has not been reported.

Golf ball emerged in the early 1900s is unique, which has a hollow core and hierarchically organized surface topographies with arrays of dimples and indentations. The geometrical array of dimples (indentations) influences the aerodynamic flowfield^[15] by modifying the boundary layer from laminar to turbulent, delaying the separation of the boundary layer and ultimately results in a reduction in drag force^[16]. Due to a special microstructure, the prototype of golf balls attracts considerably scientific and technological interest and offers far-reaching potential for the synthesis of novel types of hollow or partly filled micro- and nanoparticles with similar dimples or holes. For example, a new templating method referred as textured isomorphic synthesis was reported to synthesize highly porous Cu/CuO golf balls in highly viscous solutions. The procedure undergoes three stages: synthesis of anodized rational alumina templates, conformal copper metallization of the alumina templates and treatment with phosphoric acid at high temperature^[15].

Many reports have considered that surfactants play an important role in shape-controlled synthesis of materials in solution. Due to the special amphiphilic structure, surfactants contain both hydrophobic and hydrophilic groups, which can not only effectively prevent the produced particles from aggregating but also direct the morphology development of the products. In this work, using PVP (polyvinylpyrrolidone) as surfactants, a special kind of porous CuS golf balls have been prepared via a facile and rapid hydrothermal route in which CuCl reacted with thiourea. This process involves CuCl powers as raw material, which is converted to CuS golf balls via reaction with H_2S . The formation of CuS and the consumption of CuCl occur at the same time. To the best of our knowledge, it is the first report on the unique morphological golf ball-like architecture of CuS. To demonstrate potential utilities of this interesting material, we have further studied the ammonia response of sensors built from the CuS golf balls. Although CuS has been studied in various forms for ammonia detection^[17,18], there has been no report yet on the use of CuS golf balls as a ammonia sensor material.

EXPERIMENTAL

Synthesis of CuS golf balls

Analytical grade solvents and reagents were purchased from Shanghai Chemistry Co. The detailed processes of synthesizing highly porous CuS golf balls were as follows: 0.099g gray-white CuCl and 0.500g PVP were dispersed in 20 mL of deionized water by ultrasonic vibration. After 10 min, 0.228g thiourea ($\text{CH}_4\text{N}_2\text{S}$) was added under vigorous magnetic stirring for about 15 min. Finally, the mixtures were put into a Teflon-lined stainless steel autoclave of 50 ml capacity. The autoclave was sealed and maintained at 150 $^\circ\text{C}$ for 10 h, then allowed to cool down to room temperature naturally. The color of powders changed from gray-white to black. All of the black powders were carefully collected, washed with distilled water and ethanol for several times, respectively, and dried in vacuum at 60 $^\circ\text{C}$ for 6 h.

Characterization

The phase of the final products were characterized by XRD, using a Japan Rigaku D/max- γB X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.54178 \text{ \AA}$), operated at 40 kV and 80 mA. Scanning electron microscopy (SEM) measurement was carried out with an emission microscope (JEOL JSM-6490LV) operating with the accelerating voltage of 20 kV. The photoluminescence (PL) measurements and sensing properties of the samples towards ammonia were performed on a Hitachi F-4500 FL spectrophotometer at room temperature.

Ammonia sensing experiments

All the gas-sensing experiments were performed at room temperature using a simply adapted photoluminescence installation (see Fig. S1 in supporting information), which included a gas flow control system, a colorimetric cuvette and a Hitachi F-4500 FL spectrophotometer. The sensors were made up by filling CuS golf ball powders in the concave (10 $\times$ 5 mm²) on a hard black substrate, which was cornerwise put in the colorimetric cuvette for PL measurements. The sensing properties of the products towards ammonia were investigated under the following conditions. The excitation wavelength and the emission wavelength is set at 320 nm and the maximum emission wavelength of the products respectively, and the working mode is time-scanning, using nitrogen as carrier gas at room temperature. Ammonia gas was obtained by bubbling N_2 through an aqueous NH_3 solution. Its concentration in gas phase (in ppm) was determined by performing acid-base neutralization titrations on solutions obtained from bubbling the gas effluent through distilled water in the absence of sensors, according to our previous report^[19].

RESULTS AND DISCUSSION

When the gray-white CuCl powders are subject to reaction with H_2S , which was produced through thiourea hydrolysis, their color turns to blue-black. The color change is an indication that the CuCl is sulfurized to form a copper sulfide species. The composition and phase purity of the products are examined by X-ray diffractometer. Fig.1 shows the XRD pattern of copper sulfide golf balls. All the diffraction peaks can be indexed to the hexagonal

CuS phase (JCPDS 06-0464). No peaks arising from impurities (such as CuCl, Cu₂S, Cu₇S₄, Cu₁₁9S₈, Cu₁₁8S₇, etc.) are observed, which shows that the CuCl powders converts completely to the hexagonal CuS products.

The scanning electron microscopy and transmission electron microscopy are used to observe the morphologies and structures of the as-prepared products. The SEM images of the CuS products at different magnifications are shown in Fig. 2a and b, which obviously indicate that the morphology of products is not very uniform. However, a novel kind of well-defined golf balls is seen mainly from the images. The golf balls exhibit a novel highly porous morphology with uniform arrays of dimples. The average diameter of golf balls is about 2 μm. The information process of CuS golf balls is belong to the template-directed synthesis approach^[15], here the soft template is PVP. The information mechanism of golf balls in the presence of PVP is to be further studied in the future.

Fig. 1. Powder X-ray diffraction pattern of as-prepared CuS golf balls.

Fig. 2. SEM images of as-prepared CuS golf balls. (a) low magnification, (b) high magnification.

In CuS, there exist both univalent and divalent copper cations and the oxidation states of sulfur are also hybrid^[20, 21]. The copper in CuCl exists in the oxidation state of +1, obviously, the conversion of CuCl to CuS must relate to a redox reaction. It has been reported that CuS nanotubes produce from CuCl nanorods and H₂S, where there is no oxidizing agents other than H₂S in the sulfurization reaction system. And it is proposed that the Cu⁺ cations in CuCl are partly oxidized to Cu²⁺ by protons of H₂S in the reaction process^[7]. Herein, proton has strong reducibility, especially at elevated temperatures. For example, protons can easily oxidize metals and low oxidation state cations even in solids^[22]. During the sulfurization reaction of CuCl, the transformation of oxidation state of Cu⁺ to Cu²⁺ can proceed smoothly due to the larger lattice energy of CuS in comparison with that of CuCl. In our work, the formation process of CuS phase is considered similar to Chen's. The difference is the formation way of H₂S, where H₂S in Chen's work is produced by reacting of H₃PO₄ with Na₂S₉H₂O, while H₂S in our work is produced by hydrolyzing thiourea. In addition, it is held that the small K_{sp} value of copper sulfide and

dissolution of CuCl by ammonia solution produced through thiourea hydrolysis allow the construction of hierarchical microstructures.

The golf balls maybe have high surface area^[15], which may favor in potential application in gas sensor because they can provide more active sites in the three-dimensional hollow structure^[23]. The new CuS golf balls we have synthesized provide opportunities for investigating their optical and gas-sensing properties. The room-temperature photoluminescence spectrum has been measured for golf balls synthesized with excitation at 320 nm. Fig. 3(a) is the emission spectra of the as-prepared copper sulfide with golf ball morphology. Although many researchers^[1, 7, 24] reported that there was no emission peak for CuS in the range of 400–800 nm, the CuS golf balls we prepared had an emission band centered at 460 nm. Our result is also different from Ref^[25], where the maximum emission wavelength is 523nm. Compared to our hierarchical CuS golf ball structures, there is an obvious red shift of the emission peak, which shows that the size and morphology may be responsible for the PL spectra of CuS. However, the origin of the observed optical properties is still far from well-understood, and more detailed investigations are needed.

Fig. 3 PL emission spectra of the products (a), room temperature time profiles of PL intensity of sensors based on CuS golf balls to NH₃ (b).

Based on their PL properties, PL-type sensors constructed of highly porous copper sulfide golf balls were fabricated in a simple adapted setup (see Fig. S in the supporting information). Here, the term “relative response amplitude” is defined by expression $-(I_{\text{NH}_3} - I_{\text{N}_2}) / I_{\text{N}_2}$, where I_{NH_3} and I_{N_2} denote the PL intensity of the samples exposed to ammonia gas and nitrogen, respectively. The response time and recovery time are defined as reaching 90% and 10% maximum response.

Fig. 3b demonstrates the time profile of PL intensity of the sensors constructed of CuS golf balls at room temperature. As shown in Fig. 3b, a sharp decrease of PL intensity for CuS golf balls sensors is observed after the introduction of 480 ppm ammonia in N₂, which is well below the fatal dose limit of 3500–7000 mg m⁻³^[26]. The PL intensity is fully reversible to its original value in a very short time after removing the detecting gas from the system by purging with pure nitrogen. Relative response amplitudes calculated from

CuS golf balls sensors is 0.12, which is larger than that of single-walled Cu₇S₄ nanobox but smaller than that of double-walled Cu₇S₄ nanobox in our previous research [27]. The response time of the sensors constructed of CuS golf balls sensors is 33 s, which is shorter than the recovery time 44 s. Very interestingly, compared to our previous research, both the response time and the recovery time of the sensors based on the CuS golf balls are shorter than not only the single-walled Cu₇S₄ nanoboxes but also the double-walled Cu₇S₄ nanoboxes, which is possibly due to the special hierarchical microstructure and the highly porous morphology.

Herein, the change in PL intensity for ammonia gas with CuS golf balls is considered to be the result of a hole trapping mechanism. As one kind of p-type semiconductors, the main carriers of CuS materials are holes. Under photoirradiation, CuS materials will be excited to generate a large amount of electron-hole pairs. Subsequently, some photoexcited electron-hole pairs will recombine and then photons with relatively low energy will be emitted which are responsible for the normally larger wavelength of emission beam than excitation beam. Due to having lone electron pairs, ammonia molecules can act as electron donors. Thus, when introduced into the sensing system, ammonia molecules will bind to the photoexcited holes as electron acceptors. Therefore, the radiative recombination process of photoexcited electron hole pairs will be blocked, which decreases the density of the luminescence centers and, thus the PL intensity becomes lower^[28-30].

The special microstructure is also believed to be responsible for the shorter response time and slightly longer recovery time. The golf ball owns uniform arrays of dimples with distinct hierarchical microstructures, which may result in some differences for the natures of the binding sites between on the outer-wall and inner-wall. It can supply more sites for ammonia molecules binding with photogenerated holes and thus the response time is shorter. Due to more binding sites, the interactions between ammonia gas molecules and these sites become slightly stronger, which may have an immense effect on the desorption kinetics. Therefore, a slightly longer time is needed for highly porous CuS golf balls to recover PL intensity.

CONCLUSION

In summary, highly porous CuS golf balls were successfully synthesized based on the template-directed approach by using PVP as soft templates. The construction of CuS golf balls with hierarchical microstructures are attributed to the smaller lattice energy of CuCl and the smaller K_{sp} value of copper sulfide. Gas sensing experiments based on a PL-type gas sensor revealed that these golf balls exhibited excellent sensing performances for ammonia gas with quick response and recovery, which is about 33 s and 44 s respectively.

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