Preparation and characterization of HgI₂ nanostructures via a new facile route

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Abstract

HgI₂ (mercuric iodide) nanostructures have been prepared through a new rapid co-precipitation way utilizing Hg(CH₃COO)₂ and LiI.2H₂O in presence of different capping agents at room temperature. By applying various types of capping agent, different morphologies of mercuric iodide were formed via a facile co-precipitation way for the first time. The results demonstrated that flower-like mercuric iodide microstructures composed of uniform spherical nanoparticles could be produced in presence of polyvinylpyrrolidone (PVP) as capping agent.

Keywords: Nanoparticles; Electron microscopy; Semiconductor; Optical properties.

1. Introduction

HgI₂ (mercuric iodide) as one of the most attractive semiconductor materials exhibits an extensive range of use in radiation detectors, hybrid solar cells and photocatalyst owing to its specific characteristics [1-5]. To date, vapor phase deposition (PVD), suspension method and laser ablation [3-4, 6] have been applied to produce mercuric iodide. Co-precipitation process is known as reliable, simple, reproducible and efficient synthetic way for control the size and shape of nano-sized materials. It has been reported that size and shape could largely effect on characteristics and utilizations of materials. Until now, several efforts have been devoted to the size and shape controlled production of materials [7-10].

Herein, we describe a new rapid co-precipitation way for synthesis of mercuric iodide nanostructures applying $\text{Hg}(\text{CH}_3\text{COO})_2$ and $\text{LiI} \cdot 2\text{H}_2\text{O}$ in presence of different capping agents at room temperature. To the best of our knowledge, it is the first time that different morphologies of mercuric iodide are produced by applying various types of capping agent via a facile co-precipitation way. The results demonstrated that flower-like mercuric iodide microstructures composed of uniform spherical nanoparticles could be produced in presence of polyvinylpyrrolidone (PVP) as capping agent.

2. Materials and methods

Sodium dodecyl sulphate (SDS), polyvinylpyrrolidone 40000 (PVP 40000), $\text{Hg}(\text{CH}_3\text{COO})_2$, poly ethylene glycol 6000 (PEG 6000), $\text{LiI} \cdot 2\text{H}_2\text{O}$, sodium salicylate and ethylenediaminetetraacetic acid disodium salt (Titriplex III) were purchased from Merck and were applied as received. HgI_2 nanostructures were prepared by a new rapid co-precipitation way. First, 1 mmol of PVP dissolved in distilled water and was added drop-wise into the $\text{Hg}(\text{CH}_3\text{COO})_2$ solution (1 mmol of $\text{Hg}(\text{CH}_3\text{COO})_2$ dissolved in distilled water) under magnetic stirring. Then, $\text{LiI} \cdot 2\text{H}_2\text{O}$ solution (2 mmol of $\text{LiI} \cdot 2\text{H}_2\text{O}$ dissolved in distilled water) was added drop-wise to the above mixture and the resultant mixed solution was stirred for 1/2 h (at room temperature). The obtained precipitate was filtered, washed with distilled water and air-dried (sample no. 6). Table 1 illustrates the synthesis conditions of HgI_2 samples. In order to investigate, the influence of capping agent on the size and shape of HgI_2 , one sample was prepared in absence of the capping agent. The as-synthesized mercuric iodide nanostructures have been characterized by applying EDS, DR-UV-vis, FESEM, XRD, and TEM.

Table 1. Reaction conditions for HgI₂ samples.

Sample no	Capping agent	Figure of XRD patterns	Figure of FESEM images
1	-	2a	1a
2	Sodium salicylate	-	1b
3	Titriplex III	-	1c
4	SDS	-	1d
5	PEG	-	1e and f
6	PVP	2b	1g and h

3. Results and discussion

To investigate the influence of the capping agent on the size and shape of mercuric iodide, five various capping agents namely sodium salicylate, titriplex III, SDS, PEG and PVP were applied. The sample no.1 synthesized in absence of the capping agent show amorphous micro/bulk structures (Fig. 1a). When sodium salicylate was applied, the high agglomerated particle-like structures of mercuric iodide were formed (Fig. 1b). By applying the titriplex III and SDS as capping agent, the nanostructures with less uniform sphere-like shape (Fig. 1c) and uniform spherical nanoparticles (Fig. 1d) were formed. SDS has the highest steric hindrance effect compared with the titriplex III and sodium salicylate. It seems that SDS with the highest steric hindrance effect can cover the initial HgI₂ nanoparticles surface, and hinder the additional aggregation of mercuric iodide nanoparticles and hence control growth of HgI₂ particles. When PEG and PVP as capping agent were applied, the microbundles (Fig. 1e and f) and flower-like microstructures (Fig. 1g and h) were formed, respectively. The FESEM images in Fig. 1e-h clearly reveal that microbundles and flower-like microstructures composed of uniform spherical HgI₂ nanoparticles. It seems that PEG and PVP as capping agent can induce the mercuric iodide nanoparticles to assemble in the specific directions, and

thus microbundles and flower-like microstructures were synthesized, respectively. So, the type of capping agent has a substantial impact on the shape and size control of HgI_2 samples.

Fig. 1. FESEM images of (a) sample no. 1, (b) sample no. 2, (c) sample no. 3, (d) sample no. 4, (e and f) sample no. 5 and (g and h) sample no. 6, and (i and j) TEM images of sample no. 6.

TEM images of the nanostructured HgI_2 sample prepared by PVP are depicted in Fig. 1i and j. As illustrated in Fig. 1i and j, spherical nanoparticles of mercuric iodide with diameter about 12–37 nm were prepared.

The XRD patterns of sample nos. 1 and 6 are depicted in Fig. 2a and b, respectively. The reflection peaks seen in these patterns can be indexed to tetragonal phase HgI₂ (JCPDS card no. 73-0455). The mean crystallite size of sample nos. 1 and 6 calculated applying the Scherrer equation [10] are 29 and 26 nm, respectively.

Fig. 2c presents EDS spectrum of HgI₂ sample prepared by PVP (sample no. 6). In this spectrum, Hg and I lines are detectable. According to XRD, FESEM and EDS results, it was found that employing PVP as capping agent leads to pure tetragonal phase flower-like HgI₂ microstructures composed of uniform spherical nanoparticles are formed via a new rapid co-precipitation way (Fig. 2d).

The DR-UV-vis spectrum of HgI₂ sample prepared by PVP (sample no. 6) reveals a band at 358 nm (Fig. 3a). The energy gap (*E_g*) as substantial parameter in the photocatalytic efficiency has been calculated utilizing DR-UV-vis data and Tauc's equation [8]. The *E_g* quantity of HgI₂ sample has been estimated through extrapolating the linear section of the plot of $(\alpha h\nu)^2$ against $h\nu$ to the energy axis (Fig. 3b). The *E_g* quantity of HgI₂ sample prepared by PVP was estimated to be 3.37 eV. The estimated energy gap quantity indicates that HgI₂ sample prepared by PVP (sample no. 6) may be employed as photocatalyst under UV light.

Fig. 2. XRD patterns of sample nos. 1 (a) and 6 (b), EDS pattern of HgI₂ sample prepared by PVP (sample no. 6) (c), and schematic diagram of preparation of nanostructured HgI₂ sample (d).

To evaluate the photocatalytic behavior of the nanostructured HgI₂ sample prepared by PVP (sample no. 6), the photocatalytic degradation of methyl orange pollutant was done under ultraviolet illumination. Fig. 3c presents the result of photocatalysis experiment. From photocatalytic calculations, the pollutant decomposition was about 98.53% after 10 min ultraviolet illumination. This result demonstrates that as-produced nanostructured HgI₂ sample is effective and proper photocatalyst under UV illumination.

Fig. 3. DR-UV-vis spectrum (a), plot to determine the band gap (b) of the as-produced nanostructured HgI₂ sample (sample no. 6) and photocatalytic methyl orange pollutant degradation (c) of the as-obtained nanostructured HgI₂ sample (sample no. 6).

4. Conclusions

In summary, HgI₂ (mercuric iodide) nanostructures were synthesized through a new rapid co-precipitation way utilizing Hg(CH₃COO)₂ and LiI.2H₂O in presence of different capping agents at room temperature. To the best of our knowledge, it is the first time that different morphologies of mercuric iodide are produced by applying various types of capping agent via a facile co-precipitation way. The results demonstrated that flower-like mercuric iodide microstructures composed of uniform spherical nanoparticles could be produced in presence of polyvinylpyrrolidone (PVP) as capping agent. The results of photocatalysis experiment demonstrate that as-produced nanostructured HgI₂ sample can be utilized as effective and proper photocatalyst under UV illumination.

Acknowledgements

Authors are grateful to the council of University of Kashan for supporting this work by Grant No (159271/125).

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