A new nanocomposite superionic system (CdHgI₄/HgI₂): synthesis, characterization and experimental investigation

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Abstract

In this paper, we report a new and convenient synthetic method based on a reaction in an aqueous system, which can produce a new nanocomposite superionic system (CdHgI₄/HgI₂) at 70 °C for 20 min. It is the first time that these nanocomposites are synthesized. In this work, we have chosen lithium iodide, cadmium and mercury acetate as starting reagents. First, an aqueous solution of cadmium acetate, surfactant and lithium iodide is obtained. Second, an aqueous solution of mercury acetate and lithium iodide is prepared. Then obtained solution is added to the first solution. The effects of the surfactant and mole ratio of Cd:Hg have been optimized to achieve the best products on morphology and purity. When the molar ratio of Cd:Hg is 1:1, in the absence of surfactant also in the presence of CTAB and Triplex, pure aggregated nanostructures are formed. The nanocomposites are characterized using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and cyclic voltammetry (CV). The electrical conductivity measurement carries out at frequencies of 100 Hz, 1000 Hz, 10 kHz and 100 kHz in the temperature range 70–140 °C. Results show that the best morphology and purity have been achieved in the absence of surfactant, in 1:1 ratio of precursors.

Keywords: CdHgI₄; Co-precipitation; Nanocomposites; Superionic system; Electrical conductivity.

1. Introduction

A growing interest has developed in recent years to study the nanocomposites [1–6]. The nanocomposites as materials containing heterogeneous phases have been very interesting from the practical and fundamental points of view [7]. These materials have been developed for the important advanced uses [8]. The nanocomposite of cadmium tetra iodomercurate (CdHgI_4) has high ionic conductivity at room temperature. The superionic conductors are used as electrolyte materials and are widely applied in the field of electrochemical energy production, for example, in fuel cells, lithium batteries [9].

The solid electrolytes composed of ionic salts and insulating, chemically inert, ultrafine particles have attracted a great deal of attention and may be regarded as a new class of solid electrolytes. The nanocomposite of CdHgI_4 as a solid electrolyte exhibits high ionic conductivity and good mechanical properties and is found to be promising materials for solid state batteries, electrodes, fuel cells, sensors, etc. [10]. This composite solid electrolyte is also termed as heterogeneously a doped material or a dispersed solid electrolyte system. In $\text{CdHgI}_4/\text{HgI}_2$ nanocomposites, HgI_2 as the dopant is intercalated into the CdHgI_4 host. The HgI_2 is a semiconductor candidate for the construction of x- and δ -ray detectors for digital medical imaging due to its high atomic number ($Z_{\text{Hg}} = 80$, $Z_{\text{I}} = 53$). Also, HgI_2 has a wide optical band-gap (2.13 eV) and high photon absorption coefficient for high-energy radiation [11–13]. In fact two crystalline forms of HgI_2 (α - and β -types) exist, the former red and the latter yellow. Different structures can lead to varying electrical and optical properties of the final material [14].

Electrical conductivity and structural correlation for M_xHgI_4 type compounds have been studied, where $\text{M} = \text{Ag}, \text{Cu}, \text{Tl}, \text{Pb}, \text{Cd}$ and $x = 1, 2$ [15–17]. Diffraction thermal analysis of compounds Ag_2HgI_4 , Cu_2HgI_4 , Tl_2HgI_4 , PbHgI_4 and CdHgI_4 have been compared. A substantial change in

conductivity and thermodynamic parameters of these compounds are observed [18]. Most studies in the M_xHgI_4 nanocomposites have been focused on AgI/CuI-doped M_xHgI_4 nanocomposites [19–25], but there is no report of those containing HgI_2 , owing to the toxicity problem of mercury. Our group has been interested in the synthesis of HgI_2 -doped $CdHgI_4$ nanocomposites, because of their high ionic conductivity at room temperature. To our knowledge, it is the first time that these nanocomposite superionic systems are synthesized and their electrical conductivity measured at various frequencies. Herein, we develop the co-precipitation method to prepare $CdHgI_4/HgI_2$ nanocomposites. In comparison to other works, our method is simple, convenient and low-cost. We are used nontoxic reactants and solvent. Water is an interminable, cheap, available solvent.

2. Experimental

2.1. Materials and experiments

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and were used as received without further purification. XRD patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu $K\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Microscopic morphology of products was visualized by a LEO 1455VP scanning electron microscope (SEM). TEM images were obtained on a Philips CM30 transmission electron microscope. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Voltammetric studies were carried out by Sama 500 potentiostat (Isfahan in Iran).

2.2. Synthesis of $CdHgI_4$ nanostructures

The $CdHgI_4$ nanostructures were prepared by the co-precipitation method. First, $Cd(CH_3COO)_2 \cdot 2H_2O$ was dissolved in distilled water to form a clear solution. Then a certain amount of surfactant (polyvinylpyrrolidone (PVP), Triplex, cetyltrimethylammonium bromide (CTAB) and sodium dodecylbenzenesulfonates (SDBS)) and then aqueous solution containing LiI_2 were added into the above

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4 solution. After stirring the solution for 5 min, an aqueous solution containing $\text{Hg}(\text{CH}_3\text{COO})_2$ and
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6 $\text{LiI}_2 \cdot 2\text{H}_2\text{O}$ was added into the above solution drop-wise under magnetic stirring at room temperature for 10
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8 min. Then the solution was heated by stirring at 70 °C for 20 min. The products were obtained by
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10 evaporation of solvent and washing precipitate with distilled water and ethanol. Table 1 lists the reaction
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12 conditions for the synthesis of $\text{CdHgI}_4/\text{HgI}_2$ nanocomposites.
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15 16 **3. Results and discussion** 17

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19 The crystal structure and composition of the as-prepared products were determined by XRD. Fig. 1
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21 shows the XRD patterns of as-prepared nanocomposites. In this figure, the peaks have been indexed with
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23 red color indicate the tetragonal phase of HgI_2 (JCPDS card No. 04–0455) and correspond to diffractions
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25 from the (002), (003), (102), (004), (112) and (114) planes. The peaks which have been indexed with blue
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27 color indicate the tetragonal phase of CdHgI_4 with JCPDS card No. 44–0159 and correspond to diffractions
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29 from the (002), (101), (102), (004), (103), (112), (104), (114), (200), (105), (006), (211), (106) and (212)
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31 planes. As shown in the figure, in the absent of surfactant and also in the presence of CTAB and Triplex,
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33 the samples are found to be the mixture of two products, tetragonal HgI_2 and CdHgI_4 (Fig. 1a, b and c).
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35 Intense and sharp diffraction peaks suggest that the obtained products are well crystallized. No remarkable
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37 diffractions of other phases can be found in these figures. When SDBS (sample no. 5) is used as surfactant,
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39 there are still the peaks of HgI_2 and CdHgI_4 , but the intensities have been decreased. Also many other
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41 peaks are observed, which failed to be identified from among the JCPDS cards. In our experimental
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43 conditions, the $\text{CdHgI}_4/\text{HgI}_2$ nanocomposites with best morphology, purity and crystallinity are obtained in
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45 the absent of surfactant. In continuation, the effect of the ratio of Cd:Hg on the purity of the products is
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47 investigated. The ratios are changed and other conditions are constant. Changing of the ratio of Cd:Hg from
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49 1:1 to 2:1 (sample no. 6), the products have the peaks corresponding to CdHgI_4 and HgI_2 and crystallinity
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of the as-prepared products is decreased, as shown in Fig. 1 e. In our experimental conditions, the ideal ratio between Cd:Hg is 1:1.

Fig. 2a–d illustrates SEM images of the products synthesized in the presence of different surfactants at 70 °C after 20 min of co-precipitation condition. Fig. 2a shows the SEM image of the product obtained in the absence of surfactant (sample no. 1). The formation of agglomerated nanoparticles is seen in this figure. When the triplex is used as surfactant (sample no. 3), agglomerated flakes are formed (Fig. 2b). The SEM images in Fig. 2c and d show formation of agglomerated structures with unregular shapes, in the presence of CTAB (sample no. 4) and SDBS (sample no. 5).

In other side, the effect of the reaction time on the morphology and type of product was investigated. With increase of reaction time from 20 min to 24 h, coalesced particles and bulk structures are formed.

Fig. 3 shows the TEM images of the CdHgI₄/HgI₂ nanocomposites prepared with 1:1 ratio of Cd:Hg in the absence of surfactant. The images show the formation of the aggregated nanoparticles with nearly spherical and hexagonal morphologies and diameters in the range 50–120 nm.

The electrochemical behavior of CdHgI₄/HgI₂ nanocomposites is investigated by CV technique at the surface of a glassy carbon electrode (GCE). A three electrode system comprising of a GCE modified CdHgI₄/HgI₂ nanocomposites, a saturated Ag/AgCl/KCl and Pt wire are used as working, reference and counter electrode, respectively. The CV experiment is performed in a 0.2 M phosphate buffer solution at a scanning rate of 100 mVs⁻¹. The pH of the buffer solution, which was applied as a supporting electrolyte in the voltammetric experiment, is adjusted by PH meter. The voltammogram of GCE/CdHgI₄/HgI₂ nanocomposites is shown with violet color in Fig. 4. As can be observed, the electrochemical property of GCE after modification by CdHgI₄/HgI₂ nanocomposites is better than the bare GCE. The increase in current response of GCE is clear evidence of the catalytic effect of GCE/CdHgI₄/HgI₂ nanocomposites.

In this paper the electrical conductivity behavior in the nanocomposites is investigated. The electrical conductivity measurement carries out at frequencies of 100 Hz, 1000 Hz, 10 kHz and 100 kHz in the temperature range 70–140 °C. Fig. 5 shows plot of electrical conductivity of sample no. 1. According to the figure, with increases at the frequency, the conductivity of the nanocomposites is increased. It can be seen that the conductivity of the sample no. 1 is high. The high conductivity is due to the formation of CdHgI₄/HgI₂ nanocomposite which is a solid fast ion conductor. The formation of product was also suggested by XRD (Fig. 1a). Fig. 5 also shows the temperature dependence of the ionic conductivity. In general, the conductivity increases with temperature and obeys the Arrhenius relation [19]. The equation can be written in a simpler form as:

$$\sigma_{\text{ionic}} T = \sigma_0 \exp (-E_a / kT) \quad (1)$$

Where σ_0 is the pre-exponential-factor of the ionic conductivity, k the Boltzmann constant, T the absolute temperature and E_a is the activation energy for the ionic conductivity. The log σT vs. $1/T$ plot shift from a lower temperature to a high temperature is responsible for the phase change of CdHgI₄ and is associated with a charge transfer process between electron levels of Hg, Cd and I [24].

4. Conclusions

In summary, CdHgI₄/ HgI₂ nanocomposites have been successfully synthesized from reaction of CdI₂ and HgI₂ as precursors, using a simple co-precipitation method. The ratio between Cd and Hg has a significant effect on the purity of obtained product. Under our reaction conditions, the optimal ratio of Cd:Hg to synthesize the CdHgI₄/HgI₂ nanocomposites is found to be 1:1. The presence or absence of the surfactant and also the Cd:Hg ratio adjustment are two important considerations in this synthesis. This method is proved to be a new, simple, efficient and quick way.

Acknowledgment

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Figure captions

Fig. 1. XRD patterns of $\text{CdHgI}_4/\text{HgI}_2$ nanocomposites prepared with 1:1 ratio of Cd:Hg in the presence of different surfactants: (a) absent of surfactant (sample no. 1) , (b) CTAB (sample no. 4) , (c) Triplex (sample no. 3) , (d) SDBS (sample no. 5) , (e) 2:1 ratio of Cd:Hg (sample no. 6).

Fig. 2. SEM images of $\text{CdHgI}_4/\text{HgI}_2$ nanocomposites prepared with 1:1 ratio of Cd:Hg in the presence of different surfactants: (a) absent of surfactant (sample no. 1) , (b) Triplex (sample no. 3) , (c) CTAB (sample no. 4) , (d) SDBS (sample no. 5).

Fig. 3. TEM images of $\text{CdHgI}_4/\text{HgI}_2$ nanocomposites prepared with 1:1 ratio of Cd:Hg in the absent of surfactant.

Fig. 4. Cyclic voltammogram of GCE and $\text{GCE}/\text{CdHgI}_4/\text{HgI}_2$ nanocomposites (sample no. 2).

Fig. 5. Plot of electrical conductivity of $\text{CdHgI}_4/\text{HgI}_2$ nanocomposite (sample no. 1) at different frequencies.

Table 1. The reaction conditions of $\text{CdHgI}_4/\text{HgI}_2$ nanocomposites synthesized in this work.

Table 1.

Sample no.	Cd source	Hg source	I source	Temperature (°C)	Time (min)	Surfactant	Cd:Hg ratio
1	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Hg}(\text{CH}_3\text{COO})_2$	$\text{LiI}_2 \cdot 2\text{H}_2\text{O}$	70	20	–	1:1
2	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Hg}(\text{CH}_3\text{COO})_2$	$\text{LiI}_2 \cdot 2\text{H}_2\text{O}$	70	20	PVP	1:1
3	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Hg}(\text{CH}_3\text{COO})_2$	$\text{LiI}_2 \cdot 2\text{H}_2\text{O}$	70	20	Triplex	1:1
4	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Hg}(\text{CH}_3\text{COO})_2$	$\text{LiI}_2 \cdot 2\text{H}_2\text{O}$	70	20	CTAB	1:1
5	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Hg}(\text{CH}_3\text{COO})_2$	$\text{LiI}_2 \cdot 2\text{H}_2\text{O}$	70	20	SDBS	1:1
6	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Hg}(\text{CH}_3\text{COO})_2$	$\text{LiI}_2 \cdot 2\text{H}_2\text{O}$	70	20	–	2:1
7	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	$\text{Hg}(\text{CH}_3\text{COO})_2$	$\text{LiI}_2 \cdot 2\text{H}_2\text{O}$	70	20	–	4:3

Fig. 1.

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