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“Ag_2HgI_4” a thermochromic compound with superionic conducting properties: Synthesis, characterization and investigation of graphene-based nanocomposites

Faezeh Soofivand [a], Masoud Salavati-Niasari [b,*]

[a] Young Researchers and Elite Club, Bandar Abbas Branch, Islamic Azad University, Bandar Abbas, Iran
[b] Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box. 87317-51167, Iran

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ABSTRACT

In this work, silver tetraiodomercurate (Ag_2HgI_4) nanoparticles as a compound with two properties: thermochromism with performance as sensor and superionic conducting with solid electrolytic application were synthesized by simple co-precipitation method. According to the results, it was found that decreasing the size to nano-scale increases transition temperature and conductivity of Ag_2HgI_4. Also, the investigation showed that frequency can be effective on conductivity so that increasing it increases the conductivity. Besides, the effect of graphene as a substrate with unique properties on conductivity, phase transition temperature and optical properties of Ag_2HgI_4 was studied. As expected, the transition temperature and energy of optical absorption of nanocomposites were lower than the pure nanoparticles that is due to high thermal conductivity of graphene. On the other sides, the conductivity of nanocomposites increased by creating the new conductance channel for moving the mobile ions. The findings confirmed that the properties of thermochromic compounds and superionic conductors can be changed by impurities, size and component.

1. Introduction

Smart materials are materials that have one or more properties that can be changed by various stimuli, such as stress, temperature, moisture, pH, electric or magnetic fields under a controlled condition. Smart materials are categorized into two main groups: the first group are compounds that answer to stimuli as colour change and the second group are the compounds that can convert the energy from one form to another.

Recently, changing the life style has increased tendency to use the fantastic materials and products with unique properties. Smart materials have received considerable attention because of various subsets and fascinating properties. These materials have different applications in various fields, so that it should be chosen by matching the desired application to the answer of these materials to a certain stimulant. However, using the smart materials has a long history but these compounds is still of interest to scientists and researchers because of their remarkable and unique properties [1–3].

Thermochromic compounds are one of the most popular smart materials that are categorized in the first group of these materials. Reversibly, the colour of these compounds change against temperature at the certain range, so they can use as sensors, warning signals and commercial applications [4–6]. Ag_2HgI_4 is a thermochromic compound that undergoes a reversible colour change from yellow (before transition temperature) to orange (after transition temperature) at $T \approx 45$–50 °C [7–10]. The colour change of Ag_2HgI_4 is due to rearrangement of ions in crystalline structure at before and after transition temperature. Ketelaar characterized the crystalline structure of this compound at before and after colour change. According to that reported, in temperature before colour change (β phase), the ionic arrangement closely resembled zincblende, so that F.C.C. (face-centered cubic) sublattice of iodide anions distorted slightly and Ag and Hg cations ordered over the tetrahedral sites that are occupied in, so mobility of mobile ions is low and conductivity decreases. In after colour change, four tetrahedral (zinc blende) sites of ideal F.C.C. sublattice formed by iodide anions are occupied by two cations of Ag, one cation of Hg and one vacancy, randomly [11]. In this state, Ag^+ ions can transform to vacancies of F.C.C. lattice of iodide, easily and increase the conductivity. So, high temperature phase of this compound is considered as superionic conductor that can be used as solid electrolyte [12]. By considering the previous reports about this compound, it was found that the various parameters can change the transition temperature of this compound such as components, size, type and amount of impurities [9,13–16]. On the other words, the defects in these systems have the significant role to determine the transition temperature, so amount or position of defects can increase or

* Corresponding author.
E-mail address: salavati@kashanu.ac.ir (M. Salavati-Niasari).

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decrease this temperature. Also, synthesis of these materials in nano-scale (increasing the defects by changing the scale), preparation of various nanocomposites (changing the defect position and the amount and type of impurities) and investigation of the effect of each of these parameters on various properties of them can be considered as a noticeable research option.

In this work, pure Ag_2HgI_4 as a thermochromic compound with superionic conducting properties in nano-scale was synthesized at the first time using HSal ligand as an effective capping agent and the effect of particle size on conductivity and transition temperature was studied. However, conductivity in nanomaterials increased because of the more defects that act as new channel for moving the mobile ions but thermal conductivity decreased by scattering the phonons in grain boundaries, so the transition temperature increased. To the best of our knowledge, it is the first time that the effect of graphene as substrate on various properties of Ag_2HgI_4 was investigated by preparation of graphene-based nanocomposites with different molar ratios of nanoparticles to substrate. According to the results, increasing the effect of graphene in nanocomposites led to decrease the transition temperature through increasing the thermal conductivity and increase the conductivity because of the unique properties and high surface area of graphene.

2. Experimental

2.1. Materials and physical measurements

All of the chemicals used in synthesis of nanostructures were purchased from Merck Company and didn't purify any more. X-ray diffraction (XRD) patterns were recorded by a Philips-X'pertpro, X-ray diffractometer using Ni-filtered Cu Ka radiation. Fourier transform infrared (FT-IR) spectra were recorded on Nicolet Magna-550 spectrometer in KBr pellets. The electronic spectrum of the sample was taken on Perkin–Elmer LS-55 luminescence spectrometer. GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. Scanning electron microscopy (SEM) images were obtained on LEO-1455VP equipped with an energy dispersive X-ray spectroscopy. The EDX analysis with 20 kV accelerated voltage was done. Transmission electron microscopy (TEM) image was found by a Philips EM208 transmission electron microscope with an accelerating voltage of 200 kV. The diffused reflectance UV–visible spectrum (DRS) of the sample was recorded by a V-670 UV–Vis–NIR Spectrophotometer (Jasco). Thermogravimetric analysis (TG) was carried out using a thermal gravimetric analysis instrument, Bahr-STA 503 (Germany).

2.2. Synthetic procedures

Synthesis of Ag_2HgI_4 nanoparticles was carried out during three-steps including: A, B and C as follows:

A: 0.1 g of $AgNO_3$ was dissolved in 50 ml of distilled water, then it was added to an aqueous solution containing 0.5 mmol of $LiI{\cdot}2H_2O$ (0.07 g), gradually. The obtained yellow precipitate indicated success synthesis of AgI.

B: In this step HgI_2 was synthesized by reacting 0.1 g of $Hg(OAc)_2$ (0.006 M) with 0.11 g of $LiI{\cdot}2H_2O$ (0.01 M), the molar ratio of I^-/Hg^{+2} was adjusted at 2. The orange precipitate confirmed that HgI_2 was formed.

C: In the final step, solution "A" was added to solution "B" under stirring at 90 °C for 30 min. The colour of orange solution changed to yellow, gradually. The obtained precipitate was washed by ethanol and distilled water and it was dried in a vacuum oven in 80 °C. The colour of Ag_2HgI_4 as the final product was yellow in room temperature and the colour of it was being orange in the oven. The product was characterized by various analyses. This process was repeated to investigate the effect of Ag^+/Hg^{+2} molar ratios on the purity of products. The details were given in Table 1. The Conclusions section should come in this section at the end of the article, before the Acknowledgements.

Table 1
The details of preparation of sample 1–10.

Sample no.	Ag^+:Hg^{+2} molar ratio	The obtained product	Capping agent	Graphene:nanoparticle weight ratio
1	2:1	AgI, Ag_2HgI_4	–	–
2	1:1	Ag_2HgI_4	–	–
3	1:2	HgI_2, Ag_2HgI_4	–	–
4	1:1	Ag_2HgI_4	SDS	–
5	1:1	Ag_2HgI_4	PEG-8000	–
6	1:1	Ag_2HgI_4	PVP-40000	–
7	1:1	Ag_2HgI_4	Triplex	–
8	1:1	Ag_2HgI_4	HSal	–
9	1:1	Ag_2HgI_4/graphene	HSal	1:1
10	1:1	Ag_2HgI_4/graphene	HSal	2:1

3. Results and discussion

The X-ray powder diffraction (XRD) is a rapid analytical technique primarily used for phase identification of crystalline materials, so it used to investigate the effect of molar ratio of Ag^+ to Hg^{+2} on the purity of the products. The XRD patterns of samples 1–3 are shown in Fig. 1(a–c), respectively. In Fig. 1a, the XRD pattern of sample 1 with molar ratio of $Ag^+/Hg^{+2} = 2$ was represented. According to this figure is shown two phases: Ag_2HgI_4 (JCPDS No. 74-0168, tetragonal structure) as main phase and AgI (JCPDS No. 78-0641) as impurity. Fig. 1b reveals the XRD pattern of sample 2 with molar ratio of $Ag^+/Hg^{+2} = 1$, as shown all diffraction lines correspond to the reflections of the tetragonal phase of Ag_2HgI_4 (JCPDS No. 74-0168) that is the main product with space group: I-4. XRD pattern of sample 3 indicates HgI_2 phase with tetragonal crystalline structure (JCPDS No. 01-1217) as impurity that was formed in addition to the Ag_2HgI_4 phase with tetragonal crystalline structure (JCPDS No. 74-0168) as main product. By considering the obtained results, the molar ratio $Ag^+/Hg^{+2} = 1$, was chosen as the

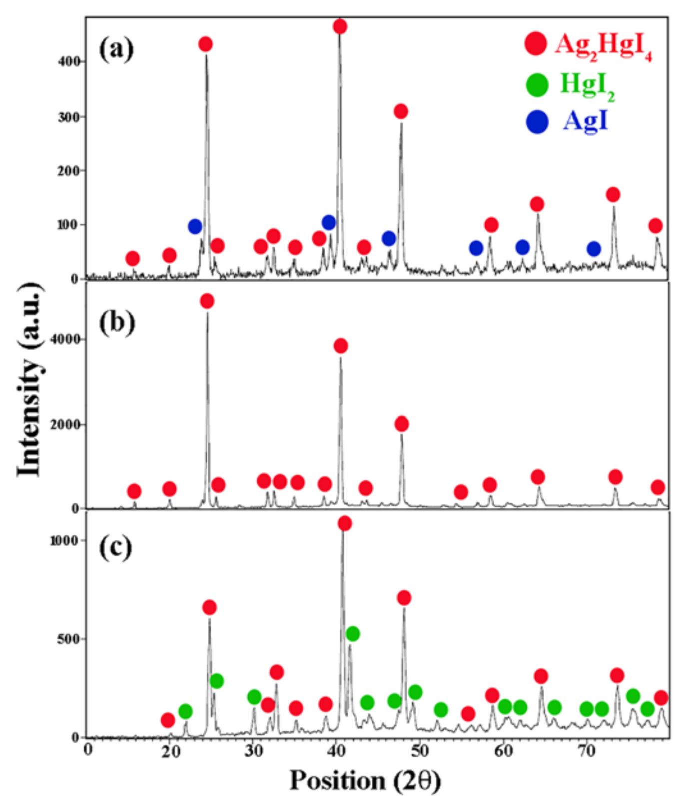

Fig. 1. XRD pattern of sample (a) 1, (b) 2 and (c) 3.