Simple synthesis-controlled fabrication of thallium cadmium iodide nanostructures via a novel route and photocatalytic investigation in degradation of toxic dyes

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Abstract The present work focused on the synthesis and characterization of TlCdI_3 nanostructures through a new **mechanical mixture of the reactants** method for the first time. In this work, thallium nitrate, cadmium nitrate and lithium iodide were chosen as starting reagents. The preparation of CdI_2 and TlI for synthesis of TlCdI_3 were performed at ambient condition. The morphology, phase structure, and phase purity of TlCdI_3 can be controlled by the $\text{TlI}:\text{CdI}_2$ ratio and also adjusting type of surfactant. In our experimental conditions, the ideal ratios between $\text{TlI}:\text{CdI}_2$ was 1:1, Also the ideal surfactant was SDS. The nanostructures were characterized by using XRD, SEM, TEM, EDS and FT-IR. The photocatalytic activity of the synthesized products has been compared in the photodegradation activity of methyl orange (MO) and methylen blue (MB).

Keywords: Nanostructure; TlCdI_3 ; Surfactant; Photocatalytic; Optical property; Electron microscopy.

1. Introduction

In recent years Metal halide perovskites are currently under intense investigations because of their potential application in photoelectronic devices [1-4] and as light emitting diodes, photodetectors, and lasers [5-8]. The perovskite structure is a highly versatile and widespread mineral form, of great importance in nature and technology. They were first suggested by the Russian mineralogist Count Lev Aleksevich von Perovski, who discovered the naturally occurring mineral calcium titanate (CaTiO_3) [9]. The stability of perovskite structure is necessary for this the sum of positive and negative charges be equal to the crystal lattice charge becomes zero. In halide Perovskite the sum of halide ions charge is equal to -3, as a result the sum of cations charge must be equal to +3 [9, 10]. Many halide perovskites with the general formula AMX_3 ($\text{A} = \text{Cs, Rb, Tl}$; $\text{M} = \text{Cd, Mg, Ni}$; $\text{X} = \text{Cl, Br, I}$) are built face-shared, corner-shared, edge-shared or partly face-partly corner-shared form of $[\text{MX}_6]_4$ octahedrons [11-14] of special interest are the group 14 iodometalates, since they can adopt perovskitic structures that are amenable to compositional variation. In the perovskite formula, AMX_3 , when the A-site in structure, is occupied by a small monovalent cation, such as Rb, Cs, K is obtained a three-dimensional (3D) framework [15, 16]. If a larger cation is used instead two-dimensional (2D) layered [17, 18] or one-dimensional (1D) chain [19, 20]. Materials are obtained with formulas AMI_3 , A_2MI_4 and A_3MI which still retain their perovskite [21, 22]. The structure of these compounds is extremely dependent on the stoichiometry of the final material and the metal-halide linkages [23].

Nanomaterials have been synthesized by hydrothermal [24], reverse-micelle [25], chemical co-precipitation [26], auto-combustion sol-gel technique [27-30], glass-crystallization [31], and salt melt methods [32]. But precipitation is an effective method for the synthesis because this technique provides a simple and appropriate approach for preparation of nanomaterials and has many advantages: low cost, easy component adjustment, and high homogeneity of the obtained nanomaterials [33]. In this work the nanostructures of TlCdI_3 were synthesized by simple mechanical mixture of the reactants method in ambient condition, Accordingly, neither high-

temperature, complex chemical reactions nor high-vacuum deposition processes are required, contrary to most conventional methods that have been used for synthesis these materials. Finally products were characterized by XRD, SEM, TEM, EDS, FT-IR, DRS and UV-Vis

2. Experimental

2.1. Materials and experiments

All the chemicals used in our experiments were of analytical grade, were purchased from Merck and used as received without further purification. XRD patterns were collected from a diffractometer of Philips Company with X'PertPro monochromatized Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). GC-2550TG (Teif Gostar Faraz Company, Iran) were used for all chemical analyses. FE-SEM images were obtained on MIRA3 FEG-SEM.. The EDS analysis was studied by XL30, Philips microscope.

2.2. Synthetic of TlCdI_3

TlCdI_3 has been synthesized from precursor TlI and CdI_2 . For synthesis of TlI stoichiometry amount of TlNO_3 and LiI were dissolved in separate Beakers in distilled water. The preparation of CdI_2 is similar to TlI for this point $\text{Cd}(\text{NO}_3)_2$ was used as Cd source and stoichiometry amount of $\text{Cd}(\text{NO}_3)_2$ and LiI were dissolved in separate Beakers in distilled water to form a clear solution. Following TlI and CdI_2 were mixed together with a curtained ratio and grinded in mortar for 2h and the result powder were dried in oven at 70°C . the effect of different parameters was investigated on the morphology and phase purity of the products. Table 1 lists the reaction conditions for the synthesis of TlCdI_3 . Scheme 1 shows a schematic diagram of the formation process of the TlCdI_3 nanostructures.

2.3. Photocatalytic experiment

The photocatalytic activities of the samples are determined by the degradation of aqueous methyl orange (MO) and methylene blue (MB) under UV light in presence of TiCdI_3 (0.005 g/L) is first inserted to a reactor that included about (0.1 mM) of aqueous MO and MB. Then the suspension is transferred into a self-designed glass reactor, and stirred in darkness to attain the adsorption equilibrium. In the investigation of photodegradation using UV light, a 125 W high-pressure mercury lamp with a water cooling cylindrical jacket is utilized. The concentration of MO and MB is checked on the basis of its UV-visible absorption.

3. Results and discussion

XRD analysis, which is the most useful technique for identification of crystalline structure, was employed to investigate the prepared samples. The XRD patterns for the samples no: 1, 2, 3 and 4 are shown in Fig. 1a-d, respectively. When the ratio of TiI/CdI_2 is 1:1 and 1:0.75 (sample no. 1 and 4), the products have the peaks corresponding to pure TiCdI_3 (JCPDS NO 70-2182), as shown in XRD patterns in Fig. 1a. Changing of the ratio of TiI/CdI_2 from 1:1 to 2:1 (sample no. 2) and 1:2 (sample no. 3), a mixture of TiCdI_3 and Ti_4CdI_6 (JCPDS NO 79-1303), in Fig. 1b and TiCdI_3 and CdI_2 (JCPDS NO 33-0239) in Fig. 1c are obtained respectively.

In the following the effect of surfactants (NaHSal, CTAB, SDS, Triplex and PVA) on the purity of the products were investigated. Fig. 2a-f shows the XRD patterns of products (sample no. 5, 6, 7, 8 and 9) obtained in the presence of different surfactants. This figure clearly shows the formation of TiCdI_3 only occur in the presence of SDS.

The morphology of the samples was investigated by SEM images. Fig. 3 shows the SEM images of samples achieved with different ratios of TiI/CdI_2 involving (a) 1:1, (b) 2:1, (c) 1:2 and 1:0.75 (d). It can be seen that the bulk structures are formed when the molar ratio of TiI/CdI_2 is 2:1 and 1:0.75 (sample no. 2 and 4). The sphere-like nanostructures in sample no. 1 and 3 are aggregated as shown in Fig. 3 c and d, whereas in the sample no. 1

these structures are apart from one another (Fig. 3 c). Thus, in our experimental conditions, the ideal ratio between TlI/CdI_2 is 1:1. In continuation, the effect of the surfactant on the morphology of the products was investigated, whereas the molar ratio between TlI and CdI_2 was selected to be 1:1. Fig. 4 shows the SEM images of the TlCdI_3 obtained in the presence of different surfactants. It can be observed that agglomerated nanostructures with different shapes and sizes have been formed in the presence of NaHSal (Fig. 3a), CTAB (Fig. 3b), SDS (Fig. 3c) PVA (Fig. 3d) and Triplex (Fig. 3f). In the presence of NaHSal, CTAB, SDS, Triplex and PVA The morphology of product are not suitable and not regular. The sample obtained in the presence SDS has spherical morphology as shown in Fig. 4 c. The nanoparticles in this figure have more even distribution than other samples. Thus, in our experimental conditions, the ideal surfactant is SDS. Typical histograms of the particle diameters for the samples Nos. 1, 2, 3, 5, 6, 7, 8 and 9 are seen in Fig. 5a–h, respectively.

The detailed morphology and particle size of the as-obtained TlCdI_3 nanostructures (sample no. 1) was investigated by transmission electron microscopy (TEM). The TEM image (Fig. 5) demonstrates that thallium cadmium iodide nanoparticles with diameter from 10 to 50 nm have sphere-like shape.

EDS analysis measurement was employed to investigate the chemical composition and purity of as-synthesized TlCdI_3 nanostructures. Fig. 6 shows the EDS spectrum of the sample no 1. This figure shows only the presence of Tl , Cd and I elements in the product.

The optical absorption spectrum of TlCdI_3 nanoparticles represents in Fig. 7a The DRS spectrum was used to further access their quality and electronic structure information. It demonstrates a major absorption peaks about 80 nm and different low intensity absorption peaks in 100-300 nm. The others absorption bands have been attributed to the impurities or vacancies. The optical band gap of TlCdI_3 has been evaluated using the optical density (OD) vs. energy (E) plot (Fig. 7a). The value of band gap energy for this nanoparticle is ~ 2.9 eV. To

prove the photocatalytic activity of samples for the degradation pollutants, the photocatalytic degradation of MO and MB experiments were performed as a model reaction under UV light irradiation. The percentage of degradation %D was determined as follows:

$$\%D = \frac{A_0 - A}{A_0} \times 100 \quad (1)$$

Where A_0 and A are the absorbencies of the liquid sample before and after degradation, respectively. The photocatalytic activity of TiCdI_3 powder was investigated by degradation of MO and MB as organic pollution. Fig. 7b illustrates the UV-Vis spectra of aqueous solution of MO and MB (0.1 mM) in presence of TiCdI_3 (0.005 g/L) at different irradiation times. When TiCdI_3 nanopowder is irradiated by light with energy greater than or equal to band-gap, an electron in the valence band could be excited to the conduction band, as a result a hole generated in the valence band. These electron-hole pair that generated by UV-light can also recombines or interacts independently with other molecules in aqueous solution. The holes in the valence band could be reacted with water on the surface of TiCdI_3 or hydroxide ions and produced extremely reactive hydroxyl radicals ($\cdot\text{OH}$) whereas electrons could accept oxygen by adsorption and shaped superoxide radical anion (O_2^-). This radical may form organic peroxides or H_2O_2 in presence of organic adsorbent. The hydroxyl radical is a very strong oxidizing agent and aggress the dye molecule to provide the oxidized product. The reactions could be summarized in following reactions [34-35].

4. Conclusions

In this work the nanostructures of $TlCdI_3$ were synthesized by simple **mechanical mixture of the reactants** method in ambient condition, Accordingly, neither high-temperature, complex chemical reactions nor high-vacuum deposition processes are required, contrary to most conventional methods that have been used for synthesis of these materials. The effect of molar ratio of $TlI:CdI_2$ and different surfactants on morphology, purity and crystallinity of products were investigated. we could obtain the nanostructures with desired morphology. To the best of our knowledge, it is the first time that nanostructures of $TlCdI_3$ are synthesized in ambient condition also it is the first time that precipitation route are used for the synthesis of these materials. The method is proved to be a new, simple, efficient and quick way.

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Figure captions

Fig. 1. XRD patterns of samples prepared: (a) with ratio of 1:1 of TlI:CdI₂ (sample no. 1) , (b) ratio of 1:2 TlI:CdI₂ (sample no. 2), (c) ratio of 2:1 of TlI:CdI₂ (sample no. 3), (d) ratio of 1:0.75 of TlI:CdI₂ (sample no. 4).

Fig. 2. XRD patterns of samples prepared with 1:1 ratio of TlI:CdI₂, in the presence of: (a) NaHsal (sample no. 5), (b) CTAB (sample no. 6) , (c) SDS (sample no. 7) , (d) triplex (sample no. 8) and (f) PVA (sample no. 9).

Fig. 3. SEM images of TlCdI₃ nanostructures prepared with different ratios of TlI:CdI₂: (a) with ratio of 1:1 (sample no. 1) , (b) ratio of 1:2 (sample no. 2) , (c) ratio of 2:1 (sample no. 3) , (d) ratio of 1:0.75 (sample no. 4).

Fig. 4. SEM images of TlCdI₃ prepared with 1:1 ratio of TlI:CdI₂, in the presence of: (a) NaHsal (sample no. 5), (b) CTAB (sample no. 6) , (c) SDS (sample no. 7) , (d) triplex (sample no. 8) and (f) PVA (sample no. 9).

Fig. 5. Particle size distribution of samples Nos. (a) 1, (b) 2, (c) 3, (d) 5, (e) 6, (f) 7, (g) 8 and (h) 9.

Fig. 6. TEM images of TlCdI₃ nanostructures prepared with ratio of 1:1 of TlI:CdI₂ (sample no. 1).

Fig. 7. EDS patterns of TlCdI₃ nanostructures (sample no. 1).

Fig. 8. (a) DRS spectrum (b) optical density ($\alpha h\nu$)² vs. energy (c) UV-Vis spectra of photodegradation of MO and MB with TlCdI₃ as a function of time.

Table 1. The reaction conditions of TlCdI₃ synthesized in this work.

Scheme 1. shows a schematic diagram of the formation process of the TlCdI₃ nanostructures.

Fig 1.

Fig 2.

Fig 3.

Fig 4.

Fig. 5

Fig 6.

Fig. 7.

Fig. 8.

Table 1.

Sample. no	Precursors Ratio	Surfactant
1	TII + CdI ₂	-
2	TII + 2CdI ₂	-
3	2TII + CdI ₂	-
4	TII + 0.75CdI ₂	-
5	TII + CdI ₂	NaHSal
6	TII + CdI ₂	CTAB
7	TII + CdI ₂	SDS
8	TII + CdI ₂	Triplex
9	TII + CdI ₂	PVA

Scheme 1.