



Fabrication and Characterization of Cesium Mercury tetraiodide Nanostructures as a water pollution removal catalyst

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Abstract

In the current research, cesium mercury tetraiodide (Cs_2HgI_4) nanostructures have been fabricated successfully by a simple and cost-effective sonochemical technique. The influence of varied factors such as CsI: HgI_2 molar ratio, variety of surfactant, time and power of ultrasound were studied on purity, morphology, and size of samples. The as-fabricated samples were identified by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and X-ray energy dispersive spectroscopy (EDS) analysis. Cs_2HgI_4 nanostructures were used as a catalyst for the destruction of organic dye (methyl orange) under UV light, and degrade methyl orange about 84.3%, for the first time. The result indicated these nanoparticles can be used as high-performance catalysts for water pollution removal.

Keywords: Cs_2HgI_4 , nanostructures, sonochemical method, photocatalytic degradation.

Introduction

Cesium mercury tetraiodide, Cs_2HgI_4 , is an optically biaxial crystal relating to an interesting group of A_2BX_4 compounds ($\text{B} = \text{Cd}, \text{Mn}, \text{Co}, \text{Zn}, \text{Hg}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) including detached tetrahedral BX_4^{2-} ions [1]. In the A_2BX_4 compounds, there are two groups which exist at room temperature either in a monoclinic Sr_2GeS_4 -type formation with a space group $P2_1/m$ [2, 3] or an orthorhombic $\text{b-K}_2\text{SO}_4$ -type formation with a space group Pnma [4]. Concerning Cs-containing A_2BX_4 compounds, nearly all of them are located to form in the orthorhombic $\text{b-K}_2\text{SO}_4$ -type formation [5–7]; nevertheless, just two compounds, specifically Cs_2HgI_4 and Cs_2CdI_4 , form in the monoclinic Sr_2GeS_4 -type formation [8,9]. Although, when heating, Cs_2HgI_4 and Cs_2CdI_4 compounds change from the monoclinic Sr_2GeS_4 -type formation (the named α -phase) to the orthorhombic $\text{b-K}_2\text{SO}_4$ -type formation (named β -phase) and this conversion is identified as $\alpha \rightarrow \beta$ transformation [4,10].

In addition to problems related to energy insufficiency and attempts to save that, problems associated with contamination of manufacturing wastewater and their entrance into nature are also very significant. Concerns about water pollution are widespread because the release of the excess dyes into different water bodies not only affects the human life but also the entire biosphere - plants and organisms, living in these water bodies [11]. For this reason, the methods



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and materials needed to decompose toxins into wastewater such as organic dyes are being studied by many researchers today. So far, various techniques have been employed for water treatment like as membrane filtration, adsorption, flocculation, coagulation and particularly the photocatalytic degradation [12, 13].

In this study, Cs₂HgI₄ nanostructures were successfully fabricated by facile sonochemical method. The effect of various factors including, molar ratio of precursors, type of different surfactant, reaction time, and power of ultrasound were investigated on purity, size, shape and morphology of products. The photocatalytic properties of as-fabricated Cs₂HgI₄ were studied to remove the organic pollutant present in the waste water.

Experimental

First, the CsI precursor was synthesized via a co-precipitation method using LiI.2H₂O and CsCl as starting materials. Primarily, stoichiometric amount of CsCl (0.2 g) and LiI.2H₂O (0.18 g) were dissolved in distilled water in separated beakers. the certain amount of capping agent was added to Cs⁺ solution. Then, these two beakers were mixed up to obtained a clear solution. The HgI₂ was obtained by mixing the Hg(OAc)₂ (0.25 g) with stoichiometric amount of LiI.2H₂O (0.2 g). Finally, the solution containing CsI was added into the HgI₂ container and sonicated for 20 min. The orange precipitates were filtered, washed using distilled water and finally dried in an oven at 75 °C. Different experimental setups were changed to achieve the optimum condition. Details information of various formulation ingredients are illustrated in Table 1.

Table 1 The condition preparation of Cs₂HgI₄

Sample no.	CsI:HgI ₂ Molar ratio	Type of surfactant	Time of soniation (min)	Power of soniation (W)
1	2	-	20	60
2	1	-	20	60
3	0.5	-	20	60
4	2	EDTA	20	60
5	2	SDS	20	60
6	2	PVP	20	60
7	2	NaHsal	20	60
8	2	SDS	20	40
9	2	SDS	20	80
10	2	SDS	30	60
11	2	SDS	10	60



Results and discussion

Figure 1 indicated XRD pattern of Cs₂HgI₄ nanostructures fabricated with molar ratio of CsI to HgI₂ 2: 1. In this figure, all diffraction lines are well-matched with monoclinic phase of Cs₂HgI₄ (JCPDS card No. 078-1916), and having P21/m space group.

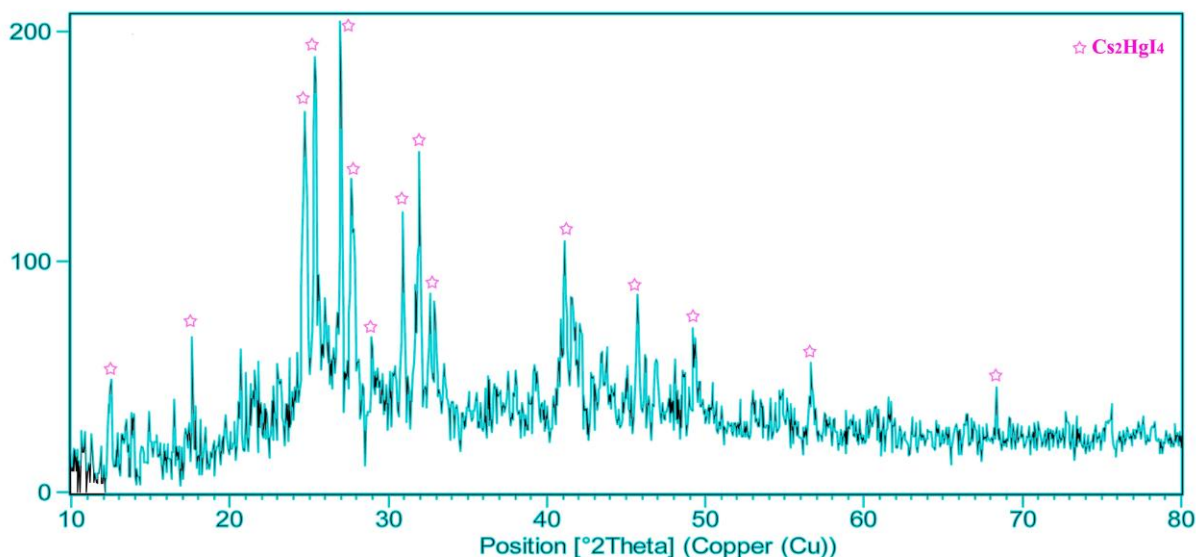


Figure 1. XRD pattern of sample 5.

Figure 2 (a-e) shows the FESEM images of the samples. Figure 2a indicates the FESEM image of sample 1 when the molar ratio of CsI to HgI₂ was 2:1. As shown in this figure tiny nanoparticles are composed and a small number of nanoparticles are aggregated. Figure 2b shows the SEM image of sample 4 in the presence of EDTA as a chelating capping agent. Bulk structures are made up of the presence of this surfactant. Using SDS as an anionic capping agent tiny nanoparticles are formed on the surface of microparticles (Figure 2c). Utilizing PVP as a polymeric capping agent caused the bulk and microstructures (Figure 2d). Figure 2e shows the FESEM image of the sample in the presence of NaHsal as a complexing agent. As shown in this figure nanoparticles are aggregated. So, we can conclude that using surfactants has a negative effect on the morphology and size of samples. Figure 2f demonstrates the EDS spectrum of sample 1. As shown in this figure the peaks of Cs, Hg, and I elements can be noticed, and the purity of the sample is high.

The photocatalytic performance of Cs₂HgI₄ nanostructures was investigated through checking the degradation methyl orange as an organic colorant agent in an aqueous solvent, following radiation among UV light (Figure 3). Without light or nanostructures, almost no methyl orange degraded after 70 min, confirming that the part of self-degradation was insignificant. The rate of degradation %D was defined as follows:

$$\%D = (C_0 - C_t) / C_0 \times 100 \quad (1)$$

Where C_0 and C_t are the absorbencies of the liquid sample before and after degradation, respectively [14]. Figure 3 indicates the photocatalytic degradation about 84.3 % methyl orange,



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decolorized after 70 min. The photocatalytic mechanism to degrade the organic contaminant can be noted as below [14]:

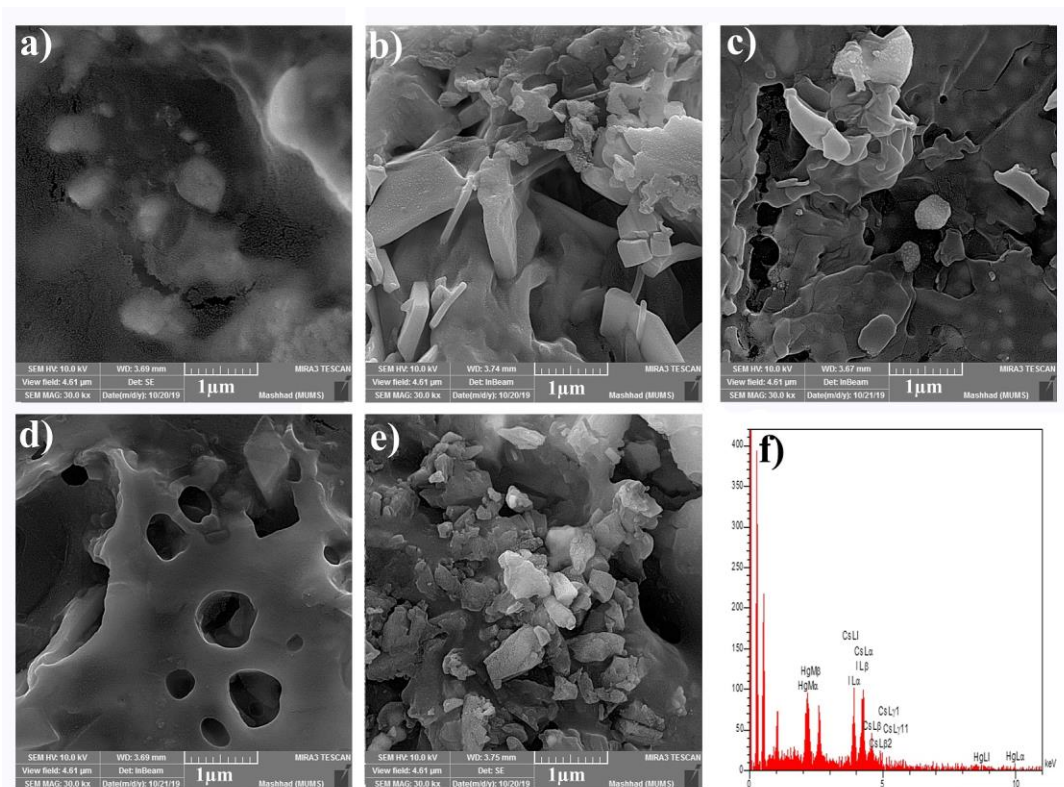
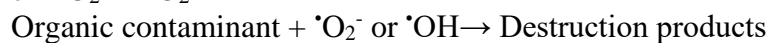
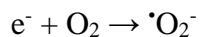
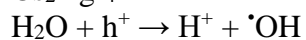
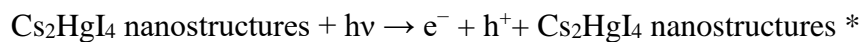


Figure 2 FESEM images of samples a) 1, b) 4, c) 5, d) 6, e) 7 and f) EDS spectrum of sample 1.

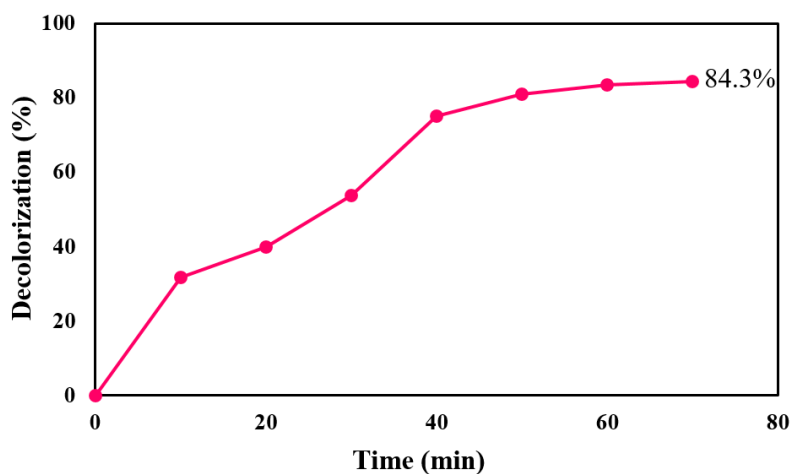


Figure 3 Photocatalytic destruction of methyl orange over sample 6.



Conclusions

In the current study, Cs₂HgI₄ nanostructures have been successfully synthesized via simple and cost-effective sonochemical method. Various parameters were optimized to obtain pure phase and small products. The molar ratio of CsI to HgI₂, the type of capping agent, the reaction time and power of ultrasound can affect the purity and particle sizes. The role of capping agent and particle size of the products confirmed by the SEM images and XRD patterns. The results clearly showed that the homogenous particles were formed in molar ratio of 2:1 without any surfactant. The photocatalytic behavior of the product studied by using methyl orange as an organic pollutant. The results confirmed that the products can successfully degrade the dye in high value.

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