Preparation, characterization and photocatalytic properties of $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites via a new simple hydrothermal approach

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Abstract: Silver zinc tetraiodide/silver iodide ($\text{Ag}_2\text{ZnI}_4/\text{AgI}$) nanocomposites are produced through a new simple hydrothermal approach. It is found that the Ag^+ molar ratio to Zn^{+2} , during and temperature of reaction play significant roles in controlling the purity, shape and grain size of products. The techniques of FESEM, EDX, XRD, TEM and DR-UV-vis are utilized to characterize the as-obtained products and investigate their optical characteristics. Application of the as-obtained $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites as photocatalyst via photodegradation of methyl orange pollutant under UV illumination was also evaluated.

Keywords: Ag_2ZnI_4 ; Nanocomposite; Hydrothermal; Photocatalytic property; Optical property.

1. Introduction

...There has been increasing interest in the preparation of nanostructures in recent years owing to their considerable features as well as excellent usages in different fields [1-5]. To date, several technologies including precipitation, salt-assisted combustion, ultrasound irradiation, solid-state reaction, thermal decomposition and hydrothermal way have been explored to produce nanostructures [6-14]. The features and usages of nanostructures have been determined by their shape, grain size and chemical composition. By controlling the shape, grain size and chemical composition of nanostructures can be tuned their features. So far our group have

prepared several sorts of nanosized structures and studied their effects on the various usages [15-19]. Herein, we prepared silver zinc tetraiodide/silver iodide ($\text{Ag}_2\text{ZnI}_4/\text{AgI}$) nanocomposites and evaluated their photocatalytic behavior. To the best of our knowledge, investigations on the preparation of $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites through a hydrothermal route have not been reported to date. In this study, the dependence of the purity, shape and grain size of products on the Ag^+ molar ratio to Zn^{+2} , during and temperature of reaction was presented. The optical features of the $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites were obtained utilizing DR-UV-vis spectrum. Moreover, the photocatalytic behavior was evaluated by decompose of methyl orange contaminant.

2. Experimental

2.1. Materials and characterization

$\text{LiI} \cdot 2\text{H}_2\text{O}$, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and AgNO_3 with analytical grade applied in the experiments purchased from Merck and applied as received. X-ray diffraction (XRD) patterns of the as-synthesized silver zinc tetraiodide/silver iodide nanocomposites were recorded by employing a diffractometer of Philips Company with X'PertPromonochromatized $\text{Cu K}\alpha$ radiation ($\lambda = 1.54 \text{ \AA}$). Transmission electron microscope (TEM) micrographs of as-produced $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites were taken on a Philips EM208S transmission electron microscope with an accelerating voltage of 100 Kv. The DR-UV-vis spectrum of the as-synthesized silver zinc tetraiodide/silver iodide nanocomposites was recorded by a UV-vis spectrophotometer (Shimadzu, UV-2550, Japan). The compositional analysis (EDS) of the as-prepared silver zinc tetraiodide/silver iodide nanocomposites was obtained on MIRA3 FEG-SEM. Microscopic morphology of as-prepared $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites was studied by a MIRA3 FEG-SEM.

2.2. Preparation of silver zinc tetraiodide/silver iodide ($\text{Ag}_2\text{ZnI}_4/\text{AgI}$) nanocomposites

The silver zinc tetraiodide/silver iodide ($\text{Ag}_2\text{ZnI}_4/\text{AgI}$) nanocomposites were prepared through a new simple hydrothermal route. In a typical experiment, first, 1mmol of AgNO_3 dissolved in distilled water (25 ml) was added

to the $\text{LiI} \cdot 2\text{H}_2\text{O}$ solution (1 mmol of $\text{LiI} \cdot 2\text{H}_2\text{O}$ in 25 ml of distilled water) to synthesize AgI product. Then, 1 mmol of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ dissolved in distilled water (25 ml) was added to the $\text{LiI} \cdot 2\text{H}_2\text{O}$ solution (2 mmol of $\text{LiI} \cdot 2\text{H}_2\text{O}$ in 25 ml of distilled water) to synthesize ZnI_2 product. $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3) were prepared by adding AgI and ZnI_2 in the autoclave. Finally, the autoclave was maintained at 140°C for 10 h. The resultant precipitate was washed out with ethanol and distilled water several times and air-dried (Scheme 1). The effect of the Ag^+ molar ratio to Zn^{+2} , during and temperature of reaction on the purity, shape and grain size of products were also evaluated. Table 1 presents the reaction conditions of the obtained nanocomposites.

2.3. Photocatalytic experiment

The photocatalytic performance of as-obtained $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3) was examined by employing methyl orange pollutant solution. The solution comprising 1 mg of the pollutant and 40 mg of the as-produced $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3) in the quartz reactor was employed to perform the photocatalytic test. After aerating for 1/2 h, the mixture was subjected to the UV illumination from the 400 W mercury lamps. The amount of pollutant was checked on the basis of its UV–visible absorption quantity.

3. Results and discussion

Fig. 1a–f depicts FESEM images of the sample nos. 1-3 prepared by various molar ratios of Ag^+ to Zn^{+2} at 140°C after 10 h of hydrothermal reaction. The FESEM images reveal that the irregular micro/nanostructures (Fig. 1a and b), the agglomerated particles/irregular micro/nanobundles (Fig. 1c and d) and the uniform nanoparticles with sphere-like shape (Fig. 1e and f) can be prepared by applying 1:1, 2:1 and 3:1 molar ratios of Ag^+ to Zn^{+2} , respectively.

To identify the crystal phase of the as-synthesized nanocomposites (sample nos. 1-3), XRD analysis was performed. Fig. 2a-c illustrates XRD patterns of sample nos. 1-3 produced by employing 1:1, 2:1 and 3:1 molar ratios of Ag^+ to Zn^{+2} , respectively. XRD results indicate that the sample nos. 1 and 2 consist of the $\text{Zn}(\text{OH})_2$ and

ZnO, and that the Ag₂ZnI₄/AgI nanocomposites have not been produced (Fig. 2a, b). By employing 3:1 molar ratios of Ag⁺ to Zn⁺², Ag₂ZnI₄/AgI nanocomposites have been formed. All diffraction peaks in the XRD pattern (Fig. 2c) can be indexed to the Ag₂ZnI₄ (JCPDS Card file no. 42-0071) along with AgI (JCPDS Card file no. 01-0502). By employing Scherrer equation and XRD results [12], the mean crystallite size of the as-produced Ag₂ZnI₄/AgI nanocomposites (sample no. 3) was estimated to be about 26 nm. The possible mechanism for preparation of products:

The preparation of ZnO may be explained using a possible mechanism as follows: ZnI₂ has high affinity to the H₂O and transforms to Zn(OH)₂. The formed Zn(OH)₂ (as intermediate product) may be transformed to ZnO in hydrothermal condition [20].

FESEM and XRD results reveal that 3:1 is the most favorable molar ratio of Ag⁺ to Zn⁺² for preparing pure Ag₂ZnI₄/AgI nanocomposites with homogeneous sphere-like shape (Figs. 1e and f and 2c), thus other samples were produced by employing this molar ratio of Ag⁺ to Zn⁺².

The influence of reaction temperature on the shape and grain size of the as-prepared samples are illustrated in Fig. 3a-d. According to Fig. 3a-d, the agglomerated particles/irregular micro/nanobundles (Fig. 3a and b) and high agglomerated particle-like structures/irregular micro/nanostructures with large grain size (Fig. 3c and d) are formed at 160 and 180 °C (sample nos. 4 and 5), respectively. It seems that when reaction temperature changed from 140 to 160 and 180 °C, the homogeneous sphere-like Ag₂ZnI₄/AgI nanoparticles with fine size which were produced at 140

°C, agglomerated and fused to each other and hence the agglomerated particles/irregular micro/nanobundles and high agglomerated particle-like structures/irregular micro/nanostructures with large grain size were prepared.

Fig. 4a and b depicts XRD patterns of sample nos. 4 and 5 synthesized by employing 3:1 molar ratios of Ag^+ to Zn^{+2} at 160 and 180 °C, respectively. XRD results reveal that the sample nos. 4 and 5 consist of the $\text{Zn}(\text{OH})_2$, and that the $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites have not been formed (Fig. 4a and b).

Fig. 5a-d illustrates the influence of the reaction during on the shape and grain size of the as-synthesized samples. FESEM images reveal that the irregular sphere-like nanostructures (Fig. 5a and b) and high agglomerated particle-like structures decorated by irregular micro/nanostructures with large grain size (Fig. 5c and d) are formed at 14 and 18 h (sample nos. 6 and 7), respectively. It can be seen that the grain size becomes larger and the amount of homogeneous sphere-like $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanoparticles diminishes via prolonging the hydrothermal duration from 10 to 14 and 18 h. This happened increment in grain size can be attributed to the Ostwald ripening process.

Fig. 6a and b presents XRD patterns of sample nos. 6 and 7 produced by employing 3:1 molar ratios of Ag^+ to Zn^{+2} at 140 °C during 14 and 18 h, respectively. The sample nos. 6 and 7 comprising the $\text{Zn}(\text{OH})_2$, and the pure $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites have not been produced, as illustrated in Fig. 6a and b.

According to the FESEM images and XRD results, employing 3:1 molar ratio of Ag^+ to Zn^{+2} at 140 °C during 10 h is the optimum condition for preparing pure $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites with homogeneous sphere-like shape (Fig. 1e and f and 2c).

To elucidate the detailed morphological features of the as-synthesized $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3) TEM images were taken (Fig 7a-d). TEM images demonstrate the formation of nanoparticles with quasi-spherical shape.

EDS analysis provide additional information for the investigation of the chemical purity level of as-produced $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3). In the EDS spectrum in Fig. 8 the characteristic bands of Ag, Zn and I are seen, which reveal preparation pure silver zinc tetraiodide/silver iodide nanocomposites.

To elucidate the optical characteristics and band gap (E_g) quantity of as-produced $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3), DR-UV-vis spectrum was taken. Fig. 9a presents the DR-UV-vis spectrum of the $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ sample. The absorption peak at 352 nm is seen in Fig. 9a. The E_g quantity can be calculated based on the DR-UV-vis spectrum by applying Tauc's formula [15]. The E_g quantity of the $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ sample (sample no. 3) may be estimated via extrapolating $(\alpha h\nu)^2$ against $h\nu$ at $(\alpha h\nu)^2 = 0$ [6, 15] (Fig. 9b). The energy gap quantity of the $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ sample (sample no. 3) calculated to be 3.28 eV. According to the estimated E_g quantity, the as-prepared $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ sample may be applied as the photocatalyst under UV illumination.

The photocatalytic performance of as-obtained $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3) was examined by monitoring the decomposition of methyl orange pollutant solution in an aqueous solution under UV illumination (Fig. 10). No pollutant was practically broken down after 20 min in absence of the as-obtained $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites or UV light. According to this obtained result, it was found that the contribution of self-degradation was negligible.

The percentage of pollutant decomposition was calculated as follows:

$$D.P.(t) = \frac{A_0 - A_t}{A_0} \times 100 \quad (1)$$

where A_0 and A_t are the absorbance value of pollutant solution at before and after decomposition by a UV-vis spectrometer, respectively. The pollutant decomposition was about 89.3% after 20 min illumination of UV light. This result suggests as-produced $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites as novel, desirable and promising candidate for

photocatalytic usages under UV illumination. The probable mechanism of the decomposition of pollutant can be assumed as:

4. Conclusions

In this study, we describe a new simple hydrothermal approach for the preparation of silver zinc tetraiodide/silver iodide ($\text{Ag}_2\text{ZnI}_4/\text{AgI}$) nanocomposites. It is shown that the Ag^+ molar ratio to Zn^{+2} , during and temperature of reaction play significant roles in controlling the purity, shape and grain size of products. When as-synthesized silver zinc tetraiodide/silver iodide nanocomposites was employed as photocatalyst, the percentage of the methyl orange pollutant decomposition was about 89.3 after 20 min illumination of UV light. This result suggests as-produced $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites as novel, desirable and promising candidate for photocatalytic usages under UV illumination. This investigation suggests a novel, convenient, cost-effective and simple approach for the preparation of silver zinc tetraiodide/silver iodide ($\text{Ag}_2\text{ZnI}_4/\text{AgI}$) nanocomposites.

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Table 1. The synthesis conditions of the products prepared in this study.

Sample No.	Molar ratio (Ag ⁺ :Zn ⁺²)	Reaction temperature (°C)	Reaction duration (h)	Figure of XRD patterns	Figure of FESEM images
1	1:1	140	10	2a	1a and b
2	2:1	140	10	2b	1c and d
3	3:1	140	10	2c	1e and f
4	3:1	160	10	4a	3a and b
5	3:1	180	10	4b	3c and d
6	3:1	140	14	6a	5a and b
7	3:1	140	18	6b	5c and d

Figure Captions:

Figure 1. FESEM images of sample nos. 1-3 produced by employing 1:1 (a and b), 2:1 (c and d) and 3:1 (e and f) molar ratios of Ag^+ to Zn^{+2} , respectively.

Figure 2. XRD patterns of sample nos. 1-3 produced by employing 1:1 (a), 2:1 (b) and 3:1 (c) molar ratios of Ag^+ to Zn^{+2} , respectively.

Figure 3. FESEM images of sample nos. 4 and 5 synthesized by employing 3:1 molar ratios of Ag^+ to Zn^{+2} at 160 (a and b) and 180 °C (c and d).

Figure 4. XRD patterns of sample nos. 4 and 5 synthesized by employing 3:1 molar ratios of Ag^+ to Zn^{+2} at 160 (a) and 180 °C (b).

Figure 5. FESEM images of sample nos. 6 and 7 produced by employing 3:1 molar ratios of Ag^+ to Zn^{+2} at 140 °C during 14 (a and b) and 18 h (c and d).

Figure 6. XRD patterns of sample nos. 6 and 7 produced by employing 3:1 molar ratios of Ag^+ to Zn^{+2} at 140 °C during 14 (a) and 18 h (b).

Figure 7. (a-d) TEM images of the as-prepared $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3) at different scales.

Figure 8. EDS pattern of the as-synthesized $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3).

Figure 9. UV-vis diffuse reflectance spectrum (a) and plot to determine the band gap (b) of $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3).

Figure 10. Photocatalytic methyl orange pollutant degradation of $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites (sample no. 3).

Scheme 1. Schematic diagram of the preparation of $\text{Ag}_2\text{ZnI}_4/\text{AgI}$ nanocomposites.

Scheme 1.

Fig 1.

Fig 2.

Fig 3.

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Fig. 6.

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