Synthesis and Characterization of Zn Doped CuWO₄ Nanoparticles and Their Opto-structural Properties

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Abstract: CuWO₄ and Zn doped CuWO₄ nanoparticles were prepared by a solid-state reaction method. The XRD study confirms the triclinic crystal structure for both samples and the peak shift is noticed for Zn doped CuWO₄ particles with high crystallinity. The FTIR spectra shows metal oxide vibration which arose from the CuWO₄ and Zn doped CuWO₄ particles. The optical absorption spectra exhibit strong absorption in the visible region and the band gap of Zn doped CuWO₄ is found to be increased to 2.44 eV compared to that of CuWO₄ (2.36 eV), which is due to the elevated conduction band levels after Zn-doping. The SEM images of both CuWO₄ and Zn doped CuWO₄ nanoparticles show densely aggregated particles.

Keywords: Copper Tungstate, Zn doped CuWO₄, Absorption, Nanoparticles.

1. Introduction

The copper (Cu) containing oxides have wide potential applications in the field of catalysis and electrochemistry. Among them, Cu-ternary oxides showed more stability against the photocorrosion than Cu-binary oxides [1]. When introducing CuO into WO₃ for the formation of CuWO₄ results in reduced bandgap between 2.1-2.3 eV with increased stability [2]. CuWO₄ can easily oxidize water due to maximum absorption of visible light from the solar spectrum [3]. It is observed that CuWO₄ has the ability to degrade methanol, methylene blue, methyl orange and phenol under visible light. However the reported efficiencies are lower due to high charge recombination. Wen Yan et al. (2019) reported that ZnWO₄ nanocrystals exhibited improved photocatalytic activity for the degradation of Methylene Blue dye and it is highly active in UV range due to its large bandgap [4]. It is learnt from the literature that the noble metal oxides such as CoWO₄, Ag₂WO₄, and Bi₂WO₆ have potentially tune its structural and optical properties by doping [5-7]. In the present work, Zn was chosen as doping element owing to (i) similar oxidation state and ionic radius of Cu, (ii) absorbs the entire visible region in the solar spectrum, (iii) cost effective and available in abundance when comparable with other elements such as Ni, Nb, Zr, Mo, Ru and Rh. Doping of Molybdenum, Fluorine cations with CuWO₄ has been already investigated and the incorporation of Zinc has not been explored well [8, 9]. Thus, the results suggests that doping of Zn into CuWO₄ particles can increase the efficiency of the photocatalyst due to large electron density. Besides, Zinc is an effective strategy to retard...
the surface modification due to similar ionic radius.[10] Herein, we synthesize CuWO₄ and Zn doped CuWO₄ nanoparticles via solid state reaction method. The enhancement in structural, optical and morphological properties is analyzed with Zinc doped CuWO₄ nanoparticles.

2. Experimental details

Facile solid state reaction method was adopted for the preparation of CuWO₄ nanoparticles. First, 0.1 M of CuO and WO₃ were taken and well grounded for one hour with the help of mortar and pestle. The well grounded particle was transferred to alumina crucible which was kept in a muffle furnace at 600°C for three hours. Then, the CuWO₄ particle was allowed to cool within the furnace itself. To synthesis Zn doped CuWO₄ nanoparticles, 0.5 M of CuO, 0.5 M of ZnO and 1 M of WO₃ were taken and the aforesaid process was adopted as that of CuWO₄ particles. The structural, optical and morphological studies were carried out using PANalytical XPERT-PRO diffractometer system with Cu Kα radiation (λ=1.5406 Å) for recording X-ray diffraction patterns, Perkin Elmer spectrometer (Model: C92107) with resolution of 4cm⁻¹ was used for recording the FTIR spectra, JEOL - JSM 5610LV Scanning electron microscope was used to analyse the surface morphology and Shimadzu UV-2700 for recording the UV-DRS analysis respectively.

3. Results and discussion

The reaction mechanism involved in the formation of CuWO₄ and Zn doped CuWO₄ is given below:

\[ \text{CuO} + \text{WO}_3 \rightarrow \text{CuWO}_4 \]  \hspace{1cm} (1)

\[ 0.5 \text{CuO} + 0.5 \text{ZnO} + \text{WO}_3 \rightarrow \text{Cu}_{0.5}\text{Zn}_{0.5}\text{WO}_4 \]  \hspace{1cm} (2)

The XRD pattern of CuWO₄ and Zn doped CuWO₄ is shown in Fig.1. The CuWO₄ nanoparticles show the prominent peak at 2θ = 28.77° belonging to (-1-11) plane and some high intense peaks are seen at 2θ = 30.24°, 2θ = 31.76°, 2θ = 32.24°, 2θ = 35.74°, 2θ = 38.67° belongs to (111), (1-11), (0-21), (-120) plane respectively of triclinic crystal system (JCPDS card: 72-0616). All the sharp and intense diffraction peaks suggested the highly crystalline nature of CuWO₄. While introducing Zn, the major diffraction peak shifted with high intensity at 2θ = 30.48° belongs to 1-11 plane. The shift in peaks from 2θ = 28.77° to 2θ = 30.48° indicates the incorporation of Zn into CuWO₄. Besides, the other intense peaks are seen at 2θ=30.89°, 2θ = 36.34°, 2θ = 23.14°, 2θ = 23.64° belongs to 020, 0-21, -110, 011 plane respectively. Some additional peaks are also observed in the pattern at 2θ = 24.43°, 2θ = 33.30°, 2θ = 34.23° may be due to excess ZnO or WO₃ which are not involved in the reaction to completely transform into Cu₀.₅Zn₀.₅WO₄. All the peaks obtained are well matched with the standard JCPDS card: 88-0260 has the triclinic system. The crystalline size was calculated using scherrer formula and it is found to be 34 nm and 40 nm for CuWO₄ and Zn doped CuWO₄ nanoparticles respectively.

Fig.2. shows the FTIR spectra of CuWO₄ and Zn doped CuWO₄ nanoparticles. In the spectrum for CuWO₄, a band appears around 904 cm⁻¹ attributed to stretching vibration of W=O in WO₃ octahedron associates with CuWO₄ [11]. Besides, a vibrational band is seen around 530 cm⁻¹ corresponds to bending vibration of Cu-O of CuWO₄ due to 3d¹⁰ configuration of CuO [12]. A broad band is also seen between 800 cm⁻¹ and 650 cm⁻¹. In the case of Zn doped CuWO₄, the broad band appeared at 904 cm⁻¹ becomes widened. It is important to note that the vibrational band observed at 536 cm⁻¹ is shifted to 520 cm⁻¹ respectively. These findings confirmed the incorporation of Zn into CuWO₄ nanoparticles and it is well agreed with the XRD results.

Fig.3. shows the SEM image of CuWO₄ and Zn doped CuWO₄ nanoparticles. In CuWO₄ image, the uniformly synthesized particles distributed over the surface which are strongly aggregated with one another in the form of network-like structure [13]. In the case of Zn doped CuWO₄, the strongly aggregated particles are randomly distributed over the surface with fine grains. These observations strongly suggest that the incorporation of Zinc into CuWO₄. Interestingly, the surface decoration of Zinc into CuWO₄ promotes efficient charge separation and it may increase the efficiency of the photocatalyst [14].

The EDX spectrum clearly evidenced the W-rich CuWO₄ and Zn-CuWO₄ nanocomposites. From the EDX analysis, the existence of Cu, W, O and Zn signals confirm the synthesized product. The elemental composition of both
CuWO₄ and Zn-CuWO₄ nanoparticles is given in Table 1 and Table 2. The non-stoichiometric ratio of the obtained nanoparticles is due to the formation of WO₃ as an additional product which in turn reflected by W rich CuWO₄ and Zn-CuWO₄ nanoparticles.

FIG. 1. XRD patterns of CuWO₄ and Zn doped CuWO₄ nanoparticles.

FIG. 2. FTIR Spectra of CuWO₄ and Zn doped CuWO₄ nanoparticles.
FIG. 3. SEM images of (a) CuWO$_4$ and (b) Zn doped CuWO$_4$ nanoparticles.

Fig. 4. EDX Spectrum of (a) CuWO$_4$ and (b) Zn doped CuWO$_4$ nanoparticles.

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TABLE 2. Elemental composition of Zn doped CuWO$_4$.  

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The UV-Vis absorption spectra of CuWO$_4$ and Zn doped CuWO$_4$ are shown in Fig.5.a. From the spectra it is observed that both the CuWO$_4$ and Zn doped CuWO$_4$ possess maximum absorption in the visible region. The band gap values are estimated from Tauc's plot and it is found to be 2.36 eV and 2.44 eV for CuWO$_4$ and Zn doped CuWO$_4$ respectively. The increase in bandgap values of Zn doped CuWO$_4$ may be attributed to incorporation of Zinc ions which usually possess elevated conduction band levels [15]. However, the obtained bandgap values for CuWO$_4$ are lower than the previously reported results [16, 17]. Moreover, the relatively lower bandgap of CuWO$_4$ allows it to absorb a wider range of visible region and hence it can be effectively used as a photoanode for solar water splitting [18].

4. Conclusion

In this work, we report CuWO$_4$ and Zn doped CuWO$_4$ nanoparticles synthesized by solid state reaction method. The XRD study confirms the triclinic crystal structure for both samples. For Zn doped CuWO$_4$ nanoparticle, the shift in peak position indicates the successful incorporation of Zinc into CuWO$_4$ without affecting the crystal structure. The FTIR spectrum shows the presence of Cu-O, W-O and Zn-O stretching vibrations which confirm the formation of CuWO$_4$ and Zn doped CuWO$_4$ particles. The SEM images of CuWO$_4$ nanoparticles show densely aggregated particles in which zinc was decorated over the surface of CuWO$_4$ particles. The band gap value is found to be 2.36 eV for CuWO$_4$ and 2.44 eV for Zn doped CuWO$_4$. Hence, it is concluded that dopant Zinc could modify the structural, optical and morphological properties and thus it can be used as a photoanode for solar water splitting.

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