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ARTICLE

Synthesis and Characterization of Zn-doped $CuWO_4$Nanoparticles and Their Opto-structural Properties

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Abstract: $CuWO_4$ and Zn-doped $CuWO_4$ 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 $CuWO_4$ particles with high crystallinity. The FTIR spectra show metal oxide vibration which arose from the $CuWO_4$ and Zn-doped $CuWO_4$ particles. The optical absorption spectra exhibit strong absorption in the visible region and the band gap of Zn-doped $CuWO_4$ is found to be increased to 2.44 eV compared to that of $CuWO_4$ (2.36 eV), which is due to the elevated conduction band levels after Zn-doping. The SEM images of both $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles show densely aggregated particles.

Keywords: Copper tungstate, Zn-doped $CuWO_4$, Absorption, Nanoparticles.

1. Introduction

Copper (Cu) - containing oxides have wide potential applications in the fields of catalysis and electrochemistry. Among them, Cu-ternary oxides showed more stability against photocorrosion than Cu-binary oxides [1]. Introducing CuO into WO_3 for the formation of $CuWO_4$ results in reduced bandgap between 2.1-2.3 eV with increased stability [2]. $CuWO_4$ can easily oxidize water due to maximum absorption of visible light from the solar spectrum [3]. It is observed that $CuWO_4$ 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 $ZnWO_4$nanocystals exhibited improved photocatalytic activity for the degradation of methylene blue dye and are highly active in UV range due to their large bandgap[4]. It is learnt from the literature that noble metal oxides, such as $CoWO_4$, Ag_2WO_4 and Bi_2WO_6, have potentially tuned their 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) it absorbs the entire visible region in the solar spectrum, (iii) it is cost-effective and available in abundance when compared with other elements, such as Ni, Nb, Zr, Mo, Ru and Rh. Doping of molybdenum, fluorine cations with $CuWO_4$ have been already investigated and the incorporation of zinc has not been explored well [8, 9]. Thus, the results suggest that doping of Zn into $CuWO_4$ particles can increase the efficiency of the photocatalyst due to large electron density. Besides, zinc is an

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effective strategy to retard the surface modification due to similar ionic radius[10]. Herein, we synthesizes $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles *via* solid-state reaction method. The enhancement in structural, optical and morphological properties is analyzed with zinc-doped $CuWO_4$ nanoparticles.

2. Experimental Details

Facile solid-state reaction method was adopted for the preparation of $CuWO_4$ nanoparticles. First, 0.1 M of CuO and WO_3 were taken and well ground for one hour with the help of mortar and pestle. The well-ground particleswere transferred to alumina crucible which was kept in a muffle furnace at 600°C for three hours. Then, the $CuWO_4$ particles were allowed to cool within the furnace itself. To synthesize Zn-doped $CuWO_4$ nanoparticles, 0.5 M of CuO, 0.5 M of ZnO and 1 M of WO_3 were taken and the aforesaid process was adopted as that of $CuWO_4$ 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 (Spectrum Two, Model: C92107) with resolution of 4cm^{-1} was used for recording the FTIR spectra, JEOL - JSM 5610LV Scanning electron microscope was used to analyze 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 $CuWO_4$ and Zn-doped $CuWO_4$ is given below:

$$CuO + WO_3 \longrightarrow CuWO_4 \quad (1)$$

$$0.5\ CuO + 0.5\ ZnO + WO_3 \longrightarrow Cu_{0.5}Zn_{0.5}WO_4 \quad (2)$$

The XRD pattern of $CuWO_4$ and Zn-doped $CuWO_4$is shown in Fig.1. The $CuWO_4$ 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° and 2θ = 38.67° belonging to (111), (-111), (1-11), (0-21) and (-120) plane, respectively, of triclinic crystal system (JCPDS card: 72-0616). All the sharp and intense diffraction peaks suggested the highly crystalline nature of $CuWO_4$. While introducing Zn, the major diffraction peak shifted with high intensity at 2θ=30.48° belonging to 1-11 plane. The shift in peaks from 2θ = 28.77° to 2θ = 30.48° indicates the incorporation of Zn into $CuWO_4$. Besides, the other intense peaks are seen at 2θ = 30.89°, 2θ = 36.34°, 2θ = 23.14° and 2θ = 23.64° belonging to 020, 0-21, -110 and 011 plane, respectively. Some additional peaks are also observed in the pattern at 2θ = 24.43°, 2θ = 33.30° and 2θ = 34.23°, which may be due to excess ZnO or WO_3 which are not involved in the reaction to completely transform into $Cu_{0.5}Zn_{0.5}WO_4$. 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 $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles, respectively.

Fig.2 shows the FTIR spectra of $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles. In the spectrum for $CuWO_4$, a band appears around 904 cm^{-1} attributed to stretching vibration of W=O in WO_3 octahedron associates with $CuWO_4$ [11]. Besides, a vibrational band is seen around 530 cm^{-1} corresponding to bending vibration of Cu-O of $CuWO_4$ due to $3d^{10}$ configuration of Cu_2O [12]. A broad band is also seen between 800 cm^{-1} and 650 cm^{-1}. In the case of Zn-doped $CuWO_4$, the broad band which 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 $CuWO_4$ nanoparticles and well-agreed with the XRD results.

Fig.3 shows the SEM image of $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles. In $CuWO_4$ image, the uniformly synthesized particles are distributed over the surface and are strongly aggregated with one another in the form of network-like structure [13]. In the case of Zn-doped $CuWO_4$, the strongly aggregated particles are randomly distributed over the surface with fine grains. These observations strongly suggest the incorporation of zinc into $CuWO_4$. Interestingly, the surface decoration of zinc into $CuWO_4$ promotes efficient charge separation and it may increase the efficiency of the photocatalyst [14].

The EDX spectrum clearly evidenced the W-rich $CuWO_4$ and Zn-$CuWO_4$ nanocomposites. From the EDX analysis, the existence of Cu, W, O and Zn signals confirms the synthesized product. The elemental composition of both $CuWO_4$ and Zn-$CuWO_4$ nanoparticles is given in Table 1 and Table 2. The non-stoichiometric ratio of the obtained nanoparticles is due to the formation of WO_3 as an additional product which is in turn reflected by W-rich $CuWO_4$ andZn-$CuWO_4$ nanoparticles.

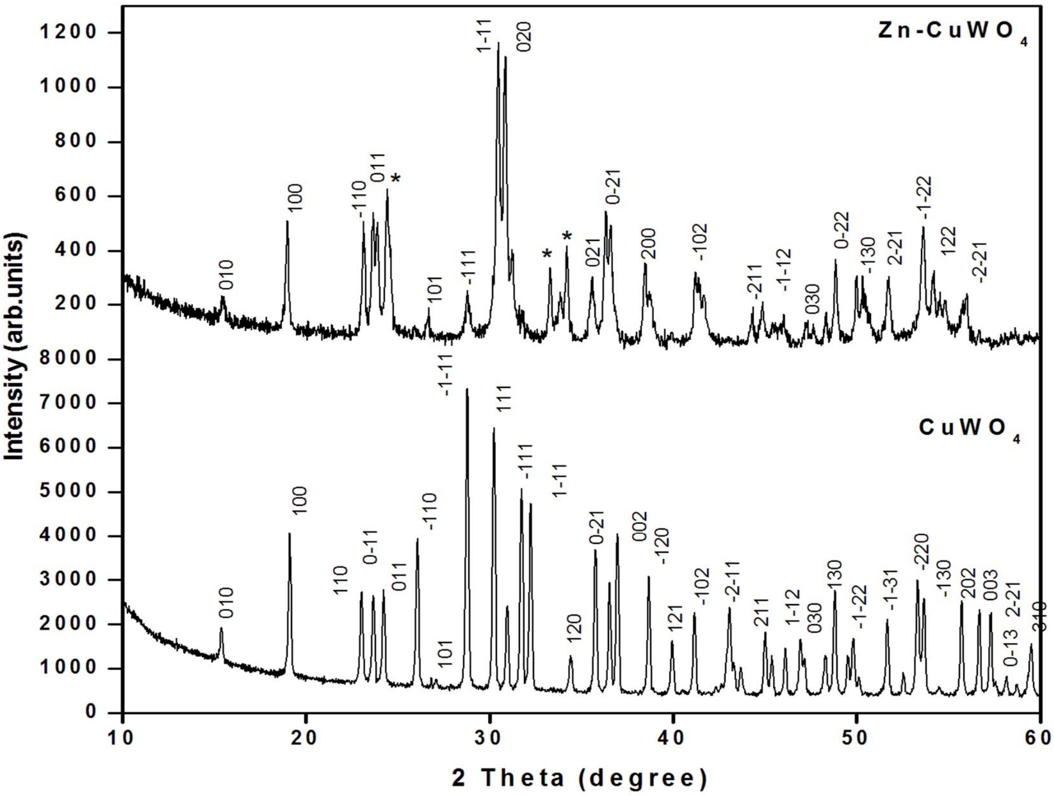

FIG. 1. XRD patterns of $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles.

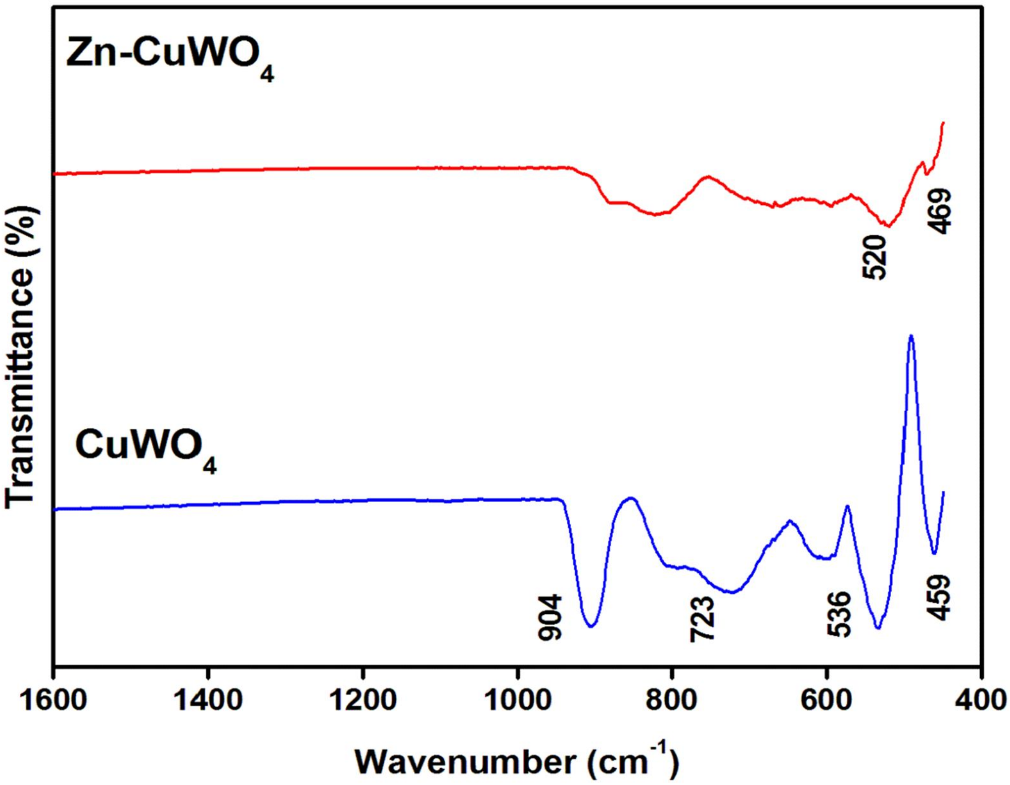

FIG.2.FTIR Spectra of $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles.

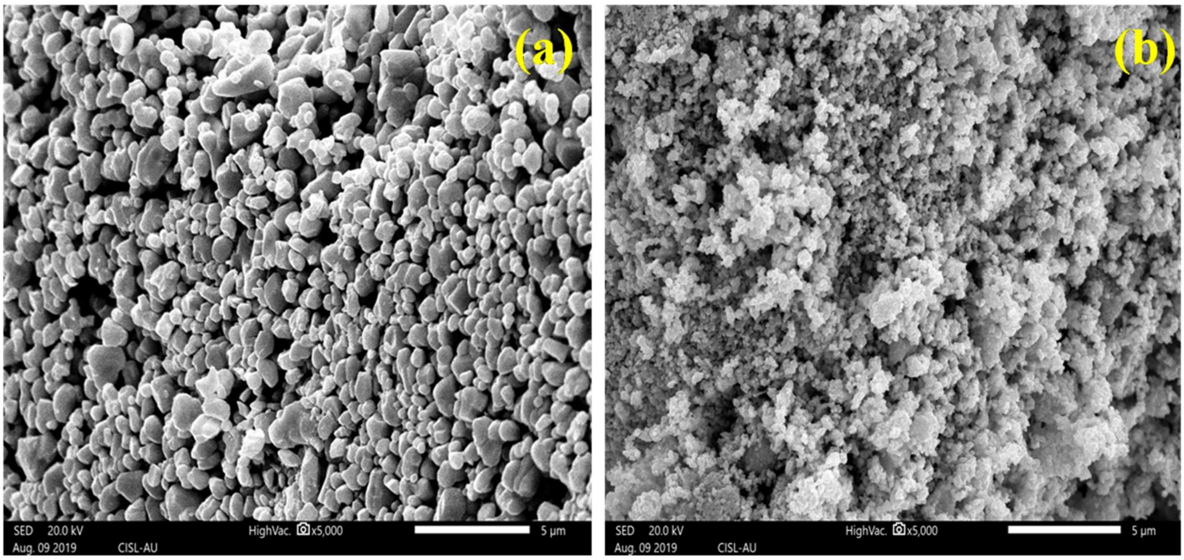

FIG.3. SEM images of (a) $CuWO_4$ and (b) Zn-doped $CuWO_4$ nanoparticles.

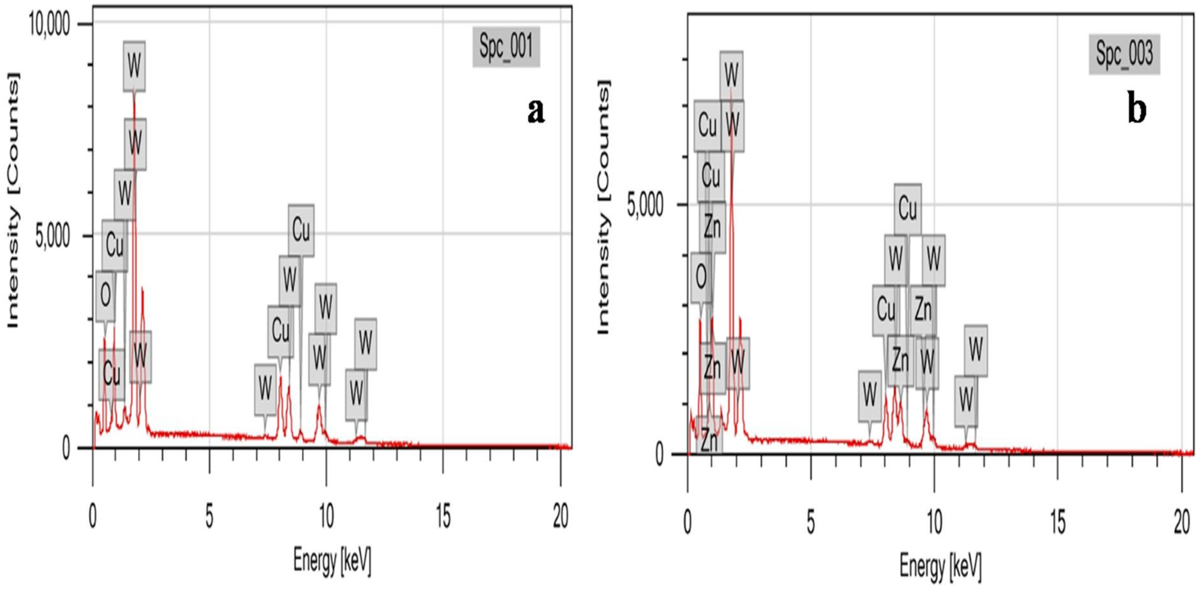

FIG.4. EDX Spectrum of (a) $CuWO_4$ and (b) Zn-doped $CuWO_4$ nanoparticles.

TABLE 1.Elemental composition of $CuWO_4$.

S. No.	Element	Mass (%)	Atom (%)
1	O	11.68	50.03
2	Cu	24.13	26.04
3	W	64.19	23.93
Total		100.00	100.00

TABLE 2. Elemental composition of Zn doped $CuWO_4$.

S. No.	Element	Mass (%)	Atom (%)
1	O	12.03	48.52
2	Cu	15.06	15.30
3	Zn	16.62	16.41
4	W	56.29	19.77
Total		100.00	100.00

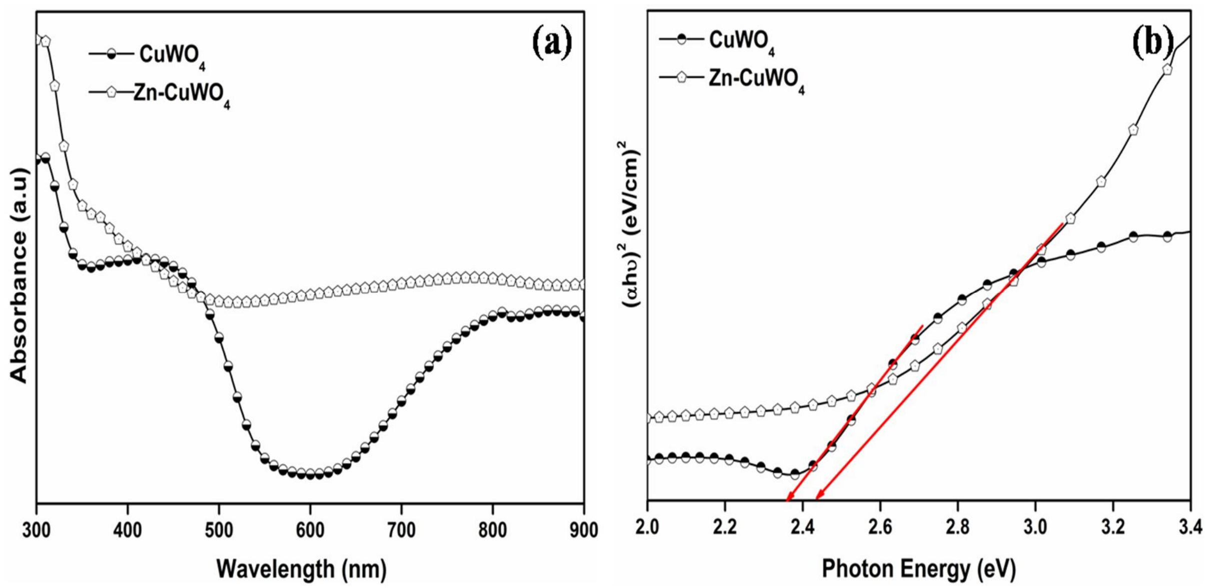

FIG.5.(a) UV-vis absorption spectra and (b) Tauc's plot of $CuWO_4$ and Zn-doped $CuWO_4$ nanoparticles.

The UV-vis absorption spectra of $CuWO_4$ and Zn-doped $CuWO_4$ are shown in Fig.5a. 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 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 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 confirms 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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