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Low Temperature Novel Photosynthesis Method and Characterization of ZnO/CuO Nano composite

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Abstract

Metallic oxides have been largely taken into consideration due to the prospect of modelling the properties of these materials for different applications. The ZnO/CuO nanocomposites were successfully synthesized using photolysis method. The product characterized using XRD, SEM, EDXS, PSA and PL techniques and all the obtained results prepared pure nanoparticles. The calculation of the percentage ratio for metals in compounds was done using EDXS, and the obtained results demonstrated that the Zn ratio was less than Cu. The measurements of XRD, SEM and PSA showed the size of the particles in the nano range by using Scherrer equation and program counting. At 380nm, a strong emission appeared and this indicated that the particles were useful for electronic devices.

Keywords: Novel, ZnO/CuO, Nanocomposite, Photosynthesis, Characterization

Introduction

As it has been known, nanomaterial is a material with the nanoscale size of (1-100 nm). This material has a unique property for commercial applications. The key properties of nanoparticles are their small particle size, narrow size distribution, low agglomeration and high dispersion (Saravanan et al., 2013). The addition of CuO to ZnO could form the CuO-ZnO composite that increased the particle size and reduced the band gap energy. With the higher concentration of CuO in composites, the smaller band gap energy could be achieved. Mixed oxide semiconductors have won the applicability for many applications such as solar cell, piezoelectric devices, sensors, microelectronic circuits, catalyst, fuel cells, surface, and coating to prevent corrosion (Saravanan et al., 2013; Bandara et al., 2005; Anicai et al., 2015; Mariammal et al., 2012; Yang et al., 2008; Fang et al., 2011). Many enjoyable properties of these semiconductors include their high allergy to moisture changes, the speedy dynamic restraint, the normal p-n characteristics, and the wide light absorption (Ohtomo et al., 1998). The energy gap (via inserting two different materials) is another substantial advantage of nanocomposites. Great interest in studying mixed oxide semiconductors has been notified where the semiconductor metal oxide (p-type) is mixed with n-type (Li et al., 2008; Mumjitha et al., 2015; Zaid et al., 2018; Cun et al., 2002; Bandara et al., 2006; Zheng et al., 2009; Liu et al., 2014; Hameed et al., 2009) and among all, ZnO/CuO nanocomposite has attracted the interest of researchers. (ZnO) is a n-type semiconductor with a property like low cost, non-toxicity, ample availability, conductivity of about 10−7–10−3 S/cm, a band gap of 3.37 eV, and also having comparatively large stir binding energy of (60 meV), high specific energy intensity, excellent piezoelectric, optoelectronic, and electrical properties (Jun & Choi, 2005; Sini et al., 2010), while CuO is a semiconductor type-n with conductivity equal to 10−4 s/cm, 1.2 eV band gap and many applications in field emission, photovoltaic, catalysis and electrochemistry (Gajendiran & Rajendran, 2014). Many methods have been mentioned to prepare mixed ZnO/CuO composites such as, chemical vapor deposition (CVD) (Simon et al., 2012), wet impregnation (Sathishkumar et al., 2011), complex-directed hybridization (Zaid, 2017), directly heating of brass in air (Zaid et al., 2017) and sol gel one (Vijayalakshmi, Karthick, 2012). By traditional methods, the drawback has linked to the physical and chemical properties of nanomaterials compared with different methods; photolysis methods have shown the major advantage that the clarity of the prepared powders significantly overtook the clarity of the starting materials. This was because during photolysis irradiations, the reaction was successive and no more side products appeared, which did not occur during the other prepared routes. And, it has many advantages like low cost, environmental friendliness, high quantity of product, simple equipment, catalyst-free growth, large-area uniform production.

The aim of the present investigation was to prepare and characterize a CuO/ZnO nanocomposite using a novel photolysis method.

Materials and Methods

Materials

The materials used were analytical grade zinc nitrate hexahydrate, $Zn(NO_3)_2.6H_2O$, zinc nitrate trihydrate $Cu(NO_3)_2.3H_2O$, ethanol, acetone and distilled water, which were used without any purification.

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Synthesis Procedure of ZnO/CuO nanocomposite

It involved a process in which 1mole of zinc nitrate hexahydrate and 1mole of copper nitrate trihydrate were dissolved separately in 50ml of distilled water. Then, the two solutions were mixed together under continuous stirring and thus irradiating for two hours using an irradiation system, shown in (Fig 1), until the formation of a brown precipitate was filtered off, dried and finally calcined at 400C for four hours. For EDX analysis, the sample of ZnO/CuO composite was coated by gold utilizing sputter coater (Edwards S150) to increase the conductivity of the mixed ZnO/CuO after gold coating.

Characterization of metal oxide nanoparticles

The XRD spectrum of ZnO/CuO nanocomposite was recorded by utilizing an X-ray diffractometer type (Shimadzu-XRD-6000) while the surface morphology of it was imaged by a Scanning Electron Micrograph type (inspect S50 from FEI). The EDXS analysis was shown by employing an energy-dispersive X-ray spectroscopy (EDXS). Particle size distribution and photoluminescence spectrum were done by Mastersizer 3000 laser diffraction particle size analyzer and Varian Carry Eclipse PL spectrophotometer; respectively.

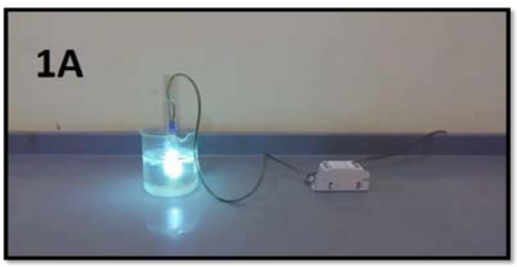

Fig. 1: irradiation system

Results and Discussion

XRD and particle size calculation of (ZnO/CuO) nanocomposite:

XRD patterns and angles and Miller indices data of prepared composite are shown in Figs.2 and Table 1. The positions and intensities of the peaks were in a good agreement with those reported in JCPDS file NO. (36-1451) for hexagonal structure ZnO and file No. (89-5899) for monoclinic structures CuO.

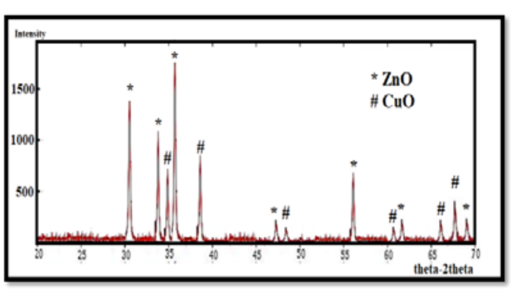

Fig. 2: XRD of pattern of (ZnO/CuO) composite

The particle size has been calculated from the XRD pattern by the use of the Debye Scherer equation.

$$D = 0.9\,\lambda / \beta \cos\theta$$

Where D is the crystalline size, λ is the wavelength of radiation, θ is the Braggs angle and β is the full width at half maximum (FWHM). The crystalline size corresponding to the highest peak in XRD pattern was found is 30.4 nm. The presence of sharp peaks in XRD patterns and crystalline size less than 100 nm suggested the nano crystalline nature of the prepared composite.

Table 1- Angles and Miller index values of XRD peaks of (CuO/ZnO)

Peaks number	2θ	Miller index
1	31°	(100)
2	34°	(002)
3	35°	$(1^{-}11)$
4	36°	(101)
5	38°	(111)
6	47°	(102)
7	48°	$(2^{-}02)$
8	56°	(021)
9	61°	$(1^{-}13)$
10	62°	(103)
11	66°	(200)
12	68°	(220)
13	69°	(201)

Scanning the electron microscope of prepared composite:

The surface morphology of the prepared CuO/ZnO composite was revealed through the SEM image and shown in Fig.3. It showed a homogeneous distribution of spherical shape like nanoparticles with irregular distribution. From SEM images, it was confirmed that the particles had a size of between 12-30 nm by simple counting, and the calculations of the number of the particles and their sizes would also confirm the nanostructure nature of the both oxides. It also showed a particle with many agglomerations and parallel shapes due to not forming large clusters (Magnus et al., 2010) and the reaction between ZnO/CuO that was followed at the time of irradiation and the linked power. Through irradiation, the acute drags and jostle of particles occurred, and therefore, the neighboring nanoparticles were self-assembled via involvement in a common crystallographic tendency. Subsequently, the particles might be constructively in a guided way to manufacture great single crystals. The irradiation of the heterogeneous system might instruct to the assorted morphology of ZnO/CuO nanocomposite. Any visible disorder was not found, and this indicated the perfect crystalline fineness of the prepared product.

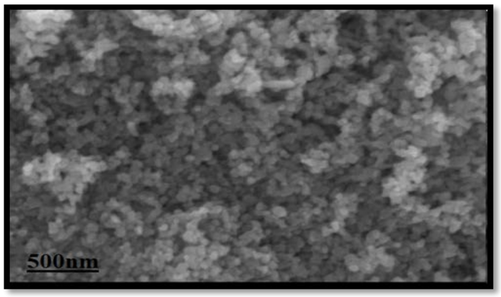

Fig. 3: SEM image of prepared (ZnO/CuO composite).

Energy-disperse X-ray spectroscopy, particle size and Photoluminescence studies

The elemental distribution percentage of nanoparticles was carried out based on an EDXS spectrum shown in (fig. 4) where the results proved the existence of Zn, Cu and O in the prepared composite. The stoichiometric structural formula estimated from EDX seemed to be $Cu_{1.20}Zn_{1.12}O_{1.00}$

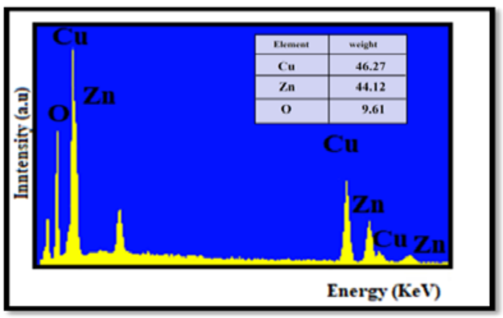

Fig. 4: EDXS of prepared (ZnO/CuO) composite.

The average particle size examining through particle size analyzer results has been shown in (fig. 5) as a histogram with the average particles of 23nm, a value that was similar to those calculated and estimated from XRD and SEM.

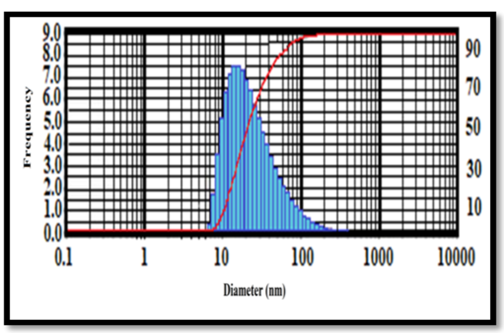

Fig. 5: Average particle size distribution of (ZnO/CuO) composite.

Finally, photoluminescence spectrum was used in the investigation of the fineness, and the purity of the prepared compound is shown in (fig.6) at the excitation wavelength of 325 nm. The free exciton played an important role in the UV emission of ZnO/CuO, appearing in 380nm due to the recomposition during an exciton / exciton conflict process (Vijayalakshmi et al., 2013; Dandan et al., 2009). Because of the radiative move from zinc interstitial to the valence band, a small shoulder peak of the emission was shown at 420nm, and it was corresponding to the ZnO band gap, and the PL spectrum of a compound showed a high intensity due to crystalline fineness, interaction between zinc and copper oxides in addition to the fundamental flow that emerged due to Zn, O vacancy and interstitial Zn which were lesser (Magnus et al., 2010; Muthukumaran et al., 2012).

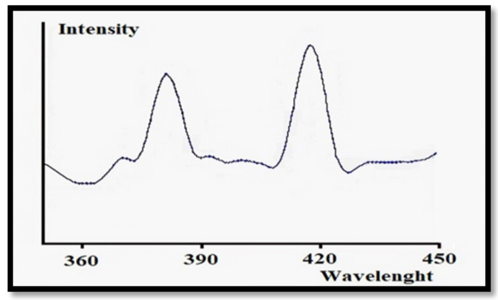

Fig. 6: PL spectrum of (ZnO/CuO)

Conclusion:

In this project, the facile UV irradiation method to fabricate ZnO/CuO nano-compoistes has been established. Photolysis has been the novel and excellent method to prepare ZnO/CuO powder due to having many advantages such as purity and fineness of the particles, low-cost, and not needing the energy to prepare it. The results of XRD patterns showed hexagonal and monoclinic phases of ZnO and CuO respectively, while the result of PSA obtained formed particles in nano range. The perfection in the crystalline fineness of the prepared product was also shown by the promoted UV emission as registered by the PL measurements.

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