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Sulfur modified ZnO nanorod as a high performance photocatalyst for degradation of Congoredazo dye

ABSTRACT

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Sol-gel derived sulfur modified and pure ZnO nanorod were prepared using zinc chloride and thiocarbamide as raw materials. Prepared nanorods were characterized by means of X-ray diffraction (XRD), thermogravimetry- differential scanning calorimetry (TG-DSC), UV- Vis absorption spectroscopy, Brunauer Emmett Teller (BET) specific surface area and Barrett Joyner Halenda (BJH) pore size distribution analyses, scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX) analyses. The band gaps of sulfur modified and pure ZnO were estimated from UV-Vis spectroscopy data to be 2.75 and 3.18 eV, respectively. The specific surface area of sulfur modified ZnO nanorod calculated to be 2.63 m²/g using BET method. Pore size distribution curve of the mater obtained via BJH method revealed that the diameter of the pores is from several to more than 20nm. Photocatalytic activity of synthesized sulfur modified and pure ZnO nanorod were tested for degradation of Congoredazo dye under ultraviolet and visible light. The results revealed that the sulfur modified ZnO nanorod has excellent photocatalytic activity towards Congored under visible light illumination.

Keywords: *Photocatalyst; Sulfur modified ZnO; Nanorod; Band gap; Congored.*

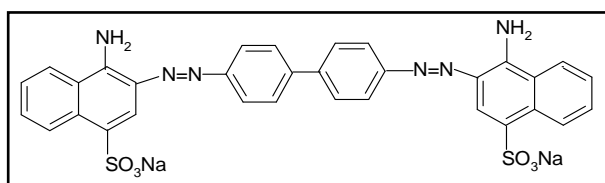
INTRODUCTION

Photocatalytic reactions using semiconductors has received much attention for destroying a wide range of environmental pollutants [1, 2]. Wide-band gap ZnO semiconductor can degrade various organic contaminants in air and water under UV irradiation [3-5]. As a result of significant optical and electrical properties of ZnO, this material has become under investigation in recent years [6]. Low cost of precursors, simplicity and high efficiency of its chemical synthesis method encourage scientists to investigate on nano-ZnO [7].

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However, a major barrier to the extensive use of ZnO as photocatalysts is its relatively large band gap, 3.18 eV, limiting its photo responsibility to visible light, which comprised of about 45% of the incoming solar energy [5]. Hence, it is essential to develop a ZnO semiconductor with high photocatalytic activity under visible light. In order to expand ZnO application under visible light, it is necessary to modify the electronic structure of the photocatalyst [8]. As is well known, impurity-doping in semiconductors with selective elements greatly affects on their physicochemical properties which are critical for their practical application. Recently, doping nonmetal atoms, such as C, N, and S, has received much attention [9-12]. Due to large electro-negativity and size difference between O and S, the electrical and optical properties of ZnO are expected to be modified by sulfur doping [13].

Hence, in this work sulfur modified and pure ZnO nanorods were prepared via sol-gel method. After that, photocatalytic efficiency of synthesized nanorods was tested for degradation of Congoredazo dye (Scheme 1) under ultraviolet and visible lights. Congored contains NH_2 and SO_3 functional groups and is an anionic azo dye. It can be metabolized to benzidine, a known human carcinogen and exposure to the dye has been known to cause an allergic reaction [14].



Scheme 1. The structure of Congored dye.

EXPERIMENTAL

Materials and Apparatus

All of raw materials used in this research were purchased from Merck. Phase identification of the produced sulfur modified ZnO was characterized by X-ray diffraction (XRD) obtained on Philips X-pert diffractometer using Cu K α line radiation. Thermogravimetry-differential scanning calorimetry (TG-DSC) was carried out using STA 150 Rhenometric Scientific unit. Measurements were taken with a heating rate of 10°C/min from 25

to 800°C in Argon atmosphere. UV-vis absorbance spectrum of prepared photocatalyst was recorded with a Shimadzu UV 2100 spectrophotometer. Brunauer-Emmett-Teller (BET) specific surface area and Barret-Joyner-Halenda (BJH) pore size distribution of the sulfur modified ZnO sample was determined through nitrogen adsorption (Quantachrome NOVA 2200 e). The morphology of the products was studied by scanning electron microscopy (SEM, Philips XL30).

Preparation of Sulfur Modified and Pure ZnO Photocatalyst

For preparation of sulfur modified ZnO, a proper amount of Zinc chloride (ZnCl_2) and thiourea (NH_2CSNH_2) were dissolved into de-ionized water under vigorous stirring. After that, ammonia was added in order to adjust the PH value to 10. Then the mixture was transferred to a round balloon. The sample was kept at 90 °C under vigorous stirring for 2 h. Then obtained solid was filtered, rinsed by de-ionized water, dried at 90 °C and finally was calcined at 250°C. synthesized powder was denoted as ZS.

The pure ZnO was prepared with the same method except no using thiourea and denoted as Z photocatalyst.

Photocatalytic Activity Determination

Photocatalytic activities of the prepared sulfur modified and pure ZnO were evaluated by the degradation of Congored dye under visible and ultraviolet lights. Photocatalytic experiments were performed in an open Pyrex vessel which was filled with 100mL of aqueous suspension of Congored (5 ppm) containing 1 g/L of photocatalysts. The UV radiation source, a lamp (30 W, UV-C, $\lambda = 253.7$ nm, manufactured by Philips, Holland), was irradiated perpendicularly to the surface of solution, and the distance between the UV source and vessel containing reaction mixture was fixed at 15 cm. Tow 18 W Osram lamps were used as the light source for visible light photocatalytic reactions. Figure 1 shows the emission spectrum of Osram lamp. Air was blown into the reaction by an air pump to maintain the solution saturated with oxygen during the course of the reaction. The experiments were performed at ambient temperature at 30 °C. Prior to irradiation, the suspension was magnetically stirred in the dark for 30 min to ensure establishment of an

adsorption/desorption equilibrium among the photocatalyst particles, dye molecules, and atmospheric oxygen. During the course of light irradiation, a suspension of about 5mL was taken out after regular time intervals. The suspension was centrifuged and then passed through milipore filters to remove suspended photocatalyst particles. Finally, the filtrates were studied by UV-vis spectroscopy.

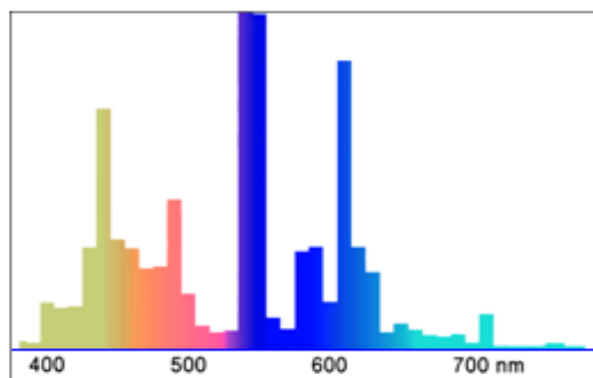


Fig. 1. Emission spectrum of Osram lamp.

RESULTS AND DISCUSSION

Characterization of Sulfur Modified and Pure ZnO Nanorods

The X-ray diffraction (XRD) analyses of sulfur modified and pure ZnO nanorods are shown in Figure 2a and 2b. According to X-ray diffraction analysis, both of pure and sulfur modified ZnO exhibited wurtzite phase of ZnO and doping with sulfur does not change the crystal structure of ZnO. However, introduction of sulfur atoms into the ZnO network causing a very small 2θ shift to smaller angle. The successful incorporation of sulfur in ZnO lattice was confirmed by lower Bragg angle shift (by 0.3°) in XRD pattern of ZS. The finding is consistent with those reported in the literatures [15, 16]. Sun and coworkers postulated that because of the larger size of S^{2-} than O^{2-} the substitution of O with S will introduce strain in ZnO and affect the lattice parameters causing smaller diffraction angle [15].

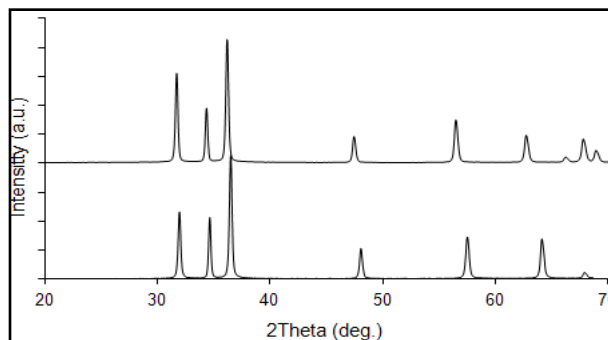


Fig. 2. X-ray diffraction (XRD) patterns of sulfur modified (a) and pure (b) ZnO samples.

Differential thermal and thermogravimetric curves of sulfur modified ZnO precipitate prior to calcination are shown in Figure 3. According to Thermogravimetry (TG) analysis, the weight loss consists of some distinct steps.

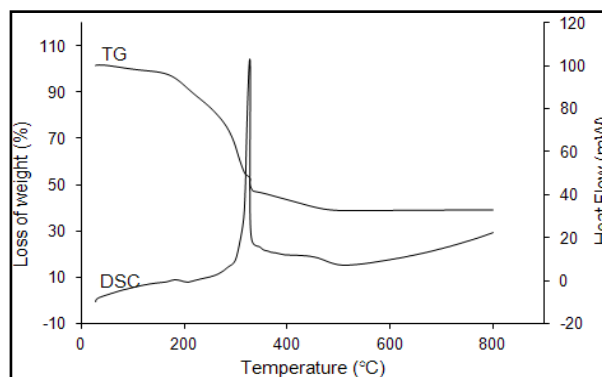


Fig. 3. Thermogravimetry-differential scanning calorimetry (TG-DSC) curves of sulfur modified ZnO before calcination.

The first stage of weight loss is corresponds to removal of physically absorbed water up to 150°C . The second step is regarding to evolution of CO_2 and carbonyl sulfide at 140°C which reach the maximum rate at 170°C and 180°C , respectively [17]. A release of ammonia has been reported to be occurred also from 170°C to 185°C [17].

X-ray diffraction (XRD) analyses exhibited that as-prepared sulfur modified ZnO powder composed of ZnS, ZnO, ZnSO_3 , ZnSO_4 , and $\text{Zn}(\text{OH})_2$ phases and only a very small amount of $\text{Zn}(\text{OH})_2$ was left beside ZnO and ZnS in the matter heat treated at 160°C (Figures are not shown). According to X-ray diffraction patterns, $\text{Zn}(\text{OH})_2$ phase was disappeared in calcined matter at 250°C . it revealed that loss of water molecules due to condensation of Zn-OH groups gradually occurs

before 250°C. Hence, complete crystallization of the amorphous phase to wurtzite ZnO at 250°C is accompanied by a weak thermal effect in DSC curve.

The significant exothermic peak in DSC curve at around 320°C is correspond to oxidation of NH_3 into the N_2O and H_2O and the small exothermic effect about 450°C is relevant to bulk oxidation of residual sulfurous species as reported by Madarasz [17].

Figure 4a and 4b display scanning electron microscopy (SEM) images of pure and sulfur modified ZnO samples, respectively. According to the images both of prepared samples have rod morphology. The obtained nanorods are approximately 120 nm in diameter and more than 1 μm in length.

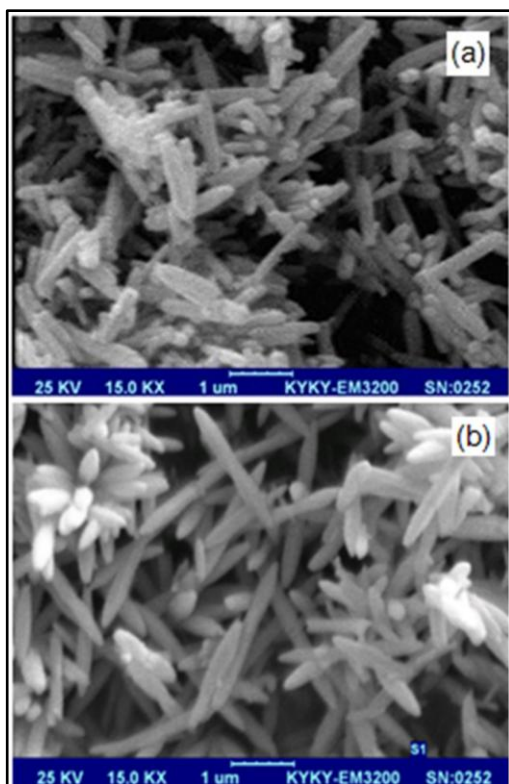


Fig. 4. Scanning Electron Microscopy (SEM) images of sulfur modified ZnO (a) and pure ZnO (b).

The composition of the sulfur modified ZnO powder is identified via Energy-dispersive X-ray spectroscopy (EDX) analysis. The EDX pattern is shown in Figure 5. This analysis indicates that

the prepared matter composed of Zn, O and a small amount of sulfur element.

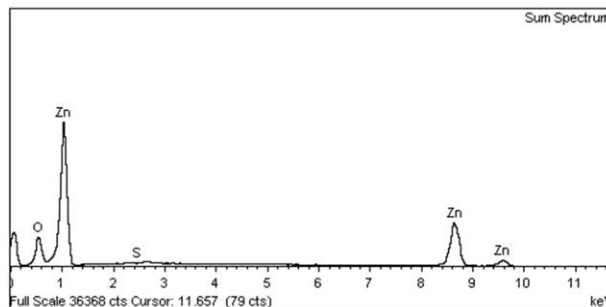


Fig. 5. Energy-dispersive X-ray spectroscopy (EDX) analyze of sulfur modified ZnO nanorods.

Figure 6a and 6b shows the absorption spectra (in the range 200–800 nm) of the pure and sulfur modified ZnO nanorods dispersed in ethanol. Pure ZnO only exhibits a strong absorption in the UV region corresponding to the band to band transition [18]. The band gaps of the sample were calculated from the straight part of the optical absorption spectra [19]. By this method, the band gaps of the pure and sulfur modified ZnO nanorods were calculated to be 3.18 and 2.75 eV, respectively. Comparing band gaps of the pure ZnO and synthesized sulfur modified ZnO nanorods revealed that by introducing S atoms into the crystalline network of ZnO, a remarkable shift in the absorption band toward higher wavelength regions is obtained. Moreover, comparison of Z and ZS spectra showed that synthesized sulfur modified ZnO nanorods have more light absorption ability than pure ZnO from 390 nm to 800 nm. This phenomenon could be related to existence of new surface states in ZS sample [20].

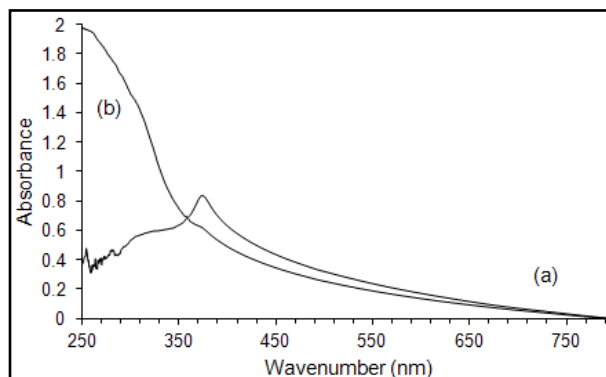


Fig. 6. UV-vis absorption spectrum of the pure ZnO (a) and Sulfur modified ZnO nanorods (b) dispersed in ethanol.

Figure 7 shows the pore size distribution curve calculated from desorption branch of the nitrogen isotherm obtained by Barrett Joyner Halenda (BJH) method and the corresponding nitrogen adsorption-desorption isotherms (inset) of the sulfur modified ZnO powder. The specific surface area of prepared mater calculated to be 2.63 m²/g using Brunauer Emmett Teller (BET) method and Pore size distribution curve of the mater obtained via BJH method revealed that the diameter of the pores is from several to more than 20 nm.

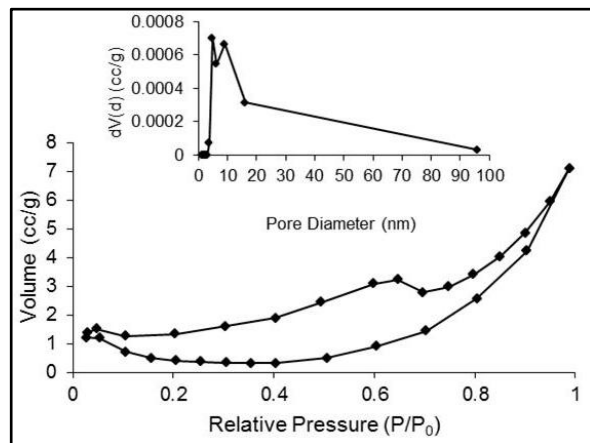


Fig. 7. Pore size distribution curve of the sulfur modified ZnO nanorods - Inset: N₂ adsorption-desorption isotherm.

Photocatalytic Activity

Figure 8a and b show changes of the UV-Vis absorption spectrum of Congored after adsorption of dye on sulfur modified ZnO at dark and during photocatalysis under visible and ultraviolet light. According to the Figure 8 sulfur modified ZnO exhibits superior photocatalytic activity under visible light compared to ultraviolet. It would be due to lower photon absorption ability of the photocatalyst in ultraviolet region.

Figure 9 shows degree of photocatalytic degradation of Congored (X) as a function of irradiation time at 497 nm using pure and sulfur modified ZnO nanorods under ultraviolet and visible light illumination. The efficiency or degree of photodegradation (X) is given by: $X = (C_0 - C)/C_0$, where C_0 is the initial concentration of dye, and C the concentration of dye at time T.

The photocatalytic experiments using sulfur modified ZnO nanorods exhibited that modification with sulfur makes the prepared

photocatalyst to be highly active under visible light. In contrast, photocatalytic activity of sulfur containing ZnO nanorods is lower than pure ZnO under ultraviolet light illumination. These phenomena are related to higher and lower photon absorption ability of sulfur modified ZnO nanorods in visible and ultraviolet region, respectively.

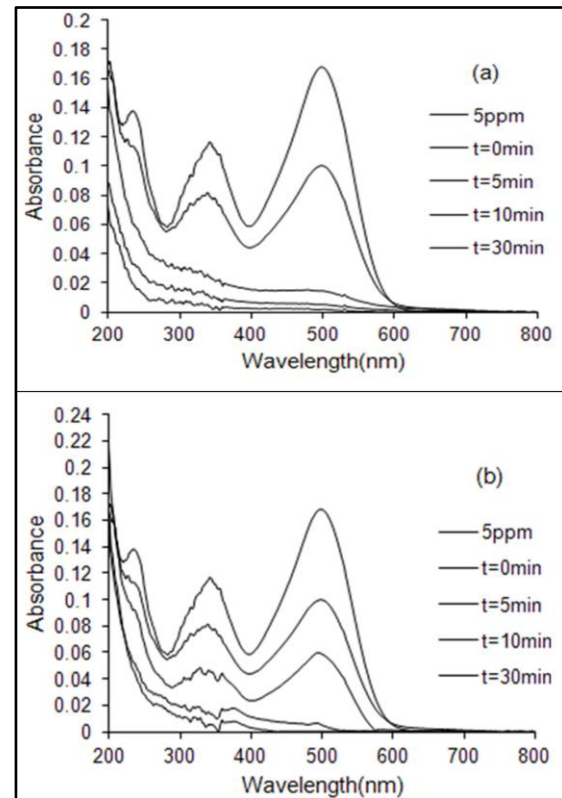


Fig. 8. Changes of UV-Vis spectrum of Congored (5 ppm) in aqueous sulfur modified ZnO dispersion (1 g/l) irradiated with two 18 W Osram lamps (a) and with a 30 W UV-C lamp light as a function of time (b).

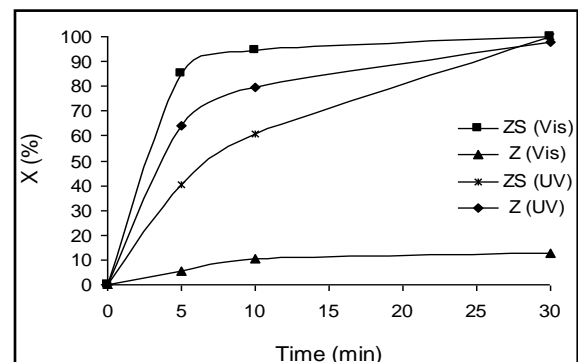


Fig. 9. Variation of photocatalytic activity of sulfur modified ZnO nanorods under ultraviolet and visible lights in comparison with pure ZnO.

CONCLUSIONS

Visible light active sulfur modified ZnO nanorods with about 120 nm in diameter and approximately 1 μm in length have been synthesized successfully. X-ray diffraction (XRD) pattern revealed that the sulfur modified ZnO nanorods have wurtzite structure. The prepared sulfur modified ZnO has a porous texture and its optical band gap estimated to be 2.75 eV. The prepared sulfur modified ZnO has high efficiency in Congo red decolorization under visible light. The visible light absorbance of sulfur modified ZnO is of great significance for its practical application point of view.

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