PHOTODEGRADATION OF CONGORED DYE USING HETEROGENEOUS PHOTOCATALYSIS UNDER ULTRA- VIOLET IRRADIATION

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ABSTRACT

Undoped Zinc oxide and Magnesium, Titanium codoped ZnO (S_A, S_B and S_C) nanoparticles were synthesized from their precursors by soft chemical method. The structural and chemical characteristics of nanoparticles synthesized were analyzed utilizing various techniques such as XRD, FTIR, SEM-EDX, UV-Visible Spectroscopy and AFM while the photodegradation study of congo red was performed by UV/VIS spectrophotometry. The XRD results showed that the undoped ZnO and Mg, Ti codoped ZnO nanoparticles were hexagonal wurtzite structure. The SEM analysis showed that synthesized nanoparticles were in the nano-range with varying morphology and also the purity of the sample was confirmed by EDX analysis. Undoped ZnO and Mg, Ti codoped ZnO nanoparticles were used as photocatalyst for the photodegradation of congo red dye in aqueous medium under UV-light irradiation. The photodegradation study revealed that the Undoped ZnO and Mg, Ti codoped ZnO nanoparticles degraded about 55% and 91.5% of dye within 180 mins respectively. The activity of recovered undoped ZnO and Mg and Ti codoped ZnO nanoparticles were studied.

Keywords: ZnO, Nanoparticles, Soft-Chemical Method, Congored, Photodegradation.

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INTRODUCTION

Zinc oxide (ZnO) has remarkable polar surfaces leading to the formation of a lot of nanostructures namely needles, films, rings, springs, bows and helices. Nowadays, ZnO has gained its popularity and consideration due to its indistinctive properties such as optical, semiconducting, piezoelectric and magnetic properties. The peculiar properties such as high catalytic efficiency and strong adsorption ability are possessed by ZnO nanostructures. The multiplicity of morphologies such as belts, ribbons, cables, rods, tubes, rings, tetrapods, spirals are the indistinctive properties of ZnO nanosystems that renders its contributions for a wide range of applications. ZnO nanomaterials is utilized as a photocatalytic agent for the photodegradation of industrial effluent, electric conductors, microbial inhibitors, etc. Technologies including alkoxide hydrolysis, gas phase thermal decomposition and micro-emulsion technologies for synthesizing ZnO nanostructures have been recorded. This investigation intended at synthesizing nano-sized ZnO and Magnesium (Mg), Titanium (Ti) codoped ZnO nanoparticles by soft chemical method and the chemical properties, compositions, particle morphology and photocatalytic performance of the synthesized nanomaterials were also studied.

EXPERIMENTAL

The chemicals required for the preparation of undoped ZnO and Mg, Ti-doped ZnO nanoparticles by soft chemical method for photodegradation efficiency were purchased from Merck and used as precursors and distilled water was used as a solvent.

Synthesis of Undoped ZnO Nanoparticles

Zinc nitrate hexahydrate (1M) was used as a starting material and dissolved in 100 ml distilled water using magnetic stirrer for 30 mins. A solution of NaOH (2M) was mixed with starting solution to get a large

amount of white precipitate under constant stirring at 45⁰ C. By using distilled water, the precipitates were filtered and washed, then dehydrated at 120⁰C in hot air oven for four hours and white precipitates of synthesized materials were powdered in an agar mortar. The final powder was calcined at 450⁰C for 3 hours and allowed for cooling in furnace. The nanomaterials were collected for further characterization studies.

Synthesis of Mg and Ti Codoped ZnO Nanoparticles

Zinc nitrate hexahydrate (0.98M), Magnesium nitrate hexahydrate (0.05,0.01&0.15M), Titanium (IV) isopropoxide (0.15,0.01&0.05M) were used as precursors for the preparation of different concentrations (S_A, S_B and S_C) of Mg and Ti codoped ZnO by above-mentioned procedure and the final powder was collected for further characterization studies.

Photodegradation Analysis

About 10 mg/L of congo red dye and 50 ml of distilled water with 40 mg of Undoped ZnO nanomaterials were placed under UV irradiation for the degradation of dye in different time stretch of (0, 30, 60, 90, 120,150 and 180 minutes). The influence of UV light sources on photo-degradation of congo red dye was supported with a 30 W mercury lamp and the decomposition effect was measured by UV-absorption measurement. The same method was applied for photodegradation efficiency of synthesized Mg and Ti codoped ZnO nanoparticles.

RESULTS AND DISCUSSION

XRD Analysis

Figure-1 evidenced the XRD configuration of undoped ZnO and Mg and Ti codoped ZnO (S_A, S_B and S_C) nanoparticles synthesized by soft chemical method at 450⁰C. All the peaks corresponded with hexagonal wurtzite structure of ZnO with lattice constants $a = b = 0.32$ nm and $c = 0.52$ nm (JCPDS Card No.36-1451). The peaks of (100), (101), (102), (110) and (103) were detected for pure ZnO. The peaks of (102), (110) and (103) disappeared when doped metals were inserted into the ZnO nanoparticles⁶. The peaks of (100), (002) and (101) intensities continuously decreased with doping agents and Debye Scherrer's formula was used to calculate the average nanoparticle size. Debye Scherrer's formula is as below:

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

As per the formula, D indicates the average particle size, λ indicates the incident wavelength of the X-ray beam, β indicates the full-width at half-maximum (FWHM) and θ indicates the Bragg's diffraction angle correspondingly. The calculated particle sizes were 51 nm for undoped ZnO and 34 nm, 32 nm, 27 nm for samples S_A, S_B and S_C of Mg, Ti codoped ZnO nanomaterials. The nanoparticles size of sample S_C was decreased when compared with undoped ZnO and samples S_A & S_B of Mg & Ti codoped ZnO.

Figure-2 evinced the Fourier Transform Infrared spectrum of prepared ZnO Np's and Mg & Ti codoped ZnO (S_A, S_B and S_C) nanoparticles. The bands were perceived at 476 cm⁻¹ for undoped ZnO, and at 441 cm⁻¹, 428 cm⁻¹ and 438 cm⁻¹ for samples S_A, S_B and S_C of Mg & Ti codoped ZnO nanoparticles were associated to metal oxide. It was acknowledged that the ranging of peak from 410 – 735 cm⁻¹ was related to Zinc oxide as elicited by Wu et al 2015⁷. Pure Zinc Oxide and synthesized samples (S_A, S_B and S_C) bands were estimated as 1371 cm⁻¹ and it was ascribed to the bending frequency of oxygen stretching mode. A band was noticed at 3443 cm⁻¹ for undoped Zinc Oxide and the bands were found at 3431, 3430 and 3430 cm⁻¹ for S_A, S_B and S_C of Mg, Ti codoped ZnO was ascribed to the stretching vibrations of O-H⁸.

Scanning Electron Microscope

Figure-3 evinced the surface morphology of Undoped ZnO and Mg and Ti codoped ZnO nanoparticles. The SEM images revealed that synthesized nanoparticles were in spherical morphology and the surface agglomeration was perceived. The nanoparticle size of undoped ZnO and Mg, Ti codoped ZnO nanoparticles were calculated to be around 80-90 nm.

EDX Analysis

Figure-4 shows EDX analysis of Undoped ZnO and Mg, Ti codoped ZnO nanoparticles. Fig.-4(i) indicated that the elements of Zn and O were present in undoped nanomaterials and Fig.-4(ii) indicated that Mg, Ti,

Zn and O were present in doped nanomaterials. The greater peak in the spectrum indicate the high concentration of element present in doped and undoped nanomaterials⁹. In Fig.-4 (i) & (ii), Zn element exhibited higher peaks than another element such as Mg, Ti and O. The result of EDX analysis confirmed that there were no impurities present in the sample.

Fig.-1: XRD Patterns of (i) Undoped ZnO and (ii) Mg_{0.05} Ti_{0.15} codoped Zn_{0.98}O (iii) Mg_{0.01} Ti_{0.01} codoped Zn_{0.98}O (iv) Mg_{0.15} Ti_{0.05} codoped Zn_{0.98}O

Fig.-2: Fourier Transform- Infrared Spectrum of (i) Undoped ZnO (ii) Mg_{0.05} Ti_{0.15} codoped Zn_{0.98}O (iii) Mg_{0.01} Ti_{0.01} codoped Zn_{0.98}O (iv) Mg_{0.15} Ti_{0.05} codoped Zn_{0.98}O

Fig.-3: SEM Analysis of (i) Undoped ZnO and (ii) Mg_{0.01} Ti_{0.01} codoped Zn_{0.98}O

Fig.-4: EDX Analysis of (i) Undoped ZnO and (ii) $\text{Mg}_{0.01}\text{Ti}_{0.01}$ codoped $\text{Zn}_{0.98}\text{O}$

Ultra Violet -Visible Spectroscopy

Figure-5 evinced the optical absorption of undoped ZnO and Mg, Ti codoped ZnO (S_A , S_B and S_C) nanoparticles. The wavelength of synthesized nanomaterials optical absorption spectra was 379 nm for undoped ZnO and 373 nm, 371 nm, 371 nm for S_A , S_B and S_C of Mg, Ti codoped ZnO nanoparticles respectively. The band gap energy values were calculated using the following equation,

$$E = (hc)/(\lambda) \quad (2)$$

As per the above equation, h indicates Planck's constant, c indicates the velocity of light and λ indicates the wavelength of light and the obtained values were 3.72eV for undoped ZnO and 3.70eV, 3.68eV, 3.64eV for samples S_A , S_B and S_C of Mg, Ti codoped ZnO nanoparticles. The small decrease in absorption was established in the presence of doping agents.

Fig.-5: Ultra-Violet –Visible Spectroscopic analysis of (i) Undoped ZnO (ii) $\text{Mg}_{0.05}\text{Ti}_{0.15}$ codoped $\text{Zn}_{0.98}\text{O}$ (iii) $\text{Mg}_{0.01}\text{Ti}_{0.01}$ codoped $\text{Zn}_{0.98}\text{O}$ (iv) $\text{Mg}_{0.15}\text{Ti}_{0.05}$ codoped $\text{Zn}_{0.98}\text{O}$

AFM Analysis

Figure.6.shows the AFM analysis of synthesized undoped ZnO & Mg, Ti codoped ZnO nanoparticles by soft chemical method. The average size of the particles was detected as 61 nm for Undoped ZnO and 41nm for Mg and Ti codoped ZnO which was in good agreement with XRD analysis. The appearance of AFM images with regular shape and the random arrangement was observed¹⁰.

Photodegradation of Undoped ZnO and Mg, Ti Codoped ZnO Np's

Figure-7 evinced the photo-degradation reaction for Congo red dye. The synthesized nanoparticles were absorbed by UV light, electrons were stimulated from the valence band to the conduction band. The light energy caused holes and reacted with water and hydroxyl radical was created. The hydroxyl radical was forceful, non-selective oxidant and oxidizing agent thereby resulting in the degradation of dyes. The light

energy on reaction with electrons and in turn with molecular oxygen resulting in the generation of superoxide radical anions, which was responsible for the degradation of dye solution.

Fig.-6: AFM Images of (i) Undoped ZnO (ii) $\text{Mg}_{0.01}\text{Ti}_{0.01}\text{Zn}_{0.98}\text{O}$

Fig.-7: Photodegradation Reaction of for Congo Red Dye

Photodegradation efficiency of Nanomaterials was calculated using the formula,

$$D (\%) = (A_0 - A_t) / (A_0) \times 100 \quad (3)$$

Where, D is the degradation efficiency (in %). A_0 is the UV absorption of dye with sunlight irradiation time (0 min) and A_t is the UV absorption of dye after UV-light irradiation (t-min).

Figure-8 (i) and (ii) shows the photodegradation efficiency of Undoped ZnO and Mg, Ti-doped ZnO nanocomposites with UV irradiation in various time stretch (30, 60, 90, 120, 150 and 180 mins). The photodegradation efficiency values calculated were 55% for Undoped ZnO and 91.5% for Mg and Ti codoped ZnO nanoparticles. The results of Photodegradation analysis of congo red dye with Undoped and doped ZnO photocatalyst clearly presented a higher dye removal efficiency of the Mg and Ti codoped ZnO nanoparticles. Therefore, the experimental results concluded that the Mg and Ti codoped ZnO nanoparticles were a respectable dye removal catalyst comparing Undoped ZnO nanoparticles. This route could be suitable for sewage and industrial water treatment.

Fig.-8: Photodegradation Efficiency of (i) Undoped ZnO (ii) $\text{Mg}_{0.01}\text{Ti}_{0.01}$ codoped ZnO

CONCLUSION

The present investigation revealed that a simple and low-cost technique of synthesis of Undoped ZnO and Mg, Ti codoped ZnO nanoparticles by soft chemical method and its photodegradation efficiency. XRD results confirmed that hexagonal wurtzite structure of Undoped ZnO and Mg, Ti codoped ZnO nanoparticles, then the average size of particle size calculated was 51 nm, 34 nm, 32 nm & 27 nm using Debye Scherrer's equation. SEM images exhibited the formation of nanoparticles and surface agglomeration was observed. EDAX analysis results clearly indicated the percentage of presence of material and its purity. The synthesized nanocomposites band gap was calculated using UV-Vis analysis and the result was 3.72 eV, 3.70 eV, 3.68 eV and 3.64 eV. From FT-IR studies, the peaks range 410 - 735 cm^{-1} verified the ZnO stretching mode. AFM study indicated the surface morphology and average particle size of nanomaterials. The photo-degradation efficiency of Mg and Ti codoped ZnO (91.5%) nanomaterials had superior performance than undoped ZnO (55%) nanomaterials against congo red dye solution under UV irradiation (180 min). This process is useful for wastewater treatment in many industries for the removal of hazardous chemicals for ecological remediation.

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