Well-organized Zinc oxide nanospheres with enhanced photocatalytic activity

S. Steplin Paul Selvin, I. Sharmila Lydia

***Abstract*— Synthesis of visible light driven ZnO nanospheres is of great importance in practical application, such as water purification. In this paper, cysteine capped ZnO (CCZ) nanospheres were prepared by microwave based biomolecule assisted chemical precipitation method. The CCZ nanospheres were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), Energy Dispersive X-ray spectrum (EDAX), photoluminescence (PL). The photocatalytic activity of CCZ nanospheres was estimated using Rhodamine B as model pollutant under visible light irradiation. The experimental results exhibited that cysteine molecule were doped into the lattices of ZnO nanospheres and shows noticeable increase in visible-light harvesting ability. The CCZ shows the highest photocatalytic activity than that of bare ZnO counterpart. The enhanced photocatalytic activity of CCZ nanospheres is ascribed owing to its adsorption capacity and enhanced visible light harvesting ability.**

***Index Terms*— Microwave processing; ZnO nanospheres; Porosity; Amino acid.**

I. INTRODUCTION

Over the years and still now, photocatalysis has been widely used in the part of environmental remediation because several types of contaminants can be decayed totally by photocatalytic active well-ordered semiconductor nanomaterials under visible light irradiation and further, it is a promising applications for renewable energy and clean environment [1]. Such well-ordered nanostructure semiconductors like nanospheres [2], nanoflowers [3], nanorods and nanosheets [4] have fascinated great attention owing to its physical and chemical properties and their significant applications in photocatalytic degradation of dyes. Among different photocatalysts zinc oxide is used as a significant semiconductor with band gap energy (3.37 eV) as well as a large exciton binding energy of 60 meV [5]. Nowadays, chemical vapor deposition, hydrothermal, Solvothermal, spray pyrolysis, sol-gel method, hydrothermal method, microwave, co-precipitation method, and biomolecule assisted synthesis [6-11] have been used to synthesize well-ordered nanostructure semiconductors. However, very few reports are presented regarding synthesis of nanoparticles (NPs) with aligned structure in a simple, short time and low cost methods. Among these methods, microwave based biomolecule assisted chemical precipitation method has new and promising focus in the preparation of zinc oxide nanospheres. Uses of biomolecules in the synthesis of nanospheres are also ways to practice green chemistry. In addition biomolecules not only control the morphology but also used as a dopant for various metal oxide nanospheres [12] Moreover, addition of amino acid not only alter the property of the photocatalyst but also used as a structural directing agent. Weilai Yu et al. [13] found that nonmetal doped ZnO is most extensively examined since its effectiveness in broadening the light responsive range of wide-bandgap semiconductors. There are several nonmetal species like C, N, S are available as an active dopant in photocatalysis. Doping ZnO with these nonmetal elements has shown to be promising approaches and induce stronger visible-light absorption. To date, several remarkable photocatalytic materials have shown exciting photocatalytic activity. Furthermore, the demand for exploring new materials with enhanced reactivity of known promising photocatalysts is also playing a crucial role in emerging technologies. Nevertheless, ZnO can only be activated by UV light and therefore, visible light driven ZnO nanospheres are highly expected. Bearing in mind, doping metal or nonmetal with ZnO is current interest to convert ZnO absorption from ultraviolet to visible region [14]. In this work, we present a visible light driven Cysteine capped ZnO nanospheres were prepared using microwave based biomolecule assisted chemical precipitation method and investigated the structure and morphology. Furthermore, it is known that the addition of cysteine onto ZnO altered their properties significantly. Therefore, the aim of the work is to investigate the Cysteine capped ZnO nanospheres and their enhanced photocatalytic activity over Rhodamine B dye degradation under CFL light irradiation. Here the CFL lamp was used as a visible light source in photodegradation of rhodamine B and it has many benefits like energy consumption, user friendly and also used in everyday life which opens an opening for practical application in photocatalytic degradation of dyes. Additionally, compared to other approaches this method is simple, low cost and environmental friendly with improved visible light responsive, more dye adsorption and show better efficiency on separation of photogenerated carriers, which shows the photocatalyst to be unique in the field of photocatalysis.

II. MATERIALS AND METHODS

All the chemicals in this study were analytical grade and used without further purification. Deionized water is used throughout the study.

A. Preparation of Cysteine capped Zinc Oxide

In a typical synthesis CCZ were prepared by the following method[10]. 0.1M $Zn(OAc)_2.2H_2O$ with calculated amount of cysteine were stirred magnetically for 30 min at 70 °C. To this 0.2 M NaOH was added and stirred continuously for 3 h and subjected to microwave irradiation for 3 min. Finally the

S. Steplin Paul Selvin, Research Scholar, PG & Research Department of Chemistry, Bishop Heber College, Tiruchirappalli- 620 017. Tamil Nadu, India. Mobile- 8870835376.

I. Sharmila Lydia, Associate Professor, PG & Research Department of Chemistry, Bishop Heber College, Tiruchirappalli- 620 017. Tamil Nadu, India Mobile- 9994293122.

precipitate was washed several times with water and ethanol. Then the resultant product was dried in oven at 80 °C for 4 h.

B. Characterization

The crystalline and phase purity of the products were examined by powder XRD on a Rigaku X-ray diffractrometer with Cu Ka radiation at 40 kV and 40 mA in steps of 0.020. The surface morphology of the as-synthesized samples was characterized using scanning electron microscopy (VEGA 3 TESCAN). EDAX spectrum was recorded using Bruker, The optical properties were analyzed by the Photoluminescence spectra, UV-Vis. Absorption studies for dye degradation were carried out using Perkin Elmer Lambda 35 UV-Vis. spectrophotometer. A low pressure CFL (70 W) were used as a visible light source respectively.

C. Photocatalytic activity

The photocatalytic activity of the CCZ nanospheres was evaluated by degradation of RhB under 70 W CFL light. The CFL was placed parallel to the 100 mL of glass tube container. The CCZ (50 mg) photocatalyst was suspended in a glass tube containing 100 mL of RhB solution (1 x 10^{-5} M). Before light irradiation, the suspensions were magnetically stirred in the dark for 10 min to ensure the adsorption equilibrium. Air was bubbled into the reactor for maintaining the required oxygen level. The suspension was (3 mL) was withdrawn at regular time interval. Then the catalyst was removed by centrifugation and the collected dye sample was monitored by UV–vis spectrophotometer.

III. Results and Discussion

A. Characterization of the as-synthesised nanospheres

The phase structure of the as synthesized ZnO and CCZ nanospheres was confirmed by **XRD** measurements (Fig. 1A). The pattern indicates strong and sharp peaks, which corresponds to standard diffraction pattern of hexagonal wurtzite structure of ZnO. The major peak shows at 31.80, 34.63, 36.63, 47.69, 56.72, 62.55, 66.57, 67.97 and 69.58 are assigned to (100), (002), (101), (102), (110), (103), (200), (112) and (201) planes of ZnO planes of the wurtzite structure, respectively. Interestingly the XRD pattern of CCZ show no much changes in the peak compared to pure ZnO which confirms the phase purity of as synthesized CCZ. Average particle size (D) of CCZ was calculated around 20 nm based on XRD peaks using Scherrer's equation (Eq.1). (1) Where D is the average crystalline size, λ is the applied wavelength, β is the line broadening at half the maximum intensity (FWHM) and Θ is Bragg's angle [15].

$$D = k\lambda/\beta \cos \Theta \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

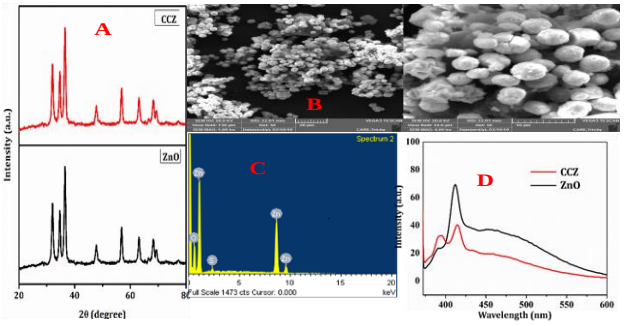

Fig.1. Characterization of the as-synthesised Cys/ZnO: A) XRD B) SEM image C) EDAX spectrum D) PL spectra

Surface morphology of nanoparticle plays an important role in photocatalytic application besides with all other applications. Fig. 1B shows the **SEM** images of the CCZ. In general, the surface morphology of the as synthesized sample was uniform and had sphere-like morphology without any aggregation.

Furthermore, the elemental composition of the catalysts was investigated with **EDX** spectra which, shows that the obtained product is CCZ (Fig. 1C).

PL studies are useful to find the different optoelectronic nature of doped semiconductor nanospheres. Fig.1D shows the room temperature PL spectra of bare ZnO and CCZ nanospheres. Photoluminescence occurs owing to the recombination of electron–hole pair in the semiconductor. The spectra show UV emission band at 388 nm for bare ZnO and CCZ exhibits UV emission at 383 nm and other luminescence band show broad green emission at 460 nm respectively. The addition of cysteine in the ZnO crystal lattice introduces distortion because sulphur has a larger Bohr radius than oxygen resulting the green light emission [16]. Further, the oxygen and zinc vacancies are produced due to the addition of sulfur resulting in the adsorption of O_2 and capture of the photo-induced electrons to help high photocatalytic efficiency of the catalyst [17].

B. Photocatalytic degradation of RhB

The **photodegradation efficiencies** of bare ZnO and CCZ photocatalysts were carried out with RhB as a model dye under CFL light with identical conditions are shown in Fig. 2a. RhB undergoes almost less than 10% degradation under CFL light irradiations even after 180 min.

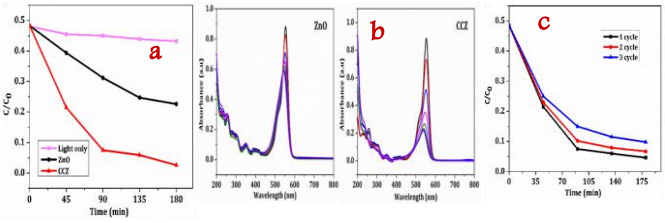

Fig.2. a) Photocatalytic activity of the as-synthesised materials b) UV-visible spectral changes for the degradation of Rhodamine B dye solution under visible light irradiation and c) Reusability

The photocatalytic activities of bare ZnO are resulted in 53.2 % degradation of RhB in the presence of CFL light. In addition, it was also observed that the CCZ had better photocatalytic activity over RhB dye under CFL light irradiation with around 94.62 % (Fig. 2a). This could be attributed to the accumulation of degradation products on the surface of photocatalyst. The photocatalytic degradation on the surface of ZnO nanospheres increases with increasing catalyst dosage in the dye solution. However, further increase in catalyst dosage above 50 mg caused a significant reduction in degradation efficiency due to the agglomeration of catalysts in solutions which in turn, reduced the degradation rate.

Fig. 2b shows the **UV–vis spectral changes** of RhB during photocatalysis under CFL light irradiation at different time intervals. The intensity at 554 nm decreases gradually during the photodegradation of RhB processes via N-deethylation and aromatic ring opening [18]. Furthermore, it revealed that the band at 554 nm decreased markedly with hypochromic

shift and almost disappeared after 180 min of irradiation in presence of CCZ nanospheres.

The photoactivity of the catalyst has been investigated in three consecutive cycles in order to find the **reusability** of the catalyst in the dye solution. Identical experimental conditions was carried out for three consecutive cycles (50 mg of CCZ, 100 mL of RhB =1 x 10^{-5} M) and the obtained results are comparatively shown in Fig. 2c. The photoactivity of the recycled photocatalyst has nearly retained its efficacy after three cycles. It clearly exposes that the synthesized CCZ nanospheres shows effective photocatalytic activity for the degradation of RhB under CFL light irradiation.

IV. Conclusion

The study results found that the preparation method exhibited a significant influence on the surface morphology, crystal structure, and photocatalytic activity of CCZ nanospheres. The experimental results proved that the CCZ catalysts exhibited higher photoactivity than bare ZnO and the 50 mg CCZ photocatalyst showed an optimum performance in the removal of RhB dye. Moreover, the enhanced photocatalytic activity could be attributed to the synergistic effect between ZnO and cysteine molecules which further reduces the particle size of the nanospheres. Hence, increases the surface area of CCZ compare to bare ZnO. Further, loading of cysteine with ZnO may suppress recombination of electron–hole pairs occurred by loading cysteine doped ZnO nanospheres. This decrease in the PL intensity will decrease the rate of electron–hole recombination, which might favored the photocatalytic degradation of dyes.

References

[1] C. C. Wang, X. D. Du, J. Li, X. X. Guo, P. Wang, J. Zhang, "Photocatalytic Cr (VI) reduction in metal-organic frameworks: A mini-review", Appl. Catal.B: Environmental, 193 (2016) 198-216.

[2] H. B. Bakrudeen, M. Sugunalakshmi, B. S. Reddy, "Auto-fluorescent mesoporous ZnO nanospheres for drug delivery carrier application", Materials Sci. and Engg: C, 56 (2015) 335-340.

[3] A. Samanta, D. K. Chanda, P. S. Das, J. Ghosh, A. Dey, S. Das, A. K. Mukhopadhyay, "Synthesis of mixed calcite–calcium oxide nanojasmine flowers", Ceramics International, 42 (2016) 2339-2348.

[4] A. A. Othman, M. A. Osman, E. M. M. Ibrahim, M. A. Ali, "Sonochemically synthesized ZnO nanosheets and nanorods: Annealing temperature effects on the structure, and optical properties", Ceramics International, 43 (2017) 527-533.

[5] K. Y. Tomizaki, S. Kubo, S. A. Ahn, M. Satake, T. Imai, "Biomimetic alignment of zinc oxide nanoparticles along a peptide nanofiber", Langmuir, 28 (2012) 13459-13466.

[7] Y. Benkhetta, A. Attaf, H. Saidi, A. Bouhdjar, H. Benjdidi, I. B. Kherchachi, M. Nouadji, and N. Lehraki. "Influence of the solution flow rate on the properties of zinc oxide (ZnO) nano-crystalline films synthesized by ultrasonic spray process", Optik-International Journal for Light and Electron Optics, 127 (2016) 3005-3008.

[8] M. Zobel, H. Chatterjee, G. Matveeva, U. Kolb, R. B. Neder, "Room-temperature sol–gel synthesis of organic ligand-capped ZnO nanoparticles", J. of Nanoparticle Res., 17 (2015) 1-11.

[9] Y. Hu, H. J. Chen, "Preparation and characterization of nanocrystalline ZnO particles from a hydrothermal process", J. of Nanoparticle Res., 10 (2008) 401-407.

[10] Y. Guo, B. Chang, T. Wen, C. Zhao, H. Yin, Y. Zhou, Y. Wang, B. Yang, S. Zhang, "One-pot synthesis of graphene/zinc oxide by microwave irradiation with enhanced supercapacitor performance", RSC Advan., 6 (2016) 19394-19403.

[11] A. N. El-Shazly, M. M. Rashad, E. A. Abdel-Aal, I. A. Ibrahim, M. F. El-Shahat, A. E. Shalan, "Nanostructured ZnO photocatalysts prepared via surfactant assisted Co-Precipitation method achieving enhanced photocatalytic activity for the degradation of methylene blue dyes". J. of Environ. Chem. Engg., 4 (2016) 3177-3184.

[12] Y. Lei, S. Song, W. Fan, Y. Xing, H. Zhang, "Facile synthesis and assemblies of flowerlike SnS_2 and In^{3+}-doped SnS_2: hierarchical structures and their enhanced photocatalytic property". The J. of Phy. Chem.C, 113 (2009) 1280-1285.

[13] K. Lv, J. Hu, X. Li, M. Li, "Cysteine modified anatase TiO_2 hollow microspheres with enhanced visible-light-driven photocatalytic activity". J. of Mole.Catalysis A: Chemical, 356 (2012) 78-84.

[14] W. Yu, J. Zhang, T. Peng, "New insight into the enhanced photocatalytic activity of N-, C-and S-doped ZnO photocatalysts". Applied Catalysis B: Environmental, 181 (2016) 220-227.

[15] W. Yu, J. Zhang, T. Peng, "New insight into the enhanced photocatalytic activity of N-, C-and S-doped ZnO photocatalysts:, Applied Catalysis B: Environmental, 181 (2016) 220-227.

[16] M. Ramani, S. Ponnusamy, C. Muthamizhchelvan, E. Marsili, "Amino acid-mediated synthesis of zinc oxide nanostructures and evaluation of their facet-dependent antimicrobial activity". Colloids and Surfaces B: Biointerfaces, 117 (2014) 233-239.

[17] X. Y. Xie, P. Zhan, L. Y. Li, D. J. Zhou, D. Y. Guo, Meng, J. X. Meng, W. J. Zheng, "Synthesis of S-doped ZnO by the interaction of sulfur with zinc salt in PEG200", Journal of Alloys and Compounds, 644 (2015) 383-389.

[18] A. Senthilraja, B. Krishnakumar, B. Subash, A. J. Sobral, M. Swaminathan, M. Shanthi, "Sn loaded Au–ZnO photocatalyst for the degradation of AR 18 dye under UV-A light", Journal of Industrial and Engineering Chemistry, 33 (2016) 51-58.

[19] Q. Wang, J. Hui, L. Yang, H. Huang, Y. Cai, S. Yin, Y. Ding, "Enhanced photocatalytic performance of Bi_2O_3/H-ZSM-5 composite for rhodamine B degradation under UV light irradiation". Applied Surface Science, 289 (2014) 224-229.