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Enhanced Photocatalytic Properties of ZnO Nanoparticles for the Degradation of Rhodamine B

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ABSTRACT

This study investigates the photocatalytic properties of hydrothermally synthesized ZnO nanoparticles for the degradation of RhB. The structural and morphological properties of the product have been characterized by XRD, EDS, SEM and TEM. Structural measurements reveal that single crystalline nanoparticles in the range of 9 to 130 nm are formed. The elemental composition is analyzed by EDX. The photocatalytic properties demonstrate that the ZnO nanoparticles stand an active photocatalyst which completely degrade RhB in 30 min. Therefore ZnO nanoparticles may have significant implications for degradation of organic contaminants and for the environment remediation.

1. Introduction

Effluents from textile, paper mills and other industries are a serious threat to environment because it contains perfumed toxic dyes which are that are challenging to decompose due to their highly stable chemical/molecular structure [1-3]. Among the variety of dyes used in the dying industries, Rhodamine B (RhB) is the most frequently used dye for paper and textile stuff dying, and in cosmetics and pharmaceuticals. Semiconductor photocatalysts have attained special attention due to their outstanding electrical, photocatalytic and optical properties [4]. Their characteristic electronic structure of filled valance band (VB) and empty conduction band (CB) [5] has made these a strong candidate for decomposition of variety of organic water pollutants.

Among the most extensively studied semiconductor photocatalysts, zinc oxide has attracted substantial interest in photocatalysis because it is physically and chemically stable having broad functionality, good oxidative ability, and availability at commercial scale on low cost [6-8]. Wide band gap of 3.37 eV and exciton binding energy of 60 meV provide significant opportunity of electronic, photonic and spin based functionalities leading to large number of applications in particular in photocatalytic activities [9], gas sensing [10], photovoltaic and high speed display devices [11-14]. ZnO has emerged as the most efficient photocatalyst in the photodegradation of some organic compounds in the presence of sunlight [15]. As the photocatalytic reaction occurs at the interface of the catalyst and the organic pollutant, therefore the surface morphology and the particle dimensions are important for the photocatalytic reaction to occur. Moreover it has been demonstrated that functional performance of ZnO is size, morphology and crystallinity dependent which are determined by synthesis conditions.

The control over the size and morphology of ZnO particles from micro to nanometer is a challenge and gradually becomes a dynamic area of research in the past decade [16-17]. Different synthesis strategies have been employed for the synthesis of ZnO nanostructures of different sizes and morphologies [9-10, 16, 18-20]. In this article we have reported the synthesis of low dimensional ZnO nanoparticles by hydrothermal method and demonstrated its photocatalytic activity for RhB degradation.

2 Experimental

The model dye Rhodamine B (RhB) and Zn sheet (99.9%) was bought from ALFA AESAR, and Sinopharm chemical reagent Co. Ltd respectively. Hydrogen per Oxide (H_2O_2) (34.5-36.5%) and NaOH were obtained from Sigma-Aldrich, Germany. analytical grade chemical were used without extra purification. De-ionized water was used during the synthesis.

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In order to synthesize ZnO NPs, stock solutions of 1.6g NaOH and 10 ml of hydrogen peroxide (H_2O_2) was prepared in 20 ml de-ionized water under continuous stirring and transferred to Teflon lined autoclave. A polished Zn sheet was inserted into the autoclave as seeding source for the collection of product and shifted in an electric oven for heat treatment at 180°C for 5-6 hrs. After the completion of reaction the autoclave was cooled down to room temperature and resultant white product was obtained over the Zn sheet surface. The sheet was rinsed several times with de-ionized water and dried at 70°C for 6 hrs.

Different characterization tools such as X-ray diffractometer (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS) was used to investigate the shape, structure and morphology of ZnO NPs. Phase purification of the product was measured by Regaku (Dmax III A) X-ray diffractometer (XRD) equipped with graphite-monochromatized high-intensity Cu Kα (λ = 1.54178 Å). Morphological and compositional analysis was performed by SEM (SEM-6301F) and EDS attached to SEM systems. Microstructure investigation was done by TEM and HRTEM. Xenon UV light source (Perfect Light, PLS-SXE 300UV) was used as ultra-violet (UV) light source and UV-vis absorption spectrum were collected by SPECORD 205 UV-Vis spectrometer (Analytikjena).

Aqueous solution of an organic model dye RhB was used to study the photocatalytic activity. Pyrex glass vessel was used as photo reactor. The reaction suspensions were prepared in 50 ml of 10 µmolar RhB aqueous solution containing 25 mg ZnO NPs as photocatalyst. The suspension was then exposed to UV light source.

Heat produced in the reaction environment was dissipated by forced convection using electric fan. Prior to irradiation the suspension was sonicated for 5 min and then magnetically stirred for 10 min in the dark to achieve the adsorption-desorption equilibrium of RhB in the presence of catalyst. Before UV-exposure a 3 ml of the sample was also taken as a reference. After UV irradiation started, a 3 ml of the irradiated sample was taken out at regular intervals, centrifuged to remove the entire catalyst and UV-Vis spectra were measured.

3 Results and discussions

The crystal structure of the synthesized ZnO NPs is characterized by XRD. Fig. 1 shows the XRD pattern of ZnO NPs. It displays that all the diffraction peaks are well matched to hexagonal wurtzite structure of ZnO (JCPDS # 00-036-1451).

The SEM images of ZnO NPs at different magnifications and the corresponding EDS pattern of the NPs is depicted in Fig. 2. It shows that most of the product mainly consists of large number of spherically shaped NPs of varying diameter between 9 to 130 nm. The EDS pattern of the NPs shows that only Zn and O are present in the specimen indicating the successful growth of ZnO NPs. The carbon peak appears from the specimen holder.

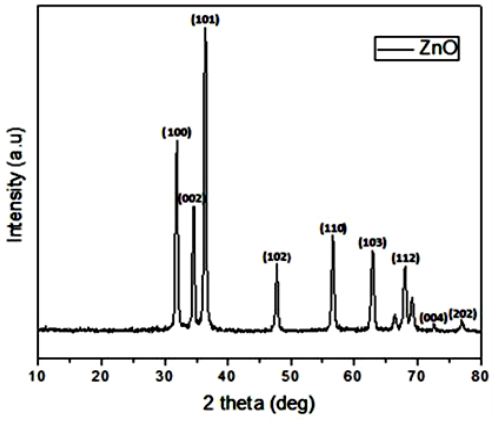

Fig. 1: XRD pattern of ZnO nanoparticles

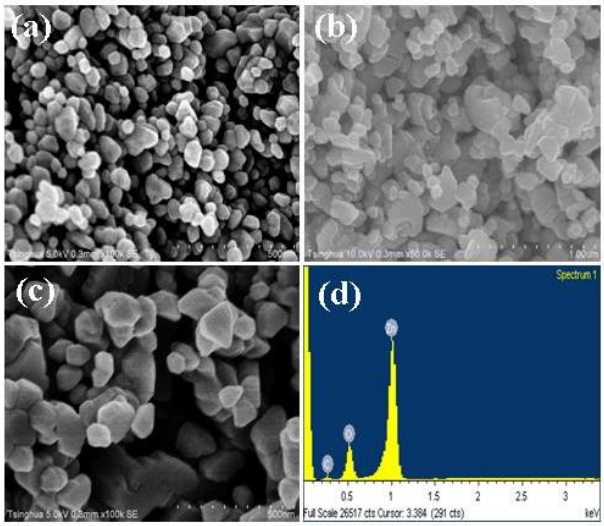

Fig. 2: (a-c) SEM images of ZnO nanoparticles, **(d)** EDS mapping analysis

The microstructural analysis of the NPs is further characterized by transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM). Fig. 3 (a, b) shows the low and high magnification images of ZnO NPs. It shows that the product contains huge amount of small nanoparticles. The HRTEM image of the nanoparticles is shown in Fig. 3 (c, d). It reveals that the nature of each nanoparticle is single crystalline. The measured inter planner distances is ~0.25 nm and 0.19 nm that corresponds to the d spacing of the diffraction planes (101) and (102) of hexagonal ZnO which agrees well with the XRD results**.**

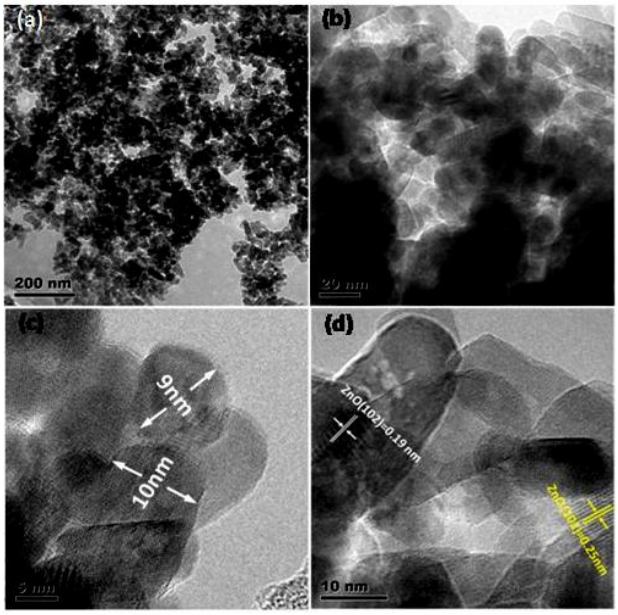

Fig 3: Transmission Electron Microscopy of (a, b) low and high magnification, (c,d) high resolution transmission TEM images of ZnO NPs

Figure 4 shows a sequence of UV-Visible absorption spectra of aqueous solution of 10 µM RhB in the presence of 30 mg of ZnO NPs as catalyst under increasing UV light irradiation time. It is evident the characteristic absorption peak decreases rapidly with increasing irradiation time and completely vanish in 30 min as shown in 4a. No change is further observed beyond this time. In contrast to this, complete degradation of RhB is not observed in the absence of ZnO NPs even after one hour as evident from Fig. 4b. It indicates that ZnO NPs are good photocatalyst under UV light source. Fig. 5 shows variation in the RhB degradation with time (C_t/C_o) in the presence and absence of photocatalyst. It is evident that blank experiment (without catalyst) shows negligible degradation on the RhB concentration under UV irradiation. Only 20 % of the dye is bleached off in 1 hr.

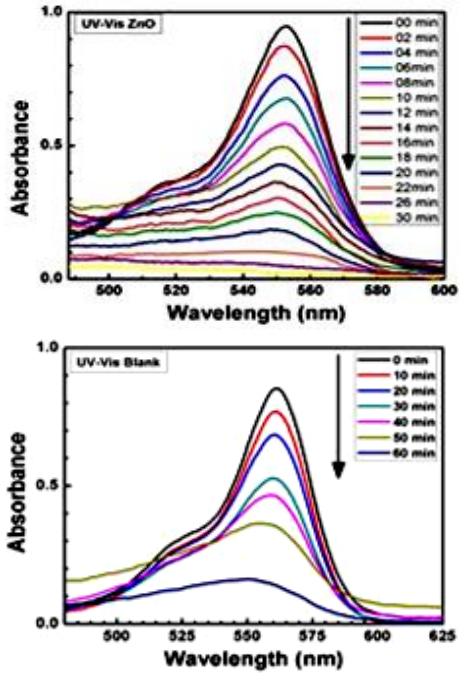

Fig 4: Photo-degradation of dye (a) in the presence of Zinc Oxide, and (b) in the absence of photo-catalyst

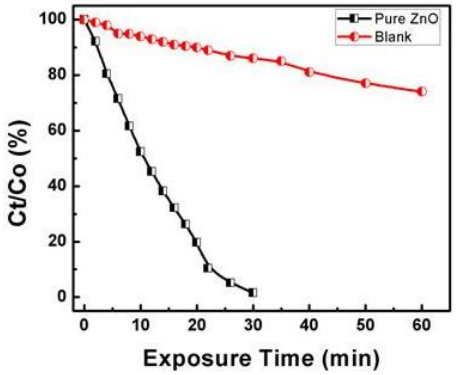

Fig 5: Photo-degradation kinetic curves of dye in the presence of ZnO catalyzed under UV-visible light irradiation

In comparison 100% of the dye is decomposed in 30 min when ZnO NPs are used as photocatalyst. Therefore, the results demonstrate that the ZnO NPs stand promising for RhB degradation. The inter spacing distances between NPs provides an essential platform for holding the photo separated carriers and plays a significant role for redox reaction, delays the recombination of the charge carriers, thus improving the catalytic activity of ZnO.

4 Conclusions

In this work ZnO nanoparticles were successfully synthesized by using hydrothermal method. The structural and morphological characterization demonstrated that the obtained product was highly crystalline and contained small nanoparticles in the range of 9-130 nm. The photocatalytic measurements reveal that these nanoparticles provide a novel pathway to decompose organic dye molecules. The enhanced photocatalytic performance is due to the high surface area of NPs. These NPs will be very useful for environmental applications.

References

[1]. T.J. Whang, M.-T. Hsieh and H.H. Chen, "Visible light photocatalytic degradation of methylene blue with laser induced Ag/ZnO nanoparticles", Appl. Surf. Sci. vol. 258, pp. 2796-2801, 2012.

[2]. N. K. Janjua, M. Mumtaz, A. Yaqub, S. Sabahat and A. Mujtaba, "Electrocatalytic activity of $LiNiPO_4$ and the copper doped analogues towards oxygen reduction" The Nucleus, vol. 51, pp. 109-115, 2014.

[3]. S. Adil, A. Mashiatullah, M. Asma, A. Ghaffar, S. Khan and J. Abid, "Adsorption of heavy metals by bio-chars produced from pyrolysis of paper mulberry from simulated industrial wastewater", The Nucleus, vol. 51, pp. 323-327, 2014.

[4]. S.A. Ansari, A. Nisar, B. Fatma, W. Khan and A.H. Naqvi, "Investigation on structural, optical and dielectric properties of Co doped ZnO nanoparticles synthesized by gel-combustion route", Mater. Sci. Eng. B, vol. 177, pp. 428-435, March 2012.

[5]. W. Lu, S. Gao and J. Wang, "One-pot synthesis of Ag/ZnO self-assembled 3D hollow microspheres with enhanced photocatalytic performance", J. Phys. Chem. C, vol. 112, pp.16792-16800, October 2008.

[6]. R. Georgekutty, M.K. Seery and S.C. Pillai, "A highly efficient Ag-ZnO photocatalyst: synthesis, properties, and mechanism" J. Phys. Chem. C, vol. 112, pp.13563-13570, 2008.

[7]. M. Afzaal, M.A. Malik and P. O'Brien, "Preparation of zinc containing materials", New J. Chem., vol. 31, pp. 2029-2040, 2007.

[8]. T.J. Kuo, C.N. Lin, C.L. Kuo and M.H. Huang, "Growth of ultra long ZnO nanowires on silicon substrates by vapor transport and their use as recyclable photocatalysts", Chem. Mater., vol. 19, pp. 5143-5147, 2007.

[9]. M. Hussain, M. Ahmad, A. Nisar, H. Sun, S. Karim, K. Maaz, S.D. Khan, M. Iqbal and S. Z. Hussain, "Enhanced photocatalytic and electrochemical properties of Au nanoparticles supported TiO_2 microspheres", New J. Chem., vol. 38, pp. 1424-1432, 2014.

[10]. X. Liu, J. Zhang, L. Wang, T. Yang, X. Guo, S. Wu and S. Wang, "3D hierarchically porous ZnO structures and their functionalization by Au nanoparticles for gas sensors", J. Mater. Chem., vol. 21, pp. 349-356, 2011.

[11]. Z. W. Pang, Z.R. Dai and Z. L. Wang, "Nanobelts of semiconducting oxides", Science, vol. 291, pp. 1947-1949, March 2001.

[12]. L. Bahadur and T.N. Rao, "Photoelectrochemical investigations on particulate ZnO thin film electrodes in non-aqueous solvents", J. Photochem. Photobiol. A, vol. 91, pp. 233-240, November 1995.

[13]. J.B. Norris, J. Anderson, J.F. Wager and D.A. Keszler, "Spin-coated zinc oxide transparent transistors", J. Phys. D: Appl. Phys., vol. 36, pp. 105-107, October 2003.

[14]. J-B Lee, H-J. Lee, S-H. Seo and J-S. Park, "Characterization of undoped and Cu-doped ZnO films for surface acoustic wave applications", Thin Solid Films, vol. 398, pp. 641-646, 2001.

[15]. S. Sakthivel, B. Neppolian, M.V. Shankar, B. Arabindoo, M. Palanichamy and V. Murugesan, "Solar photocatalytic degradation of azo dye: comparison of photocatalytic efficiency of ZnO and TiO_2", Sol. Energy Mater. Sol. C., vol. 77, pp. 65-82, April 2003.

[16]. J. Das and D. Khushalani, "Nonhydrolytic route for synthesis of ZnO and its use as a recyclable photocatalyst", J. Phys. Chem. C vol. 114, pp. 2544-2550, January 2010.

[17]. Y.H. Zheng, C.Q. Chen, Y.Y. Zhan, X.Y. Lin, Q. Zheng, K.M. Wei, J.F. Zhu and Y.J. Zhu, "Luminescence and photocatalytic activity of ZnO nanocrystals: Correlation between structure and property", Inorg. Chem., vol. 46, pp. 6675-6682, July 2007.

[18]. B. Li and Y. Wang, "Facile synthesis and enhanced photocatalytic performance of flower-like ZnO hierarchical microstructures", J. Phys. Chem. C, vol. 114, pp. 890-896, 2010.

[19]. H. Lu, S. Wang, Li Zhao, J. Li, B. Dong and Z. Xu, "Hierarchical ZnO microarchitectures assembled by ultrathin nanosheets: hydrothermal synthesis and enhanced photocatalytic activity", J. Mater. Chem., vol. 21, pp. 4228-4234, February 2011.

[20]. S.A. Ansari, M. M. Khan, J. Lee and M.H. Cho, "Highly visible light active Ag-ZnO nanocomposites synthesized by gel-combustion route", J. Ind. Engg. Chem., vol. 20, pp. 1602-1607, July 2014.