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ENHANCEMENT IN THE PHOTOCATALYTIC ACTIVITY OF TiO_2-ZnO NANOCOMPOSITES SYNTHESIZED BY MICROWAVE ASSISTED METHOD

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ABSTRACT

Objective: To develop a new class of natural fiber based polymer composites to explore the potential of coir fiber, Rice Husk and Saw Dust. To fabricate the different composite by varying the fiber fraction and matrix fraction. To fabricate the hybrid composite by using coir fiber, Rice Husk and Saw Dust as a reinforcement and Unsaturated poly propylene as a matrix material. The present work reports on study of TiO_2-ZnO photocatalyst with different ZnO content which is prepared via a microwave assisted method. This is simple, ecofriendly, an energy efficient and cost effective method.

Materials and Methods: The 99% purity of titanium tetra-isopropoxide (TTIP), 99% purity of zinc nitrate, 99% purity of surfactant Cetyltrimethylammonium bromide and Sodium dodecyl sulphate (Spectrochem Pvt. Ltd., India), absolute ethanol (99.9%), ammonia.

Result: Structural mechanism is closely related to the crystallite structure, which has been studied by using XRD technique. The X-ray diffraction patterns of various ratios of TiO_2/ZnO composites. In the sample 'T' determined characteristics 2θ values and [hkl] planes are 25.06° [101], 37.59° [004], 48.01° [200], 62.31° [204] ascribed to reflections of anatase TiO_2 which is comparable with JCPD Card No. (21-1272)

Conclusion: TiO_2-ZnO nano particles have been prepared by energy competent, cost efficient and an ecofriendly microwave assisted method.

Keywords: - Degradation, Microwave, Photo catalyst, Methyl Orange.

INTRODUCTION

A nanomaterial is most important for novel applications in different fields like semiconductor [1] gas sensor [2], antimicrobial activity [3], photocatalysis [4], and hydrogen generation [5].The photocatalytic splitting of water on TiO_2 electrodes was investigated by Fujishima and Honda in 1972 [6]. This event was noticeable for the start of new era in heterogeneous photocatalysis. TiO_2 has been widely accepted photocatalyst because of non-toxic nature, high oxidizing power, and low price [7-9]. The photocatalysis method with TiO_2 is very capable for the water cleansing, since a lot of organic compounds can be decomposed and mineralized by the oxidation and reduction reactions [10].

An elevated effectiveness of TiO_2 photocatalyst is poor due to its large band gap (3.2 eV) as well as its huge charge carrier recombination rate (nanosecond) [14,15]. Hence, it is very necessary to extend a new catalyst which holds high potential for photocatalytic activity. The modification of TiO_2 by combining with other metal oxides (e.g., WO_3, ZnO, NiO or CoO) is an approach that has received a lot of awareness to develop the photocatalytic action of TiO_2 and that has been considered as a competent route to boost the lifetime of the charge carrier also. The pairing of two semiconductors can be tune to the preferred band gap engineering [16, 17]. Photocatalytic oxidation represents a striking explanation due to the capability to oxidize organic contaminants totally for the conversion of CO_2, H_2O and mineral acids [18].

In the present work, we have synthesized TiO_2-ZnO nanocomposites, these nanomaterials are prepared by a microwave assisted process. The synthesized nanomaterials were thoroughly analyzed by numerous techniques to predict the internal structure and composition. Its photocatalytic nature was also considered by using MO as a model organic pollutant.

EXPERIMENTAL

Materials

The 99% purity of titanium tetra-isopropoxide (TTIP), 99% purity of zinc nitrate, 99% purity of surfactant Cetyltrimethylammonium bromide and Sodium dodecyl sulphate (Spectrochem Pvt. Ltd., India), absolute ethanol (99.9%), ammonia (Loba Chemie Pvt. Ltd., India) ware purchased. All analytical grade chemicals were used as received for the preparation of different solutions. Every solution ware all set in Millipore water obtainable from Millipore water system.

Preparation of mixed metal oxides with TiO_2

TiO_2-ZnO nanocomposites were prepared by the simple microwave assisted method using titanium tetra-isopropoxide, zinc nitrate, as a source of titanium and zinc. TiO_2-ZnO nanocomposites were prepared by cautiously addition of (0.1 M) TTIP in ethanol (100 mL) with constant stirring to get clear solution. Further sufficient amount of surfactant solution (1% CTAB + 1% SDS) was mixed with nonstop stirring. In the preparation of TiO_2-ZnO nanocomposite, the zinc nitrate solution was varied from 1, 3, and 5 wt%. The essential quantity of zinc nitrate solution was added to get the desired composition. The ammonia solution (aqueous) was mixed dropwise under continuous stirring condition, with special arrangement at room temperature until the solution reached up to pH=8. After the entire precipitation, the precipitate was washed with millipore water and acetone for numerous times to make sure total removal of impurities. Then precipitate was kept to microwave treatment for 20 min. in a household microwave oven (Input 900W, 250 MHz, LG Make) by on-off rotation (20s on-40s off). The dry powder was grounded with the help of agate mortar and pestle and calcined at 300°C for 3 hrs in a temperature restricted muffle furnace. These prepared samples such as TiO_2, TiO_2-ZnO (1, 3, and 5 wt. % ZnO) and ZnO were denoted as T, TZ1, TZ2, TZ3, and Z respectively.

Characterization of TiO_2-ZnO nanocomposites

Wide-angle X-ray diffraction (XRD) of the oxides were taken on a P Analytical PXRD system (Model X-Pert PRO-1712) (Cu Kα radiation, λ= 1.54Å) in the 2θ range (20-80°). The phases of nanomaterials were identified by comparison with JCPDS cards. The shape and size of the materials was gained by using transmission electron microscopy with model TEM (JEOL 3010).

Photocatalytic Experiment

Photocatalytic study of TiO_2-ZnO was calculated by testing the degradation of MO as a model impurity by using UV light (365 nm). So as to find the most photocatalytic action of composite, catalyst amount was vary from 0.75 to 1.5 g/dm^3. The quartz photoreactor was kept in steel container along with magnetic stirrer. Philips (HPL-N, 250 W) light source was used which has Lumens of 12750. Outer side of the bulb was broken and just inside filament is used as a light source. The distance of lamp was kept 5 cm above the dye solution. In the given experiment the photocatalyst was added in photoreactor having MO (100 mL, 20 ppm). At a particular time period, samples were withdrawn and centrifuged to remove photocatalyst. The absorbance of the clear solution was recorded by using UV-Vis Spectrophotometer (Shimadzu, Model-UV-3600) to monitor the concentration of dye.

RESULTS AND DISCUSSION

Characterization of TiO_2-ZnO nanoparticles

XRD

Structural mechanism is closely related to the crystallite structure, which has been studied by using XRD technique. **Fig. 1** shows the X-ray diffraction patterns of various ratios of TiO_2/ZnO composites. In Fig.1, the sample 'T' determined characteristics 2θ values and [hkl] planes are 25.06° [101], 37.59° [004], 48.01° [200], 62.31° [204] ascribed to reflections of anatase TiO_2 which is comparable with JCPD Card No. (21-1272) [19]. For the sample 'Z' determined characteristics 2θ values and [hkl] planes, all the diffraction patterns are observed at 31.82° [100], 34.47° [002], 36.34° [101], 47.69° [102], 56.63° [110] and 62.91° [103] which can be indicates a hexagonal wurtzite structure and shows the values of standard data (JCPDS 36-1451) [20]. Meanwhile, for the sample TZ1, TZ2 and TZ3 no detection of ZnO peaks in the XRD pattern due to low content of Zn. Approximately each and every diffraction peak of the samples indexed to the anatase TiO_2 showing that Zn^{2+} were dissolved into the TiO_2 host lattice without disturbing the crystal structure of TiO_2. The possibility of substitution of Zn^{2+} is ruled out due to difference in ionic radii Ti^{4+}=0.61 and Zn^{2+} = 0.74pm.

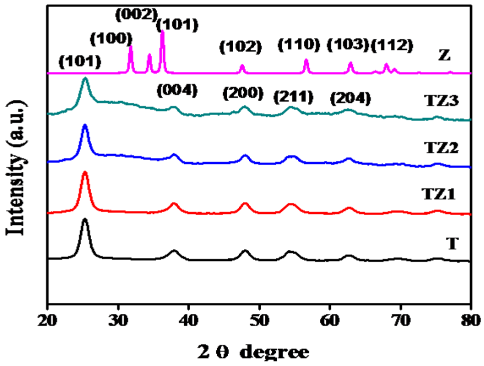

Fig.1: X-ray diffractograms of T (TiO_2), TZ1 (TiO_2-ZnO :1 wt% ZnO), TZ2 (TiO_2-ZnO :3 wt%), TZ3 (TiO_2-ZnO :5 wt%), Z (ZnO) nanoparticles

The average crystallite size of samples T, TZ1, TZ2, TZ3 and Z was calculated by using Scherrer's relation:

$$t = 0.9\lambda/\beta \cos\theta \quad \textbf{(Eq....1)}$$

where, λ is wavelength of X-ray in Å, θ is scattering angle in degree, β is [FWHM] full width at half maximum in radian. The comparatively large width of peaks of the XRD patterns suggests crystallites are lesser in size [21]. At 300°C the normal crystallite size for sample T was observed to be 15 nm, As the Zn content increase from 1 to 5 wt %, the broadening of the strong peak [101] gradually increases which indicates the smaller crystallite size of the material. It was found found that the sample 'T' has an average size of 15 nm and it reduces up to 12 nm for TZ2. The Z sample has an average crystallite size of 25 nm.

TEM Result:

Morphology of the nanomaterials was characterized by TEM analysis as indicated in Fig. 2(a). The found result reveals that as prepared TZ2 is in the form of pseudo-cube like nature with narrow size distribution. Particles size is in between 10-20 nm while the average particle size from TEM was observed to be 15 nm.

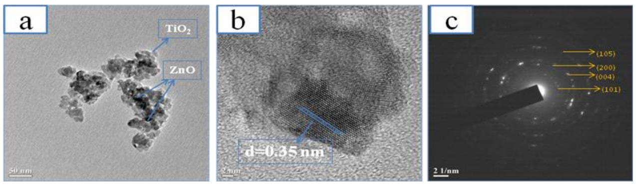

Fig.2: TEM Image of a) TZ2 (3 wt% ZnO) Nanoparticles b) HRTEM image of TZ2 c) SAED Pattern of TZ2

The HR-TEM image **(Fig.2(b))** indicates the lattice fringes, which is used for phase identification and found to be 0.35 nm. The value corresponds to lattice spacing of (101) plane in the anatase phase. Selected area electron diffraction pattern (SAED) matches to anatase phase with an excellent crystallinity as indicates **in Fig. 2(c)**. Particles shows crystalline nature with anatase phase are clearly indicated by Lattice fringes.

Factors affecting photocatalytic degradation of methyl orange

Effect of Concentration of ZnO for Photocatalysis: Fig.3 shows the photocatalytic degradation of MO on TiO_2-ZnO (TZ1-TZ3) photocatalyst with variable concentrations of 1, 3 and 5 wt % ZnO. From figure it can be accomplished that, the entire composite samples (TZ1-TZ3) shows improved degradation effectiveness of MO as compared to pristine TiO_2 and ZnO. More significantly, due to the presence of a TiO_2-ZnO composite, recombination of the photogenerated electron–hole charge carriers were noticeably reduced.

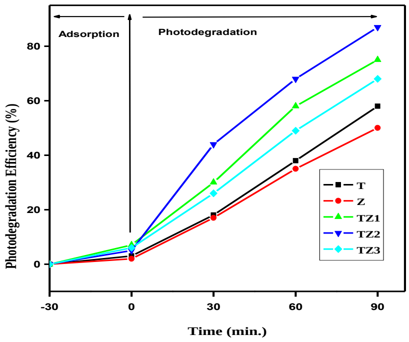

Fig. 3: Effect of concentration of ZnO on TiO_2 for MO degradation

Organic dye pollutants (MO) are oxidized by superoxide radical anions ($O_2^{-\cdot}$) and (·OH) ions which are highly active species to CO_2 and H_2O products [22]. The optimal TZ2 (3 Wt % ZnO) photocatalyst shows highest 85% degradation of methyl orange within 90 min for 1 g/dm^3 photocatalyst which seems to be excellent result.

CONCLUSIONS

In summary, TiO_2-ZnO nanoparticles have been prepared by energy competent, cost efficient and an ecofriendly microwave assisted method. It was observed that for TZ2 nanomaterials, crystallite size was observed to be 12 nm thereafter the crystallite size of the photocatalyst was more or less constant. The obtained nanomaterials are pseudo-cube in shape. A 85% degradation of MO was achieved by utilizing TZ2 (3 Wt % ZnO) photocatalyst within 90 min. for 1 g/dm^3 photocatalyst under UV- light irradiation.

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