SOL-GEL SYNTHESIZED Fe$_2$O$_3$-DOPED TiO$_2$ NANOCOMPOSITES AND ITS MORPHOLOGICAL STUDIES

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Abstract

Fe$_2$O$_3$-TiO$_2$ nanocomposites were obtained by sol-gel method using PVP-PEG as templating agent. The powder X-ray diffraction (XRD) patterns of the nanocomposites reveal the crystal structure of Fe$_2$O$_3$ as hematite and maghemite and TiO$_2$ is in anatase phase. The average crystallite sizes of Fe$_2$O$_3$-TiO$_2$ (PVP-PEG), Fe$_2$O$_3$-TiO$_2$ (PEG), Fe$_2$O$_3$-TiO$_2$ (T-80) and Fe$_2$O$_3$-TiO$_2$ (CTAB) derived from XRD are 10, 30, 15 and 15 nm, respectively.

Keywords: Fe$_2$O$_3$-TiO$_2$, sol-gel method, templating agents, nanocomposites.
INTRODUCTION

In the recent years, the ecological glitches associated to the pollution of water source have gained a lot of attention towards the natural bodies. One of the main sources for the contamination of water pollution is from the textile industries. Because the textile dyeing industries consume large quantities of water and produces large volume of waste water from different steps in the dyeing and finishing process. The worldwide dye consumption for dyeing industries are around $10^7$ kg/year. Since the dyes are stable, recalcitrant, colorant and even potentially carcinogenic and toxic, their release into the environment causes a major threats to the environment. The dye contaminated waste water cannot be easily treated because of the natural biodegradability has become increasingly difficult task to the improved properties of dyestuffs. A wide range of conventional methodologies have been used to eliminate these pollutants from the waste water but the efficiency was limited. The modern nanotechnologies have become popular for the fabrication of desirable nanomaterials with large surface-to-volume ratios of unique surface properties to treat these pollutants. Nanoparticles are the key to nanotechnology; hence in-depth study of nanomaterials is an important source for producing new principles, techniques and methods. From environmental standpoint, heterogeneous photocatalysis is an important pioneering technology for application in water purification. With advent of nanotechnology, semiconductor nanoparticles have attracted much intention due to their novel optical, electrical and mechanical properties. Among the various semiconductor nanoparticles, nanosized titanium dioxide (TiO$_2$) particles are the most frequently studied in the field of solar energy conversion,
photocatalysis, transparent UV protection films and chemical sensors etc. It has been proved to be one of the most suitable materials in environmental remediation process due to its powerful oxidation strength, low cost, non-toxicity and chemical stability against photo-corrosion. However, the conventional TiO\textsubscript{2} photocatalyst suffered an obstacle when applied in practical applications such as effective utilization of UV/solar light, large surface area requirement for the adsorption of pollutant, that is, adverse recombination of electron and holes. Many efforts have been made to extend the adsorption of light from UV to visible region and to improve the photocatalytic efficiency of TiO\textsubscript{2}. Enhancing the rate of photoreduction by doping a semiconductor with metal ions can produce a photocatalyst with an improved trapping-to-recombination rate ratio. However, when metal ions or oxides are incorporated into TiO\textsubscript{2} by doping, the impurity energy levels formed in the band gap of TiO\textsubscript{2} can also lead to an increase in the rate of recombination between photogenerated electrons and holes. Photocatalytic reactions can only occur if the trapped electron and hole are transferred to the surface of the photocatalyst. This means that metal ions should be doped near the surface of the photocatalyst to allow efficient charge transfer. Dopants like transition metals (Fe, Al, Ni, Cr, Co, W, V and Zr) and metal oxides (Fe\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, CoO\textsubscript{2}, SiO\textsubscript{2}, etc.) being used to improve its applicability. The absorption threshold of TiO\textsubscript{2} nanopowder has been shifted from UV to visible region by doping the visible light active material and the photocatalytic efficiencies can be higher than the pure TiO\textsubscript{2} and Degussa P25.

In this study, we have prepared Fe\textsubscript{2}O\textsubscript{3}-TiO\textsubscript{2} nanocomposites by employing PVP-PEG as templating agent. The nanocomposites prepared were used as photocatalyst in the degradation of the pollutant Rhodamine B under Visible light.
2. Experimental

2.1. Materials and Methods

Nanocrystalline Fe$_2$O$_3$ was purchased from Sigma-Aldrich. PEG (SD fine) and Polyvinyl pyrrolidone (PVP) (SRL) were purchased and used as received. Isopropyl alcohol, titanium tetraisoproxide (TTIP) and Methyl Orange were brought from qualigens and used without further purifications.

2.2. Preparation of Fe$_2$O$_3$-TiO$_2$ (PVP-PEG)

0.096 g of Fe$_2$O$_3$ nanoparticles were suspended in 20 ml of distilled ethanol and stirred for half an hour. 1 mg of PVP-PEG was added under stirring to the homogeneous dispersion and further stirred for 30 min. A mixture of 3 ml TTIP with 10 ml isopropyl alcohol was added drop wise into the suspension and the stirring was continued for 2 hours to get a gel. The resultant gel was filtered off and washed thoroughly with 1:1 aqueous ethanol, filtered and then oven dried at 120 ºC for 10 hours. The solid sample was kept for calcination at 500 ºC for 3 hours using muffle furnace.

2.5. Characterization techniques:

XRD patterns of the nanocomposites were recorded using PANalytical X pert pro diffractometer in the scanning range of 10-75° (2θ) employing Cu Kα as a radiation source with wavelength of 1.5406 Å at a scanning rate of 0.02° S$^{-1}$. The average crystal size (t) was calculated from the line broadening utilizing Scherrer equation.
2.6. Evaluation of photocatalytic property

Photodegradation of methyl orange was done using an immersion type photo reactor with 100 W tungsten halogen lamp. The lamp is fitted into the double walled borosilicate immersion well of 40 mm outer diameter provided with an inlet and outlet for water circulation. The reaction vessel was a 100 mL borosilicate immersion well of 50 mm outer diameter. Freshly prepared methyl orange solution of the required ppm was taken in the reaction vessel to which a known quantity of nanocomposites was added. Air was bubbled to the reaction vessel to ensure constant motion of the nanoparticles. After illumination the nanoparticles were isolated by centrifugation and the dye solution was diluted and analyzed spectrophotometrically at the wavelength of 555 nm to estimate the quantum of Rhodamine B present after degradation. A calibration curve was drawn by plotting absorbance versus different ppm of the Rhodamine B solutions.

3. Results and Discussion

3.1. Crystal Structure:

Fig. 1 reveals the XRD patterns of Fe₂O₃-TiO₂ nanocomposites prepared using CTAB as templating agent. In the synthesized nanocomposites, TiO₂ exists in anatase phase show their characteristic peaks at (101), (004), (200), (105), (211), (204), (116), (220) and (215) agrees well to standard JCPDS pattern of the anatase TiO₂ (89-4921). TiO₂ is in anatase phase with tetragonal structure indicating body centred a=b≠c (a = 3.775 Å, b = 3.775 Å, c = 9.501 Å). The presence of Fe₂O₃ and the standard JCPDS pattern of Fe₂O₃ (78-1793) matches with the recorded diffractogram. The presence of Fe₂O₃ appears as sharp peak and the 2θ value are 28.92° and 30.12° with corresponding planes {201} and {211} respectively. The crystal parameters are: Fe₂O₃, tetragonal,
primitive, \( a = 7.741 \text{ Å} \), \( b = 7.741 \text{ Å} \), \( c = 5.634 \text{ Å} \), \( \alpha = 90^\circ \), \( \beta = 90^\circ \), \( \gamma = 90^\circ \). The average crystallite sizes of the nanocomposites have been deduced from the half-width of the full maximum (HWFM) of the 101 anatase peak of TiO\(_2\) using Scherrer equation (Eq. 2),

\[
t = \frac{K\lambda}{\beta \cos \theta},
\]

(2)

Where \( t \) is the crystallite size, \( K \) is the shape factor of value 0.9, \( \lambda \) is the wavelength of the X-ray used. \( \theta \) is the Bragg’s diffraction angle, \( \beta \) is the corrected line broadening, \( \beta = \beta_b - \beta_s \), \( \beta_b \) is the broadened profile width of the experimental sample and \( \beta_s \) is the standard profile width of the reference (high purity silica) sample. Table 1 presents the average crystallite size of the prepared nanocomposites.
Figure 1 XRD pattern of Fe$_2$O$_3$-TiO$_2$ nanocomposites
3.2. Scanning Electron Microscopy (SEM)

The SEM micrographs of Fe$_2$O$_3$-TiO$_2$ nanocomposites are presented in the Fig.2. The SEM images of the Fe$_2$O$_3$-TiO$_2$ composites are in spherical shape and the size of the particles range from 28 nm to 57 nm which is about 3 to 4 times the average crystal size, determined by XRD. From the SEM analysis, it reveals that the synthesized nanocomposites are polycrystalline in nature.

3.3. Energy Dispersive X-ray Spectroscopy

The energy dispersive X-ray (EDX) spectra of the Fe$_2$O$_3$-TiO$_2$ nanocomposites are shown in Fig. 3. It confirms the composites as oxides of titanium and Bismuth. The significantly strong peak of Ti element confirms the elemental composition of the Ti in the synthesized composites. The moderately strong peak in the EDX spectra confirms the presence of Fe and O element in the Fe$_2$O$_3$-TiO$_2$ nanocomposites.
4. Conclusions

In summary, we synthesized Fe$_2$O$_3$-TiO$_2$ nanocomposites with template-assisted precipitation reaction (PVP-PEG) as templating agent to conduct a photocatalytic process towards the degradation of a xanthene dye (methyl orange) as a model organic pollutant. The results showed that Fe$_2$O$_3$-TiO$_2$ (PVP-PEG) nanocomposite is more efficient towards the degradation of Methyl Orange solution under visible light and TiO$_2$ is the least efficient photocatalyst. The results revealed that the templating agents influenced in the specific surface area of the samples.
REFERENCES
