



Enhanced Methylene Blue Dye Degradation by Newly Synthesized Ag₂O/TiO₂ Heterostructure

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Received:03.09.2014 Accepted:15.12.2014

Abstract

Silver (Ag) coated TiO₂ heterostructure was prepared by precipitation method using equal ratio of silver nitrate (AgNO₃) and as-synthesized TiO₂ nanobelt. The X-ray diffraction study results indicate high crystalline nature of the Ag₂O/TiO₂ heterostructure. The surface morphology of Ag₂O/TiO₂ heterostructure has thoroughly been investigated by Scanning Electron Microscopy (SEM). The stability and thermal studies of Ag₂O/TiO₂ heterostructure were examined by using Zeta analyzer and Differential Scanning Calorimetry, respectively. Photocatalytic activity studies were carried out using Methylene Blue (MB) as a model molecule to highlight the consequence of Ag₂O/TiO₂ heterostructure. The reuse of Ag₂O/TiO₂ nanobelt after annealing shows the excellent recovery of the catalyst. These studies may contribute to additional applications of hierarchical Ag₂O/TiO₂ heterostructure membranes, including harnessing sunlight for water treatment and photo catalytic activity.

Keywords: Ag₂O/TiO₂ heterostructure; Hydrothermal process; Methylene blue; Precipitation method; Photo catalytic activity.

1. INTRODUCTION

TiO₂ is regarded as the most efficient and environmentally benign photocatalyst. During the last three decades, titanium dioxide (TiO₂) has been comprehensively studied as a wide-band-gap photocatalyst (Xiong and Zhao, 2012; Wang *et al.* 2009; Liu *et al.* 2012; Hegde *et al.* 2005) Wide-band gap semiconductor TiO₂ nanobelt has potential use as components in electronic and optical devices because of their transparency and high carrier excitation energy. The goal of research in this area is to look for efficient materials for photocatalytic processes, including the photocatalytic decomposition of various pollutants, and killing bacteria. There is a range of recent studies suggesting other possible applications of Ti–O nano materials (Zhou *et al.* 2010).

Loading of noble metal particles, such as platinum, gold, and palladium on TiO₂ photocatalysts can improve photocatalytic activities (Henderson *et al.* 2003). Especially, the deposition of silver (Ag) nanoparticles on TiO₂ photocatalyst can highly improve its photocatalytic efficiency through the

Schottky barrier conduction band electron trapping and consequent longer electron-hole pair lifetimes; (Linsebigler *et al.* 1995). Ag coated TiO₂ catalysts have many industrial applications such as epoxidation, oxo-dehydrogenation, as well as the low-temperature selective oxidation (Zhou *et al.* 2004) At the same time, the Ag₂O/TiO₂ heterostructure also has a towering visible photocatalytic activity. The enhancement is attributed to the fact that the loading of Ag results in the formation of Schottky barriers at each Ag–TiO₂ contact regions, thus promoting charge separation and inhibiting the recombination of electron–hole pairs, leaving holes in the valence band of TiO₂ (Zhou *et al.* 2004). Ag₂O/TiO₂ heterostructure can effectively suppress the rate of electron-hole recombination under ultra violet (UV) light irradiation.

The principle of the semiconductor photocatalytic reaction is straightforward. Upon absorption of photons with energy larger than the band gap of TiO₂, electrons are excited from the valence band to the conduction band, creating electron–hole pairs. These charge carriers migrate to

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the surface and react with the chemicals adsorbed on the surface to decompose them. The holes or the surface hydroxyl radicals are generally viewed as major oxidizing agents for degrading reactants, while superoxide anions formed by scavenging the electrons from the conduction band are also capable of oxidizing reactants (Dodda *et al.* 2007). In this paper, we demonstrate that $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure can be used as an efficient electron absorbing agent under UV light irradiation and as an efficient photosensitizer under visible light irradiation in photocatalysis system. Ag nanoparticles were loaded on the surface of TiO_2 nanobelts by co-precipitation method to form $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure. TiO_2 nanobelts were chosen as the test material, because one-dimensional nanostructures have advantages over nano particles, such as enhanced visible-light scattering and absorption, rapid diffusion-free electron transport along the long direction; and the low number of grain boundaries.

2. EXPERIMENTAL METHODS

2.1 Materials & Methods

All chemicals and solvents were of analytical grade and purchased from commercial sources. TiO_2 , NaOH, HCl, AgNO_3 are purchased from Sigma Aldrich and Merck, used without any further purification.

Infra red spectra of nanobelt samples were recorded on Bruker ATR-FTIR spectrometer (Bruker Alpha – T, Germany). UV-Visible measurements were made on Analytik Jena spectrophotometer (Model SZ-100, Germany) at 298 K. Zeta potential was analyzed on Zeta analyzer (Horiba SZ-100Z, Japan) with PMT detector. The thermal stability of nanobelt was investigated by Differential Scanning Calorimetry (DSC Q20V 24) in an air stream at a heating rate of 10 °C/min. Fluorescence experiments were performed in Horiba Fluoromax-4 spectrofluorometer. The pH measurements were carried out using digital pH instrument (HANNA, Romania). X-ray diffraction studies were performed on Xpert Powder diffractometer (Panalytical, The Netherlands) with $\text{Cu K}\alpha$ ($\lambda = 0.15406$ nm). Scanning Electron Microscope (SEM) analysis was carried out using Qunata 250 model (FEI, Czech Republic) with Tungsten as electron source and Everhart Thornley Detector as detector.

2.2 Preparation of TiO_2 nanobelt

Titanate nanobelt was synthesized by the hydrothermal process in concentrated NaOH aqueous solution. A commercial anatase TiO_2 powder was used as the precursor, and a typical procedure is as follows: TiO_2 powder (0.1 g) was mixed with 20 mL

of 10 M NaOH aqueous solution, followed by hydrothermal treatment at 200 °C in a Teflon-lined autoclave for 48 h (eq. 1). The resulted powder was washed thoroughly with deionized water followed by filtration and rying process. The obtained sodium titanate nanobelts (Wang *et al.* 2008) were dipped in 0.1 M HCl aqueous solution for 24 h and then washed thoroughly with water to get hydrogen titanate nanobelts (eq. 2). By annealing the hydrogen titanate at 500 °C for 1 h, anatase TiO_2 nanobelts were obtained (eq. 3).



$\text{Na}_2\text{Ti}_3\text{O}_7$ and $\text{H}_2\text{Ti}_3\text{O}_7$ are closely related structures. $\text{Na}_2\text{Ti}_3\text{O}_7$ is a layered structure composed of $[\text{TiO}_6]$ octahedra with shared edges and vertices. The Na^+ cations are located between the $[\text{TiO}_6]$ layers. If $\text{Na}_2\text{Ti}_3\text{O}_7$ is soaked and washed with a diluted acid solution, Na^+ ions can be replaced by H_3O^+ ions to form $\text{H}_2\text{Ti}_3\text{O}_7$. Therefore, $\text{H}_2\text{Ti}_3\text{O}_7$ nanobelts can be obtained from $\text{Na}_2\text{Ti}_3\text{O}_7$ nanobelts by ion exchange and anatase TiO_2 can be obtained by heat-treatment of $\text{H}_2\text{Ti}_3\text{O}_7$ at 500 °C for 1 h through dehydration and crystal-lattice rearrangement process.

2.3 Preparation of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure

$\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure was prepared by the precipitation method. 0.12 g of newly synthesized TiO_2 nanobelts were dispersed in 50 mL of distilled water and 0.27 g of AgNO_3 was added to the suspension. The mixture was stirred magnetically for 30 min. 50 mL of 8.0 M NaOH was added drop wise to the above reaction mixture. The amount of NaOH was more than sufficient to precipitate Ag_2O from the added AgNO_3 (pH = 14). TiO_2 nanobelts coated by Ag_2O nanoparticles were centrifuged and washed thoroughly with deionized water followed by a filtration and drying.

2.4 Photocatalytic degradation of MB under UV and Visible- Light Irradiation

Methylene blue was chosen as the model organic compound to evaluate the photoactivity of the prepared $\text{Ag}_2\text{O}/\text{TiO}_2$ nanomaterials. In a typical experiment, 20 mL aqueous suspensions of MB (0.003 M) and 5 mg of $\text{Ag}_2\text{O}/\text{TiO}_2$ nanobelts powder were placed in a 50 mL beaker. Prior to irradiation, the suspension was vigorously stirred for 30 min to establish adsorption/desorption equilibrium (Hu *et al.* 2013). An 11 W UV lamp with a maximum emission at 254 nm was used as the UV resource for UV light photocatalysis and a 300 W Xe arc lamp was

used as the visible light source for visible-light photocatalysis. At given time intervals, 3 mL aliquots were sampled and centrifuged to remove the particles. The filtrates were analyzed by measuring the absorption band maximum (670 nm) using a UV-Vis spectrophotometer. The blank reaction was carried out following the same procedure without adding catalyst. Repeat tests were run to ensure data reliability.

3. RESULTS & DISCUSSION

The formation of $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes at lower temperatures is due to large surface strain energy when surface hydrogen loss exceeds a critical value. However, in our experiment, the autoclaving temperature was much higher (180 °C), which leads to a higher growth rate of nanosheets, resulting in long nanobelts. It may require larger strain energy, but there is not enough strain energy for the surface layer to overcome the coupling with the underlying layer, which may be why no $\text{Na}_2\text{Ti}_3\text{O}_7$ nanotubes appear in our experiment.

3.1 X-ray diffraction studies

X-ray diffraction patterns of TiO_2 nanobelts and $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure are shown in Fig. 1. All the diffraction peaks in the pattern of pure TiO_2 nanobelts can be indexed as anatase type structure (Fig. 1a). The diffraction peaks of the nanobelt sample are in good harmony with that reported in the literature, indicating the formation of the Ag-TiO_2 phase. The anatase TiO_2 diffraction pattern showed well resolved intense peaks (JCPDS 89-4203). After coupling with Ag, the crystal phase of TiO_2 remained unchanged except a slight shift of 38.30° (200).

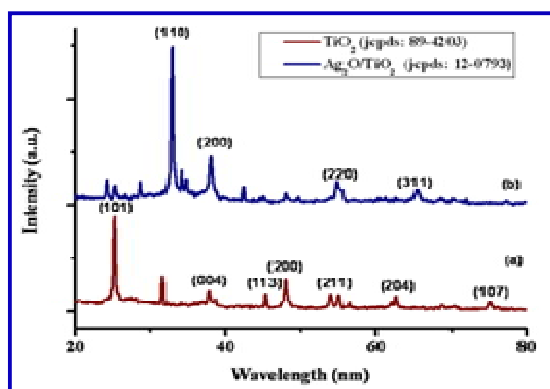


Fig. 1: (a) X-ray diffraction patterns of as-synthesized TiO_2 nanobelt synthesized by sequential autoclaving at 200 °C in NaOH solution and (b) $\text{Ag}_2\text{O}/\text{TiO}_2$ nanobelt fabricated by precipitation method

The anatase TiO_2 and Ag_2O phases coexist in the $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure crystals, and the XRD patterns match their JCPDS files (No. 12-0793).

Furthermore, the appearance of new intense peak at 32.81° (110) confirms the formation of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure (Sze-Mun Lam *et al.* 2013). Other well-resolved sharp and intense peaks indicate $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure have a relatively high degree of crystallinity.

3.2 Surface morphology studies

The morphology and microstructural features of as-synthesized TiO_2 nanobelt and $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure were examined by using Scanning Electron Microscope (SEM). It can be seen that as-synthesized TiO_2 nanobelts consisted of ~ 115 -190 nm in thickness and ~ 1.5 -2.0 μm in length (Fig. 2a). After coupling with Ag_2O , the thickness of the $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure increased to ~ 210 -225 nm width and ~ 2.0 μm length (Fig. 2b). The rough surfaces of TiO_2 nanobelts provide a very good phase to absorb Ag_2O nanoparticles in high capacity during the co-precipitation process. Considering the crystallographic symmetry of anatase nanorods, the dominant exposed facets can be identified as {101} planes, which are the most thermodynamically stable facets of anatase TiO_2 (Li *et al.* 2008; Mukhopadhyay *et al.* 2010) and constitute $\sim 95\%$ of the total exposed surface.

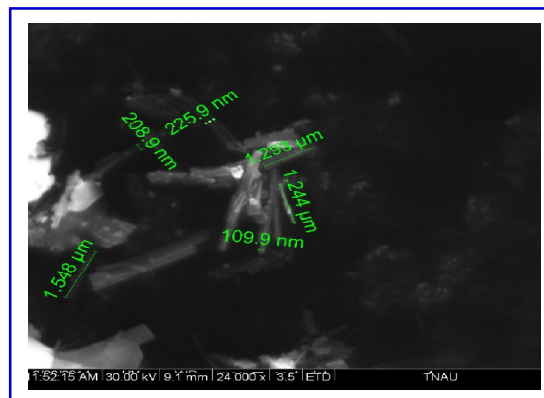
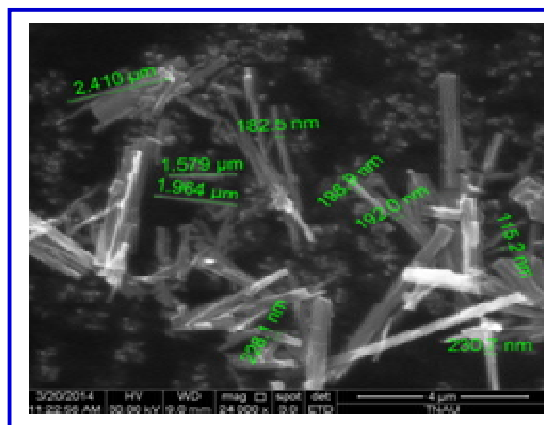


Fig. 2: SEM images of as-synthesized TiO_2 nanobelts (a) and $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure (b) with different magnification

3.3 Infra red and UV-Visible spectroscopy

The I.R. spectrum of newly synthesized $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure was compared with that of TiO_2 nanobelt in order to elucidate the formation of Ag coated TiO_2 heterostructure. In the IR spectrum of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure, a strong band was observed at *ca.* 1640 and 1410 cm^{-1} which is characteristic of stretching and bending of O-Ti-O bond. The peaks at *ca.* 510 and 430 cm^{-1} for Ag-O and Ag/ TiO_2 bonding, respectively (SI, Fig. S1), which confirms the formation of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure.

To corroborate the preparation of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure, UV-Visible absorption spectroscopy was carried out for as-synthesized TiO_2 nano belt, commercial TiO_2 , AgNO_3 and $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure at room temperature. The appearance of absorption band at *ca.* 380 nm for as-synthesized TiO_2 nanobelt confirms the preparation of TiO_2 nanobelt, which is in good agreement with commercially available sample (Fig. 3). The AgNO_3 sample showed the Ag characteristic band at *ca.* 410 nm; but in the $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure absorption spectrum, the disappearance of both 380 and 410 nm absorption bands proves the formation of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure.

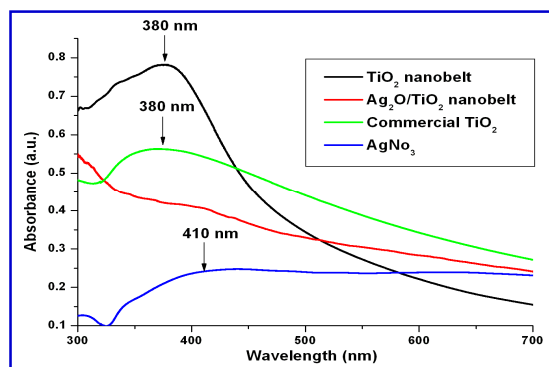


Fig. 3: UV-Visible absorption spectrum of as-synthesized TiO_2 , newly synthesized $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure, commercial TiO_2 and AgNO_3 in water at 25 °C.

The Diffused Reflectance Spectra (DRS) of as-synthesized TiO_2 nanobelts and $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure are shown in Figure 4. TiO_2 nanobelts exhibit a very steep absorption edge located at *ca.* 380 nm. In comparison to pure TiO_2 nanobelts, the absorption edge of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure red-shifts to about *ca.* 410 nm (Xu *et al.* 2012). The $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure also exhibit a narrow absorption band around 450-700 nm which is assigned as Ti-O bond. The absorption above 450 nm in $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure photocatalyst is attributed to the presence of Ag_2O nanoparticles as visible-light sensitization which has a strong and wide absorption band in the visible-light region.

3.4 Practical size analysis and Stability studies

The stability of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure was determined by calculating the zeta potential using zeta analyzer (Fig. 5) at room temperature. The zeta potential (0.1 mV) and electrophoretic mobility (0.000001 cm^2/Vs) values indicates that the newly synthesized $\text{Ag}_2\text{O}/\text{TiO}_2$ nanobelt is highly stable, can be moveable with very less current and mono dispersed.

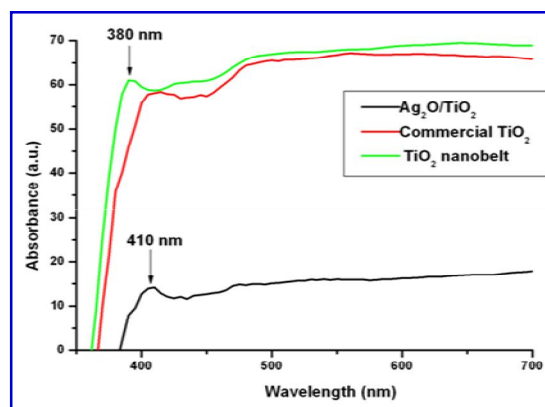


Fig. 4: Diffused reflectance spectrum of $\text{Ag}_2\text{O} / \text{TiO}_2$ heterostructure, commercial TiO_2 and as-synthesized TiO_2 nanobelts at 25 °C.

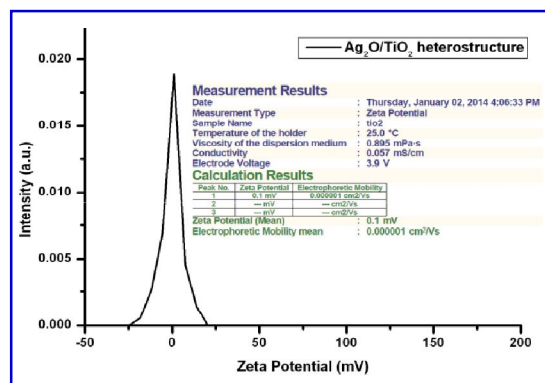


Fig. 5: Zeta potential analysis of synthesized $\text{Ag}_2\text{O} / \text{TiO}_2$ heterostructure in water at 25 °C.

3.5 Fluorescence studies

The separation and recombination of photoinduced charge carriers which is related to the transfer behavior of the photoinduced electrons and holes can be reflected in PL spectra. The PL spectra of TiO_2 nanobelts and $\text{Ag}_2\text{O}/\text{TiO}_2$ samples are shown in Fig. 6. The excitation wavelength is determined as 350 nm, and the pure TiO_2 nanobelts have a strong emission peak at *ca.* 405 nm. The PL intensities of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure decreased which is due to the Ag_2O nanoparticles deposited on the surface of

TiO₂ nanobelts act as traps to capture the photoinduced electrons, and thus inhibit recombination of electron-hole pairs (Lazzeri *et al.* 2001; Dai *et al.* 2009). The PL spectra result is in good agreement with the enhancement of photocatalytic activity of Ag₂O/TiO₂ nanobelts heterostructure under UV light.

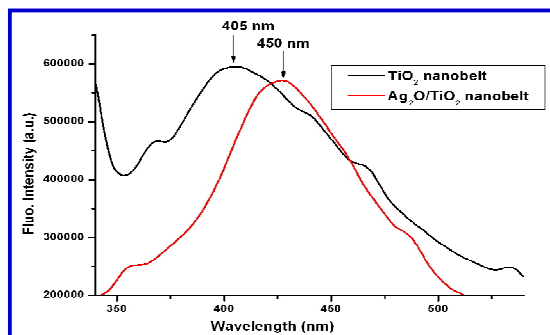


Fig. 6: Fluorescence emission intensities of as-synthesized TiO₂ nanobelts and Ag₂O/TiO₂ heterostructure (excitation : 350 nm; slit width : 1 nm) in water at 25 °C

3.6 Thermal stability studies

To measure the heat flows associated with phase transitions in Ag₂O/TiO₂ heterostructure and as-synthesized TiO₂ nanobelt as a function of time or temperature, we used differential scanning calorimetry (DSC) technique. The calorimetry is particularly applied to monitor the thermal behaviour like changes of phase transitions of the newly synthesized Ag₂O/TiO₂ heterostructures and TiO₂ nanobelt (Skoog *et al.* 1998). The samples with a mass of 20 mg were placed in aluminium crucible. The experiments were performed in synthetic air (flow rate of 1.67 cm³ s⁻¹) at 10 °C/min heating rate up to 500 °C. Fig. 7 reveals the endothermic decomposition nature of Ag₂O/TiO₂ heterostructures which includes the thermal decomposition of water molecules present in the material at 100 °C and phase transition at ~ 450 °C (Skoog *et al.* 1998).

3.7 Photocatalytic studies

To assess the photocatalytic degradation capability of Ag₂O/TiO₂, we examined the decomposition of methylene blue (MB) in water under UV-Visible light irradiation as a function of time. MB monomer consists of a sharp intense peak at 670 nm and a shoulder at 610 nm which corresponds to 0-1 vibronic transition in water (Bergmann and O'Konski, 1963). When the experiment was carried out with catalyst but in the absence of light irradiation, no change in methylene blue concentration was observed. Consequently, the decrease of concentration is attributed to the photocatalytic process. The

Ag₂O/TiO₂ heterostructure photocatalyst exhibited a 6-fold high activity for MB degradation under UV irradiation (fig. 8). More interestingly, the entire characteristic band of MB at ~ 670 nm showed a red shift (725 nm) due to enhanced intermolecular cross relaxation of the excitation energy (Wang Ya-Lan *et al.* 2013).

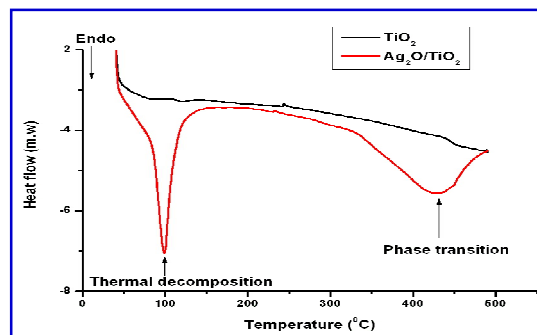


Fig. 7: Differential Scanning Calorimetry spectrum recorded for as-synthesized TiO₂ nanobelt and Ag₂O/TiO₂ heterostructure in an air stream at a heating rate of 10 °C/min.

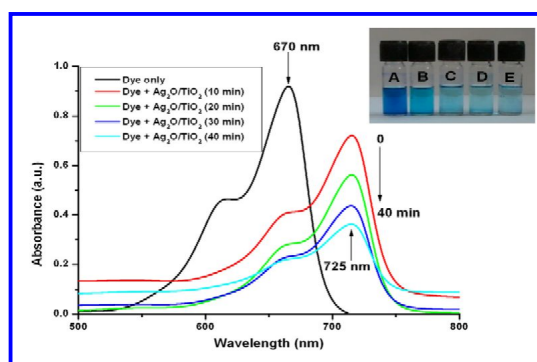


Fig. 8: Photocatalytic degradation of Methylene blue in the presence of Ag₂O/TiO₂ heterostructure under UV-Visible light irradiation; (inset) Color degradation of MB with respect to time interval: (A) dye only; (B) dye+Ag₂O/TiO₂ (10 min stirring); (C) dye+Ag₂O/TiO₂ (20 min stirring); (D) dye+Ag₂O/TiO₂ (30 min stirring); (E) dye+Ag₂O/TiO₂ (40 min stirring).

With the irradiation time increasing, the decomposition of MB dye progressed steadily and 90% completed in 40 min of UV light irradiation. The degradation activity of Ag₂O/TiO₂ heterostructure photocatalyst was much higher than those of the TiO₂ nanobelts, and the corresponding degradation rates were only ~10% after the same experimental time (SI Fig. 2). The heterostructure between Ag₂O and TiO₂ causes the enhanced photocatalysis activity of the catalysis. To reuse a photocatalyst, the photocatalyst must be easily separated from the reaction medium and maintain its activity. The Ag₂O/TiO₂

heterostructure displayed an extraordinary high stability and recyclability. It can be easily separated by simple centrifuge technique due to its large particle size. Moreover, even though the composite had been reused four times, it still exhibited high photoactivity. The enhanced performance of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure could be attributed to its unique surface and electronic properties that substantially affected the photocatalytic processes involved in the degradation, including generation of charge-hole pairs, transfer and trapping of charge carriers, and recombination of charge-hole pairs (Li and Gray, 2007).

4. CONCLUSION

We have reported a very simple and novel method to prepare $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure using as-synthesized TiO_2 nanobelt, which was synthesized by sequential autoclaving of TiO_2 at 200 °C for 48 h in the presence of 10 M NaOH solution. The preliminary characterization studies such as UV-visible absorption, particle size analyzer, zeta potential are in good agreement with the formation of stable $\text{Ag}_2\text{O}/\text{TiO}_2$ nanobelt. Highly stable and monodispersed nature of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure was confirmed by the zeta potential and electrophoretic mobility values, respectively. The X-ray diffraction study results prove the high crystalline nature of $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure which could be a good candidate for the various industrial applications. The surface morphology study results give important information that less surface area coating $\text{Ag}_2\text{O}/\text{TiO}_2$ nanobelt can be a good catalyst for the heterogeneous reactions. Furthermore, the photocatalytic studies revealed that $\text{Ag}_2\text{O}/\text{TiO}_2$ heterostructure is a stable photocatalyst for MB dye degradation within short period of time. Diverse kind of biological activity tests are ongoing in our laboratory and the results will be published in due course.

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