

Magnetic Dye-Adsorbent Catalyst: A “Core-Shell” Nanocomposite

S. Shukla^{†,*}, M.R. Varma[†], S. Suresh[§], and K.G.K. Warriar[†]

[†]Ceramic Technology Department, Materials and Minerals Division (MMD), National Institute for Interdisciplinary Science and Technology (NIIST), Council of Scientific and Industrial Research (CSIR), Thiruvananthapuram – 695019, Kerala, India, *satyajit_shukla@niist.res.in

[§]Department of Physics, Indian Institute of Technology, Mumbai 400076, India

*Present Address: Indo-US Science and Technology Forum (IUSSTF) Research Fellow, Ceramics Section, Energy Systems Division, Argonne National Laboratory, Argonne, IL 60439, sshukla@anl.gov

ABSTRACT

Hydrogen titanate nanotubes have been processed via hydrothermal using the commercially available nanocrystalline anatase-titania powder as a precursor. The samples have been characterized using TEM, XRD, and BET to determine the product morphology, structure, and specific surface-area, and have been utilized for a typical industrial application involving the removal of an organic-dye from an aqueous solution via surface-adsorption mechanism under the dark-condition. The dye-adsorption kinetics of hydrogen titanate nanotubes has been compared with that of the as-received anatase-titania nanoparticles. The nanotube morphology has been observed to play a significant role in enhancing the dye-adsorption kinetics under the dark-condition. In order to ease the separation of nanotubes after the dye-adsorption process, a magnetic dye-adsorbent catalyst has been developed. It consists of a nanocomposite particle having a “core-shell” structure, with a magnetic ceramic particle as a core and dye-adsorbent hydrogen titanate nanotubes as a shell. Due to the presence of nanotubes on the surface, the magnetic dye-adsorbent catalyst possesses an enhanced specific surface-area relative to that of the conventional magnetic photocatalyst. As a result, the former has been successfully utilized to remove an organic-dye from an aqueous solution via surface-adsorption mechanism, under the dark condition (energy-independent process), while simultaneously possessing the ferromagnetic property required for its separation, from the treated solution, using an external magnetic field. It is demonstrated that, under the given test-conditions, the magnetic dye-adsorbent catalyst removes almost ~100% of an organic-dye from an aqueous solution in dark in just 30 min, where as the conventional magnetic photocatalyst removes only ~40-55% of an organic-dye in 3 h via surface-adsorption mechanism. A surface-cleaning treatment has been developed for reusing the magnetic dye-adsorbent catalyst by removing the previously adsorbed organic-dye from its surface. The dye-adsorption and surface-cleaning treatment have been demonstrated by monitoring the variation in the original color of the catalyst-powder during the test.

Keywords: dye-adsorbent, magnetic photocatalyst, nanotubes, titania, hydrogen titanate

1 INTRODUCTION

Nanocrystalline anatase-titania (TiO_2) is a well known wide band-gap (~3.2 eV) semiconductor, which has been extensively used for photocatalysis application, which involves the generation of electron/hole pairs within the particle via radiation-exposure (ultraviolet, visible, or solar), subsequently generating hydroxyl (-OH) radicals on the surface, which attack and degrade the dye molecules in an aqueous environment. Various parameters such as the nanocrystallite size, specific surface-area, nature and relative amount of phases, dopants, surface-catalyst, and surface-purity are known to affect the photocatalytic activity of nanocrystalline anatase- TiO_2 . Although, TiO_2 -based photocatalysts are very effective for the dye-removal application, they suffer from few major drawbacks. First, the photocatalysis is highly energy-dependent process, which makes it relatively expensive. Second, for the utilization of the visible-light, band-gap tuning is required via dopants, which also increases the cost of the photocatalysis process. Third, the separation of TiO_2 -based photocatalysts after the dye decomposition, via conventional approaches such as coagulation and sedimentation, is tedious and costlier. In order to overcome these drawbacks associated with the TiO_2 -based photocatalysts, we process here the nanotubes of hydrogen titanate ($\text{H}_2\text{Ti}_3\text{O}_7$) via hydrothermal and utilize them for the removal of an organic-dye via surface-adsorption mechanism under the dark-condition. Since this is an energy-independent process, the nanotubes of $\text{H}_2\text{Ti}_3\text{O}_7$ offer significant cost-saving over the anatase- TiO_2 nanoparticles. However, being nano-magnetic, the separation of $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes with the surface-adsorbed dye, from an aqueous solution, is also a major problem. To overcome this issue, we further process a “core-shell” magnetic dye-adsorbent catalyst, which involves the core of a magnetic ceramic particle and the shell of $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes. Such nanocomposite particle possesses both the magnetic and dye-adsorption properties, which overcome almost all limitations associated with the photocatalysts based on the anatase- TiO_2 nanoparticles and $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes.

2 EXPERIMENTAL

2.1 Chemicals

Sodium hydroxide (NaOH, Assay 97 %) and methylene blue (MB, >96 %) were purchased from S.D. Fine Chemicals Limited, India; 1 M hydrochloric acid (HCl, 35 wt.%) from Ranbaxy Fine Chemicals Limited, India; ammonium hydroxide (NH₄OH, 25 wt.%) from Merk Limited, India; and anatase-TiO₂ from Central Drug House (CDH) Laboratory (P) Limited, India. All chemicals and powders were used as-received without any further purification.

2.2 Processing H₂Ti₃O₇ Nanotubes via Hydrothermal

The hydrothermal process has been already described in detail elsewhere [1]. 3 g of as-received anatase-TiO₂ (CDH) was suspended in a highly alkaline aqueous solution, containing 10 M NaOH filled up to 84 vol.% of Teflon-beaker placed in a stainless-steel (SS 316) vessel of 200 ml capacity. The process was carried out with continuous stirring in an autoclave (Amar Equipment Pvt. Ltd., Mumbai, India) at 120 °C for 30 h under an autogenous pressure. The autoclave was allowed to cool naturally to room temperature and the product was separated by decanting the top solution. The product was then washed using 100 ml of 1 M HCl solution for 1 h followed by washing using 100 ml of distilled water for 1 h (termed here as the “first washing-cycle”). The product was separated from the solution using a centrifuge (R23, Remi Instruments India Ltd.), and subjected to the “second washing-cycle”. In this cycle, the product was washed once using 100 ml of 1 M HCl and then multiple times (#8-9) using 100 ml of distilled water (1 h each) or till the pH of the filtrate became almost constant. The product was separated from the solution using a centrifuge and dried in an oven at 80 °C overnight.

2.3 Processing Magnetic Dye-Adsorbent Catalyst

The processing of magnetic dye-adsorbent catalyst has been described in detail elsewhere [2]. In short, a mixed cobalt ferrite (CoFe₂O₄)-hematite (Fe₂O₃) magnetic ceramic powder was first processed via polymerized complex technique. This was followed by the deposition of an insulating layer of silica (SiO₂) via Stober process. The SiO₂-deposited magnetic ceramic particles were then coated with the nanocrystalline anatase-TiO₂ via sol-gel to obtain the “conventional magnetic photocatalyst”. The latter was subjected to a hydrothermal process, as described in the section-2.2, to obtain the “core-shell” nanocomposite particles, with the core of a magnetic ceramic particle and the shell of H₂Ti₃O₇ nanotubes.

2.4 Characterization

The morphologies of different samples at the nanoscale were examined using the transmission electron microscope (TEM) and high-resolution TEM (Tecnai G2, FEI, Netherlands) operated at 300 kV. The selected-area electron diffraction (SAED) patterns were obtained to confirm the crystallinity and the structure of different samples. The crystalline phases present in the samples were also determined via X-ray diffraction (XRD, PW1710, Phillips, Netherlands). The broad-scan analysis was typically conducted within the 2-θ range of 10-80° using the Cu Kα (λ_{Cu}=1.542 Å) X-radiation. The Brunauer, Emmett, and Teller (BET) specific surface-area (Micrometrics Gemini 2375 Surface Area Analyzer, U.S.A.) was measured via nitrogen adsorption, using the multi-point method, after degassing the powders at 200 °C for 2 h. The magnetic properties of the magnetic dye-adsorbent catalyst were measured using a vibrating sample magnetometer attached to a Physical Property Measurement System.

2.5 Dye-Adsorption Measurements

The dye-adsorption experiments in the dark were conducted using the MB as a model catalytic dye-agent. A 75 ml aqueous suspension was prepared by dissolving 7.5 μmol·L⁻¹ of MB dye and then dispersing specific amount of the catalyst (0.4 and 1.0 g·L⁻¹ for the pure H₂Ti₃O₇ nanotubes and the magnetic dye-adsorbent catalyst). The suspension was stirred in the dark and 3 ml sample suspension was separated after each 30 min time interval for total 180 min stirring time. The catalyst powder was separated using a centrifuge and the solution was used to obtain the absorption spectra using the ultraviolet (UV)-visible absorption spectrometer (UV-2401 PC, Shimadzu, Japan). The normalized concentration of surface-adsorbed MB dye was calculated using the equation of the form,

$$MB_{Adsorbed} (\%) = \left(\frac{C_0 - C_t}{C_0} \right) \times 100 \quad (1)$$

which is equivalent of the form,

$$MB_{Adsorbed} (\%) = \left(\frac{A_0 - A_t}{A_0} \right) \times 100 \quad (2)$$

where, C_0 and C_t correspond to the MB dye concentration at the start and after string time ‘ t ’ with the corresponding absorbance of A_0 and A_t . The catalyst powders were then subjected to a typical surface-cleaning treatment in a bath of specific composition [2] either in a dark or under continuous radiation-exposure (UV, solar, or visible) with continuous stirring for 8 h. The surface-cleaned samples were utilized for the next cycle of dye-adsorption under similar test-conditions.

3 RESULTS AND DISCUSSION

The TEM image and XRD pattern as obtained for the hydrothermal product is presented in Fig. 1(a) and 1(b). The corresponding SAED pattern is shown as an inset in Fig. 1(a). It is clearly seen that, the hydrothermal product has a nanotube morphology. The SAED and XRD patterns suggest that, the nanotubes are made up of $\text{H}_2\text{Ti}_3\text{O}_7$. When the as-received anatase- TiO_2 particles are subjected to the hydrothermal treatment (autoclave) under highly alkaline condition, the exfoliation of single-layer nanosheets of $\text{Na}_2\text{Ti}_3\text{O}_7$ results from the bulk anatase- TiO_2 structure, which continuously undergo the dissolution and crystallization processes. This is supported by the fact that, $\text{Na}_2\text{Ti}_3\text{O}_7$ easily adopts a layered-structure whereas anatase- TiO_2 does not. Hence, the formation of $\text{Na}_2\text{Ti}_3\text{O}_7$ is vital for the subsequent exfoliation of single-layer nanosheets. Due to their higher specific surface-area to volume ratio and the presence of dangling bonds along the two long-edges, the nanosheets of $\text{Na}_2\text{Ti}_3\text{O}_7$ have a strong drive to rollup. However, this rollup tendency is opposed by the repulsive force produced by the charge on the nanosheets created by the presence of Na^+ -ions. These

Na^+ -ions are replaced via ion-exchange process with H^+ -ions during the washing steps, which results in the formation of pure- $\text{H}_2\text{Ti}_3\text{O}_7$; thus, reducing the repulsive force for the rollup. Hence, at the completion of an ion-exchange process, the nanosheets of pure- $\text{H}_2\text{Ti}_3\text{O}_7$ immediately rollup to form the nanotubes, Fig. 1(a). The $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes exhibit very high specific surface-area as high as $180 \text{ m}^2 \cdot \text{s}^{-1}$, which is almost 18 times larger than that of the as-received anatase- TiO_2 (CDH). As a result, the nanotubes provide large number potential sites for the removal of organic-dye from an aqueous solution via surface-adsorption mechanism under the dark-condition. The variation in the amount of surface-adsorbed MB as a function stirring time in the dark, for $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes, is presented in Fig. 2(a) and compared with that of the as-received anatase- TiO_2 nanoparticles. It is clearly seen that, the nanoparticles of as-received anatase- TiO_2 exhibit only ~50-55 % of MB adsorption under the dark condition. On the other hand, the $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes show ~100% adsorption after 30 min of stirring time. The variation in the powder-color as a function of different test-conditions is shown in Fig. 2(b). After the surface-cleaning treatment, the original high dye-adsorption capacity is regained [2].

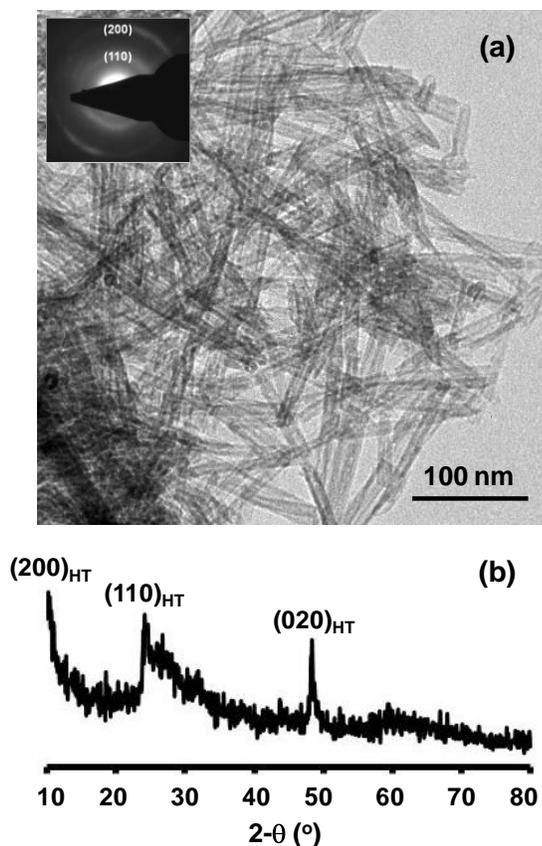


Figure 1: Typical TEM image (a) and XRD pattern (b) of hydrothermally processed $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes.

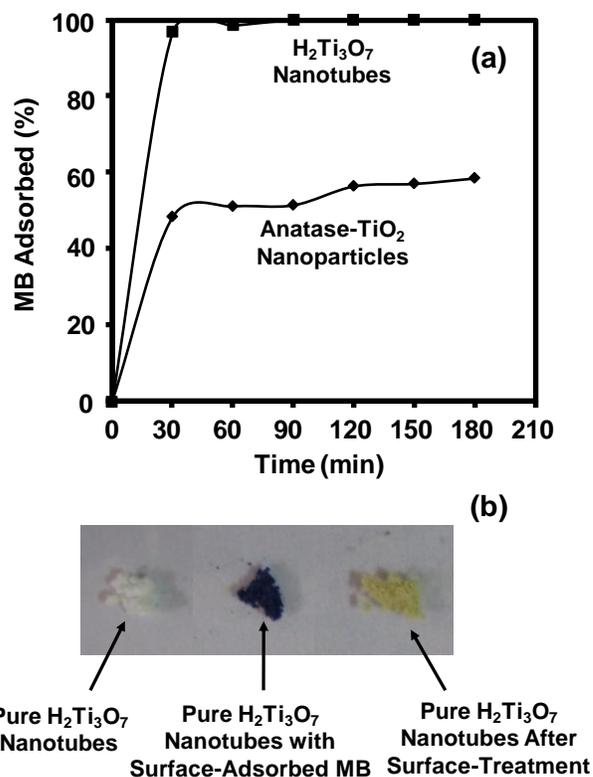


Figure 2: (a) Typical variation in the normalized concentration of surface-adsorbed MB (%) as a function of stirring time in dark. (b) Variation in the color of $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes powder as a function of different test-conditions.

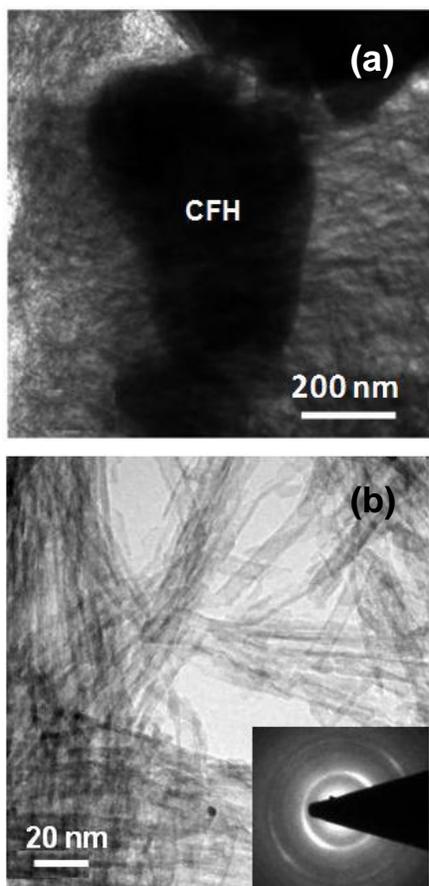


Figure 3: Typical TEM images of the magnetic dye-adsorbent catalyst at lower (a) and higher (b) magnifications.

In order to enhance the separation efficiency, a magnetic ceramic particle has been incorporated within $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes. The TEM image of a typical “core-shell” nanocomposite particle with the core of a mixed cobalt ferrite and hematite (CFH) magnetic particle and the shell of $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes is presented in Fig. 3(a). The central dark-region in Fig. 3(a) represents the core magnetic ceramic particle and the region of grey-contrast surrounding it consists of $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes, which are revealed in a higher magnification image presented in Fig. 3(b), where the corresponding SAED pattern is shown as an inset. Such “core-shell” nanocomposite structure is termed here as a “magnetic dye-adsorbent catalyst” since it possesses both the magnetic and dye-adsorption properties. The presence of a hysteresis loop, Fig. 4(a), suggests the ferromagnetic nature, which makes its separation possible using an external magnetic field. In Fig. 4(b), the magnetic dye-adsorbent catalyst is observed to remove ~100% MB dye, whereas the conventional magnetic photocatalyst removes only ~40-55% of the dye. Since MB dye is cationic, very high dye-adsorption capacity can be retained for the initial MB dye concentration as high as $60 \mu\text{mol}\cdot\text{L}^{-1}$ by adjusting the solution-pH in the basic range (~8-10) [1].

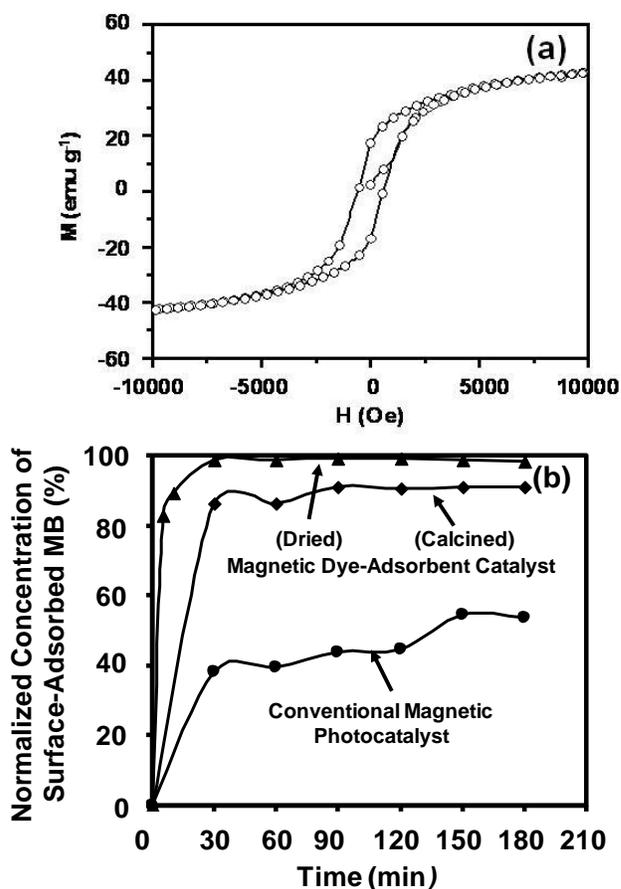


Figure 4: Magnetic (a) and dye-removal (in dark) (b) characteristics of the magnetic dye-adsorbent catalyst.

4 CONCLUSION

Hydrothermally processed magnetic dye-adsorbent catalyst consisting a nanocomposite particle, having a “core-shell” structure with a magnetic ceramic particle as a core and $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes as shell, is much superior to the nanocrystalline anatase- TiO_2 , pure- $\text{H}_2\text{Ti}_3\text{O}_7$ nanotubes, and conventional magnetic photocatalyst for the removal of an organic-dye from an aqueous solution under dark-condition.

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