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RESEARCH ARTICLE

Hydrothermally synthesized TiO_2 nanotubes and nanosheets for photocatalytic degradation of color yellow sunset

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Abstract

TiO_2 nanotubes and nanosheets were synthesized from commercially available spherical TiO_2 nanoparticles by hydrothermal method. All samples were characterized by XRD and TEM. Colour yellow sunset (E110) was used to test the photocatalytic activity of the prepared samples, it was found that all morphologies (spherical particles, nanotubes and nanosheets) were able to decompose E110 completely, where the TiO_2 nanotubes showed the highest photocatalytic activity. It was found also that the photodeposition of Ag particles on TiO_2 particles decreased the time required for complete degradation of E110.

INTRODUCTION

TiO_2 with different morphologies such as spheres (DelaiáSun 2010, Liu, Nakata et al. 2011, Xiang, Yu et al. 2011), nanorods (Wang, Zhang et al. 2007, Yun, Lee et al. 2009), fibers (Zhan, Chen et al. 2006, Zhang, Zhang et al. 2009, Zhao, Liu et al. 2010), tubes (Albu, Ghicov et al. 2007, Yu, Dai et al. 2010, Nakata, Liu et al. 2011), sheets (Shibata, Sakai et al. 2007, Chen, Tian et al. 2011, Aoyama, Oaki et al. 2012), recently has attracted considerable attention. These materials are widely used not only in photocatalysis, but also in other applications such as dye-sensitized solar cells (DSSCs) (Yang, Wan et al. 2010), lithium-ion batteries (Ding, Chen et al. 2011), and electrochromic displays (Periyat, Leyland et al. 2010). It is well known that there are many factors which can exert significant influence on photocatalytic performance, including the size, specific surface area, pore volume, pore structure, crystalline phase, and the exposed surface facets. Structural dimensionality is also a factor which can affect the photocatalytic performance and also has a significant impact on the properties of TiO_2 materials. One-dimensional fibers or tubes have advantages with regard to less recombination because of the short distance for charge carrier diffusion (Nakata, Liu et al. 2011), light-scattering properties (Yao, Haas et al. 2003), and fabrication of self-standing nonwoven mats (Lee, Kim et al. 2003). Two-dimensional nanosheets have smooth surfaces and high adhesion (Shichi and Katsumata 2010).

TiO_2 with Different morphologies nanocrystals have been synthesized by using various procedures (Dimitrijevic, Saponjic et al. 2005, Saponjic, Dimitrijevic et al. 2005) (Kasuga, Hiramatsu et al. 1998). In this work hydrothermal method was used to prepare TiO_2 with different morphologies, since hydrothermal method is environmentally friendly since the reactions are carried out in a closed system, the contents can be recovered and reused after cooling down to room temperature (Zhang, Li et al. 2002) and useful to control the size, morphology, crystalline phase and surface chemistry (Zhang, Li et al. 2002). It worth mentioning that most of the hydrothermal synthesis processes need an accurate control of low temperature and pressure systems

(Kolen'ko, Burukhin et al. 2003). The temperature of hydrothermal processes is usually under 250 ºC and the pressure in the autoclave reaches to about 2.0-6.0 atm.

Sunset yellow is one of the widely used color additives, color additives are defined as dyes, pigments or substances that can impart color when added or applied to food, drugs, or cosmetics and to certain medical devices such as contact lenses (Macioszek and Kononowicz 2004). The side effects of some food colors have been investigated in animal studies (Tsuda, Murakami et al. 2001) and it has been found that their mutagenicity varies widely, depending on the consumed dose. It worth mentioning here that most of substances which have been found to be mutagenic, also seem to have a carcinogenic action for example, carmoisine (E122), amaranth (E123), Sunset Yellow (E110), Tartrazine (E102) and Allura red (E129). Some of them have been found to cause mutations in some bacteria too (Zeiger 1993). Hence, they may affect genome integrity leading to an increase in the incidence of different types of tumours (LeBlanc and Bain 1997).

This work was designed to increase the photocatalytic activity of the commercially available TiO_2 particles by controlling its morphology by hydrothermal method.

2. Experimental

2.1. Materials

Colour yellow sunset (Figure 1) was chosen as a model compound to test the photocatalytic activity. Commercial TiO_2 was purchased from El Nasr Company for Chemicals.

2. 2. Preparation of TiO_2 nanotubes and nanosheets

All the reactants and the solvents were of analytical grade and were used without further purification. In a typical procedure, 5g of pure anatase phase TiO_2 bulk-powder was mixed with 250 ml 10N NaOH aqueous solution of under constant magnetic stirring for about 1 h. A milky white solution was appeared, which was then transferred to a Teflon-lined stainless steel autoclave with 500 ml capacity and heat treated at 160˚C for 4h nd16 h. the autoclave chambers were air-cooled to room temperature after the reactions. The formed white precipitate was recovered and washed several times with distilled water. A treatment of the products with 0.1N HCl solution was carried out, and the precipitates were finally calcinated at 500˚C for 4 h in air.

The crystalline phases of the products were determined by X-ray powder diffraction. The morphologies of the samples were studied by a scanning electron microscope (SEM) and transmission electron microscope (TEM).

2.3. Preparation of Ag loaded TiO_2

The Ag loaded TiO_2 catalysts were prepared by photoreducing Ag^+ ions to Ag on the TiO_2. In typical synthesis of Ag / $TiO_{2,}$ 0.5 g of the powder was suspended in 50 ml of 0.2M $AgNO_3$ aqueous solution. The mixture was exposed to air and irradiated with UV light by mercury lamps (12 W) for 2 h under magnetically stirring. The Ag loaded TiO_2 was filtered and washed with distilled water.

2.4. Photocatalytic experiments

The Colour solution was prepared by dissolving sunset yellow powder in distilled water to obtain a solution 1×10^{-6}M concentration. The photocatalysis experiments were carried out in 100mL beaker containing about 25mL of the prepared solution and about 0.05 g of the catalyst. The irradiation was carried out using 12W UV lamp as a source of UV radiations, which was placed vertically on the reaction vessel at a distance of 12 cm. At specific time intervals, a certain amount of the sample solution was withdrawn and the changes in concentration of the dye were observed from its characteristic absorption at around 480 nm using a UV – Vis spectrophotometer model (Thermo scientific - Evolution 600).

3. Results and discussion

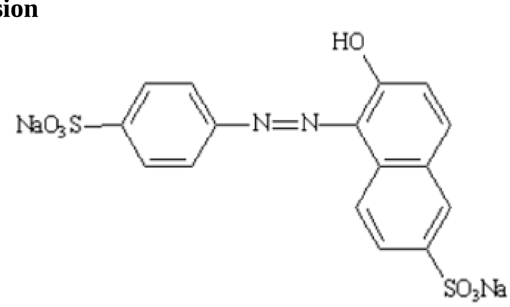

Figure 1 Structural formula of coloour yellow sunset

3.1. Physical characterization of TiO_2 and Ag loaded TiO_2.

The prepared TiO_2 samples were characterized by X-ray diffraction analysis and Transmission electron microscope. Figure 2a. shows XRD patterns of the pure TiO_2 and Ag / TiO_2 samples, results illustrated that the crystallinity of nanotubes and nanosheets was generally poor where all the detected peaks valid for the presence of anatase phase with contribution of TiO_2 (B) (Morgado Jr, de Abreu et al. 2006, Sutrisno 2010), and show no diffraction peaks due to silver species, thus suggesting that the silver particles are well dispersed on the TiO_2 surface. It is also expected that these metal sites are below the visibility limit of X-ray analysis. Figures 2 (b,c,d) show the EDX analysis of the Ag loaded samples.

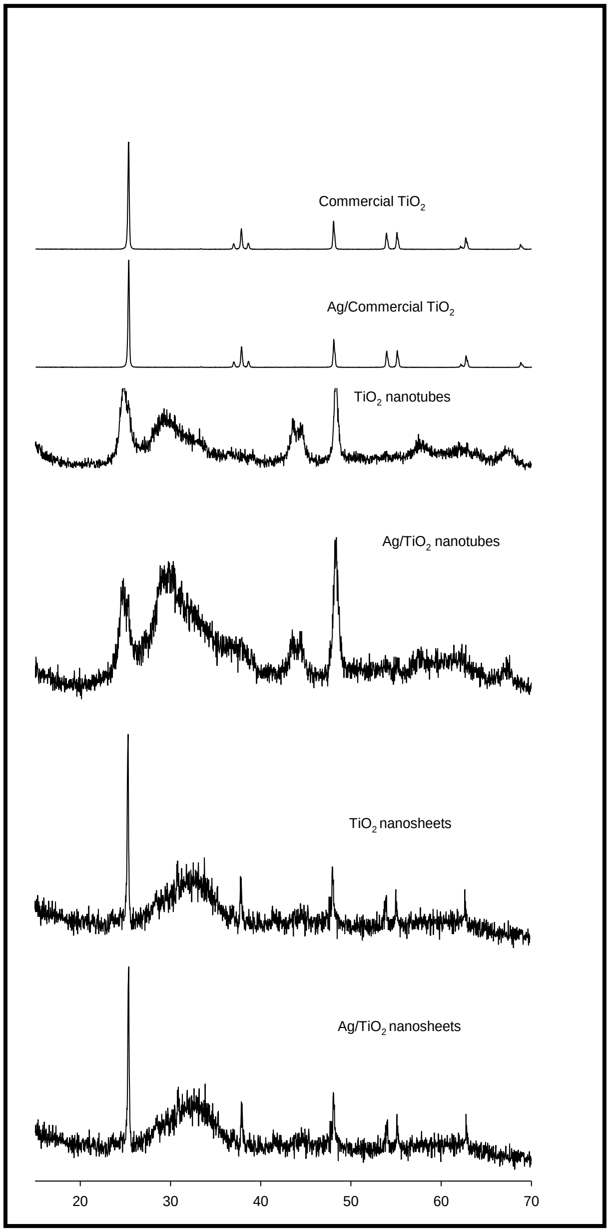

Figure 2a. XRD patterns of pure and Ag / TiO_2

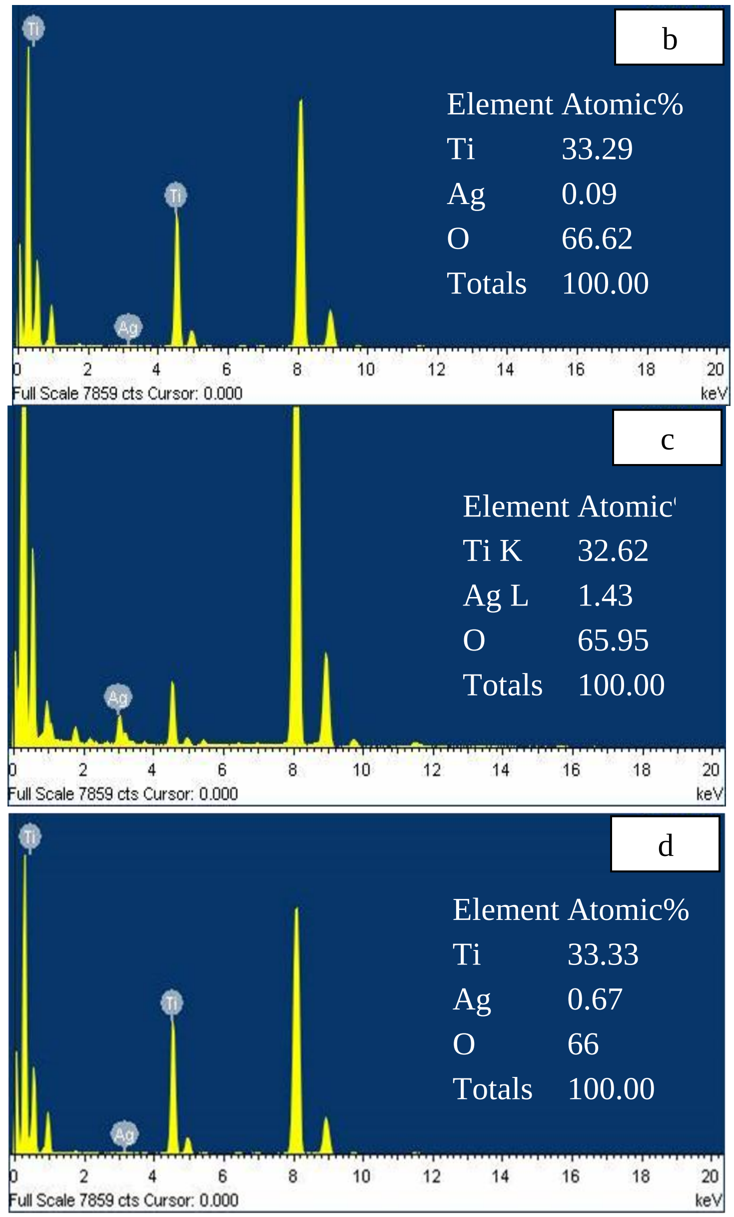

Figure 2 EDX spectrum of (b) Ag / commercial TiO_2 (C) Ag / TiO_2 nanotubes (d) Ag / TiO_2 nanosheets

The TEM images of commercial TiO_2 are shown in Figure (3a). It is observed that the TiO_2 powder consists of nanosized grains with the presence of agglomerated particles forming micro-sized grains. Figure (3b). Shows the TEM image of Ag / commercial TiO_2 nanoparticles It is observed that Ag nanoparicles evenly dispersed on larger TiO_2 grains. Figures (4 a) show the TEM images of the prepared TiO_2 nanotubes, the images demonstrated that the tubes have a diameter range of 16-70 nm. While Figure (4b) shows the TEM images of Ag / TiO_2 nanotubes, as shown in figure Ag particles with sizes of about 1-20 nm are distributed on the TiO_2 nanotubes. Figure (5a) shows the TEM image of the prepared TiO_2 nanosheets. Figure (5b) shows the TEM image of the Ag / TiO_2 nanosheets, the image demonstrated that the Ag particles are distributed on the surface of the multilayered nanosheets.

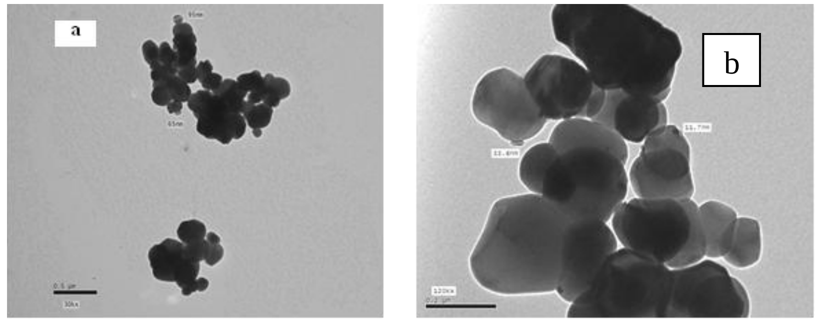

Figure 3. TEM image of (a) commercial TiO_2 nanopatricles (b) Ag/commercial TiO_2

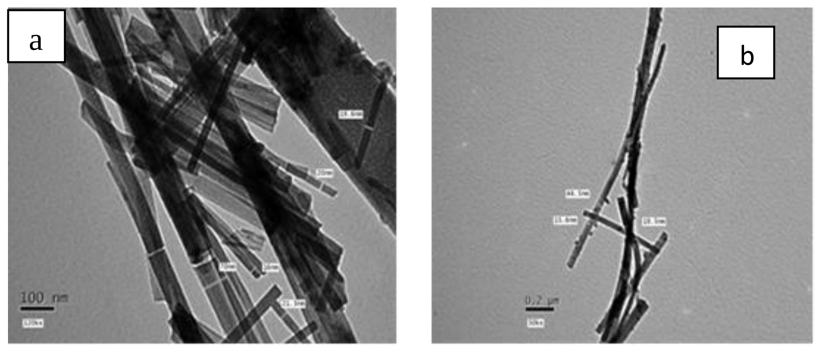

Figure 4. TEM image of (a) TiO_2 nanotubes (b) Ag / TiO_2 nanotubes

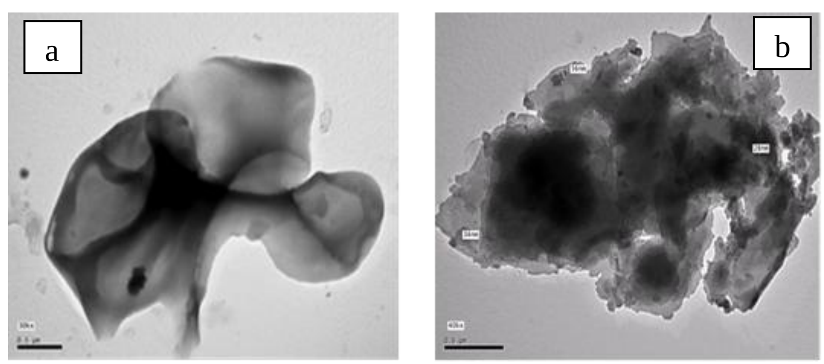

Figure 5. TEM image of (a) TiO_2 nanosheets (b) Ag / TiO_2 nanosheets

3.2. Photocatalytic activity of the prepared and Ag / TiO_2

The change in the concentration of the colour was recorded following the UV-Vis irradiation. It is observed that absorption at 480 decreases as shown in (Figure 6), resulting in complete decolorization of the solution.

It is clear from Figure (7) that all the prepared and Ag loaded samples showed higher activity than that of commercial TiO_2. The positive effect of silver on the degradation process is attributed to the most beneficial role of Ag NPs as electron acceptors. This means, Ag NPs increased the separation of photogenerated charge carriers and effectively transferred the trapped electrons to the adsorbed O_2, which improves the charge separation and thus enhances the photocatalytic activity of TiO_2. In case of TiO_2 nanotubes and nanosheets increasing the surface area and the unique morphology may be the most important factors in increasing the photocatalytic activity compared with the commecial TiO_2.

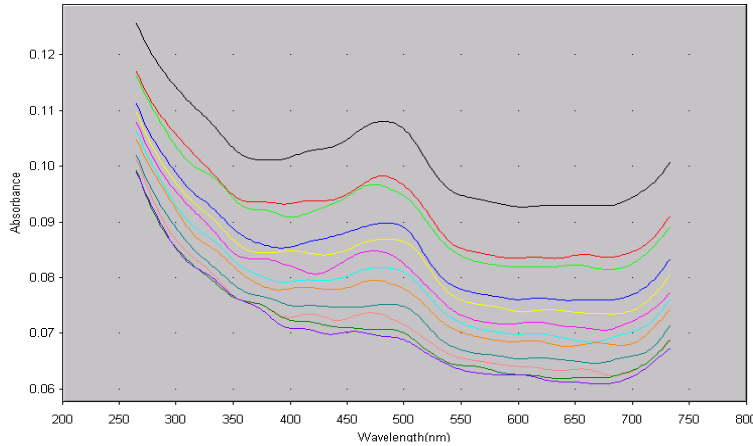

Figure 6 UV/Vis spectral changes of yellow sunset E110 with the increased irradiation time

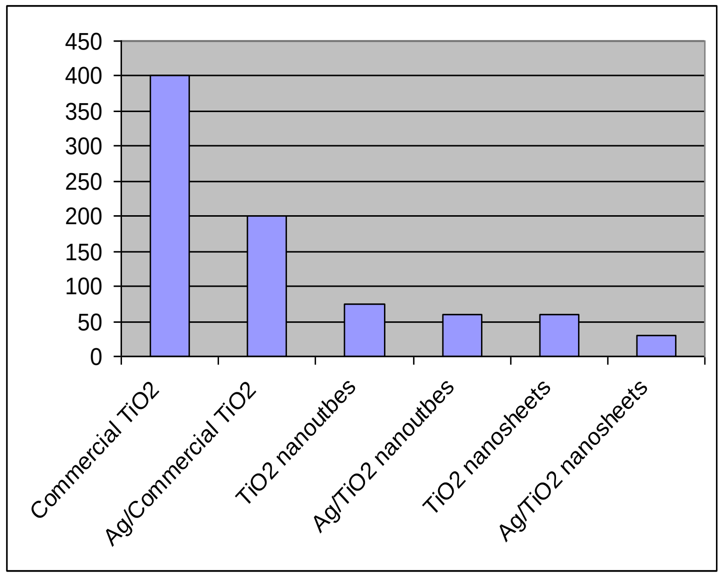

Figure 7 Effect of morphology change on the photodegrdtion of yellow sunset

4. Conclusion

TiO_2 nanotubes and nanosheets were synthesized from commercially available spherical TiO_2 nanoparticles by hydrothermal method. The photocatalytic degradation of color yellow sunset E110 over TiO_2 was studied. It was found that the change in morphology of TiO_2 played a significant role in the photodegradation process. The modification of the surface of TiO_2 with Ag also increased the rate of degradation. Hence the degradation rate of E110 over TiO_2 can be controlled by controlling the morphology of TiO_2 particles.

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