Titanate based photocatalysts for climate-efficient water treatment

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Abstract

The sol-gel dip-coating method is a simple method to synthesize TiO_2 thin film, using titanium butoxide and hydrogen peroxide as precursors. In this study in addition to TiO_2 thin film, the photocatalytic activity of its intermediate products, titanium peroxide gel and ambient dried titanium peroxide film, was evaluated. The titanium peroxide gel was used directly after gelation, ambient dried titanium peroxide film coated on glass rings was used without thermal treatment and anatase TiO_2 thin film was used after thermal treatment at 500°C. These photocatalysts were characterized by different characterization techniques and their adsorption and photocatalytic activity were evaluated by using methylene blue as a model pollutant. All three photocatalysts adsorbed the selected dye model and degraded it in the presence of sunlight but with different removal rate. It was found that the gel had the highest removal rate followed by ambient dried titanium peroxide film and TiO_2 thin film. However, this sequence was found to be vice versa in the case of life span when the photocatalysts were reused. The photocatalytic study showed that all three photocatalysts are very effective for 100% degradation of methylene blue between 5-60 minutes of contacts times under sunlight irradiation. This can be a breakthrough of using titanate based photocatalyst for cost-effective adsorption and photocatalytic degradation of pollutants based on climate and availability of sunlight.

Keywords: TiO_2; Titanium peroxide gel; amourphus; thin film; photocatalysis; methylene blue, cost-effective

1. Introduction

TiO_2 is the most commonly used effective photocatalyst for different environmental applications and its adsorption capacity is a very important factor in heterogeneous photocatalysis. In most cases of photocatalysis, the enhanced photoactivity of semiconductors has been attributed to their superior adsorption capacity [1]. Photocatalytic oxidation technology based on TiO_2 has been proven effective for degradation and mineralization of almost all of types of organic compounds and is regarded as one of the most prospectively environmental clearing technologies [2]. However, the conventional TiO_2 nano-powder has the disadvantage of requiring mixing during the reaction process and their separation also is cumbersome as it needs membrane technology to be involved. During past few decades, TiO_2 thin film has been gaining much attention as useful photocatalysts to offer practical benefits, however the available approaches are still complicated, costly and light dependent. Although, a lot of studies are revealed that TiO_2 cannot work efficiently in the visible and solar light, in this study to the best of our knowledge we could successfully synthesize and use efficient titanate based photocatalysts for pollutants adsorption and degradation in sunlight. These kind of photocatalyst have higher efficiency in adsorption and photocatalytic degradation and suggest a simple and efficient solution to solve environmental and energy problems specially in the field of water treatment based on climate and sunlight availability. For the fabrication of TiO_2, the sol-gel method has been used almost exclusively; however, it requires a subsequent thermal treatment to induce crystallization of the

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formerly amorphous titania gel, which results in particle agglomeration and hence reduction in specific surface area [3].

To meet the requirement for the practical application of photocatalyst, it should be highly photocatalytic active, cost-effective and should have high efficiency, as for practical application a large volume of photocatalyst and consequently raw materials are required. Therefore, the aim of this work was to develop a cost-effective and efficient photocatalyst for the pollutant degradation based on sunlight availability. Therefore, three types of titanate based photocatalysts including titanium peroxide gel (TPG), its amorphous ambient dried film (AmTF), and its thermal treated thin film (AnTF) were prepared and were evaluated for their adsorption and photocatalytic activity using Methylene Blue (MB) as a model pollutant. The efficiency of these photocatalysts in dark condition and under sunlight irradiation were studied and their life span were compared.

Nomenclature

A	TPG: Titanium peroxide gel
B	AmTF: Amorphous ambient dried Titanium peroxide gel film
C	AnTF: Thermal treated Anatase TiO_2 film

2. Material and methods

2.1 Synthesis of Photocatalyst

To prepare TPG, 10g titanium butoxide, was hydrolyzed and washed with 100 ml of deionized (DI) water 2 times. 100 ml 30% aqueous H_2O_2 was added to get a transparent orange sol of titanium peroxide, under continuous stirring 500 ml DI water added during the dissolution of titanium hydroxide in H_2O_2 to create transparent yellow gel which simultaneously maintains the temperature of the reaction too.

To prepare AmTF, 4.2g Titanium butoxide was hydrolyzed and washed with 100 ml of distilled water 2 times. To produce the sol of titanium peroxide, 15 ml of 30% hydrogen peroxide was added to this white precipitate with continuous stirring. When all precipitate completely dissolved, and orange color sol appears the glass rings and glass slides were added to this sol for coating purpose. An amorphous titanium peroxide gel film was formed on the surface of glass rings and were thereafter left to dry at ambient temperature for 3-4 days.

To prepare AnTF, the AmTF explained above thermally treated at 500ºC in a furnace at an ascending heating rate of 2ºC/min (up to 100ºC), 5, 10 and 20ºC/min.

2.2 Characterization

The ζ-potential of TPG was measured a Zeta Puls Analyzer. Zeta Potential measurement are used to assess the stability of colloidal systems. To study the optical properties of the as-prepared photocatalysts UV-Visible spectroscopy (UV-Vis) of the photocatalysts was recorded by a UV-Visible Spectrophotometer (Shimadzu UV-2101PC, JASCO model V-670). The crystal structure and phase purity of the AmTF and AnTF samples were measured by powder X-ray diffraction (XRD) using an XRD spectrometer (Bruker AXS D8). The morphology of the photocatalysts were analyzed by a scanning electron microscope (SEM) (JSM 6360A, JEOL). FTIR was conducted to determine the functional group available on the surface of prepared catalyst using FTIR spectroscope (JASCO model FT/IR-6100typeA).

2.3 Photocatalytic activity

MB solution (10^{-7} and 10^{-4}M) was used as a model pollutant for photocatalysts activity evaluation. For this purpose, known amount of photocatalyst was measured and used (TPG:10g gel in 50ml MB solutions, AmTF and AnTF: 3g coated glass rings (0.001g film) in 10 ml MB). Sunlight was a source of irradiation. UV-Vis spectra of sample were recorded at different time intervals.

3. Results and discussion

3.1 Structural and Chemical Characterizations

Gels are dispersion of macromolecules in liquid and a colloidal system. In this study TPG is formed when excess peroxides have been consumed [4]. Since one important component of this gel is the titanium-peroxy-radical, which can be called titanium peroxy gel [5]. The gel contains a superoxide or perhydroxyl radical, which may be formed in the gel and is stable for a long period of time. Normally, surface of TiO_2 is positively charged in acid media and negatively charged in alkaline one with an isoelectric point of about pH 6 -7 [6]. The isoelectric point of TPG is relatively acidic (only about pH 3-4) and negatively charged. This was confirmed by Zeta potential measurement and it was found to be between -40 to -50 for the stable gel. Strong negative or positive surface charges stabilize a suspension and avoid particle aggregation [7]. The diffuse reflectance UV-Visible spectra of TPG (Fig.1a) indicate that absorption edge is shifting to the visible light region. UV-Visible spectroscopy of AmTF, showed that the absorption threshold of the photocatalyst shifted to higher wavelength (Fig.1b). The estimated band gap for titanium complex film in this study indicates a narrowing of band gap to 2.8 eV occurred in comparing to commercial TiO_2 Degussa. Fig. 1b present the UV–Vis spectroscopy of prepared AnTF, the absorption threshold of AnTF shifted to the higher wavelengths. Band gap estimation of samples was performed, and these values show a band gap narrowing from 3.14 to 2.84 eV.

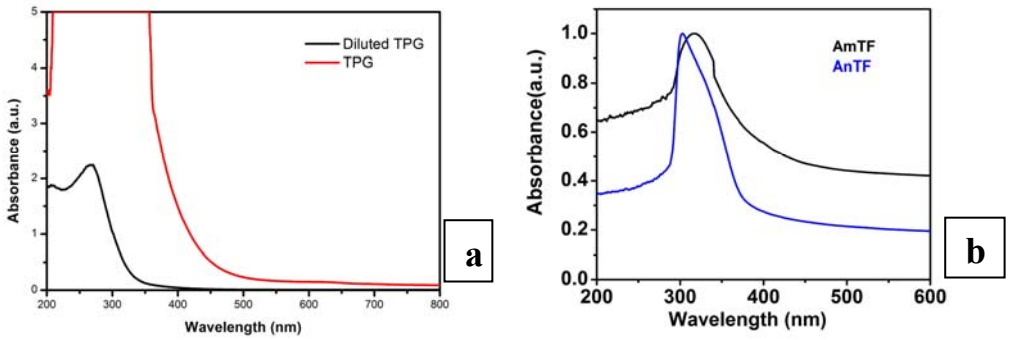

Fig. 1. UV-Vis spectra of photocatalysts, (a) TPG and (b) AmTF and AnTF

The XRD pattern (Fig. 2a) of AmTF shows that it is amorphous, as there are no sharp peaks in the spectrum, however weak peaks show that AmTF contains different oxides of titanium such as TiO_2 (002), Ti_3O_5 (110), Ti_5O_9 (102,121), Ti_7O_{13} (105,122), etc. [8]. It is suggested that the films have the structure of amorphous network in which weakly bound oxygen is trapped in the form of peroxide groups. In FTIR spectra in Fig. 2b the absorption from 3,000 to 3,600 cm^{-1} can be assigned to the stretching vibration of the hydrogen-bonded OH groups of the adsorbed water and the titanium hydroxide obtained by hydrolysis of titanium alkoxide [9]. The absorption around 1,600 cm^{-1} is due to O–H stretching and deformation mode of adsorbed H_2O [10], while the band sat 1,517 cm^{-1} and 1,430 cm^{-1} belong to carboxyl (COO) group [11]. The observed absorption at 922 and 823 cm^{-1} can respectively be assigned to the stretching vibration of the O-O bond and the Ti-O bond in the O=Ti-O-O-H bond to titanium oxide and titanium peroxy acid. The peak at 502 cm^{-1} may be due to vibration mode of Ti-O bonds in TiO_2 lattice [12]. These results are in agreement with the XRD results showing small peaks of titanium oxides.

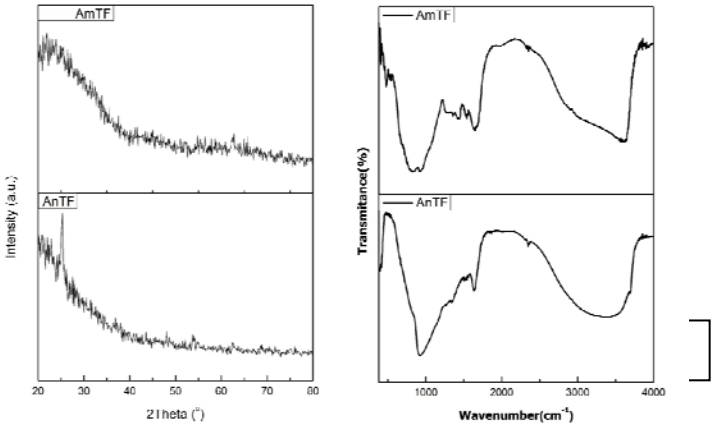

Fig. 2. XRD pattern of AmTF and AnTF photocatalyst (a) and their FTIR (b)

SEM of AnTF was recorded to investigate its structural and surface characteristics. It was observed that the coating was transparent and sufficiently strong to sustain for all the cycles (Fig. 4). The size of nanoparticles could be estimated to be about 50 nm. XRD patterns of the AnTF (Fig. 2a) are characterized by one major peak at $2\theta = 25.32°$ which corresponds to (101) reflections of the anatase phase of TiO_2. Bragg reflections at angles of 25.3°, 48.1°, and 55.6° corresponded to (101), (200), and (211) tetragonal crystal planes of anatase phase TiO_2, respectively. The calculated particle size of TiO_2 in the thin film was 37 nm as calculated by Scherrer's formula.

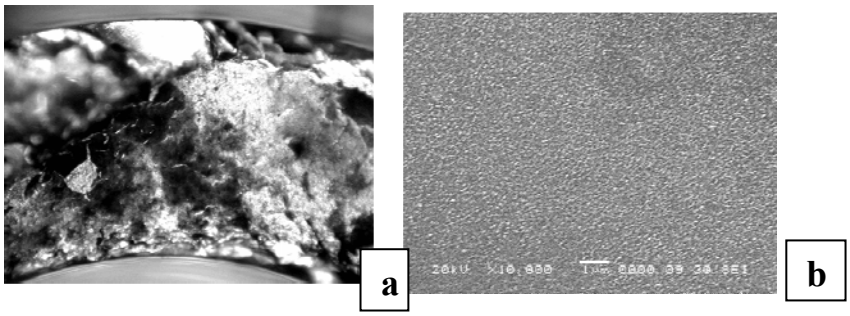

Fig. 3 (a) Micrograpgh of AmTD and (b) SEM of AnTF

3.2 Photocatalytic activity and reuse evaluation of photocatalyst

Photocatalytic activity of gel, chips and thin film were evaluated for removal of MB under dark and solar radiation. A cationic form of MB can be reduced and changed from blue to colorless by accepting a photo-catalytically generated electron. The 100% adsorption and degradation of MB by TPG, AmTF and AnTF was achieved under sunlight. In the case of TPG 100% of MB removal happened even in the absence of sunlight. It was found that there is direct relation between the zeta potential and TPG adsorption capacity.

The results of MB removal in the presence of photocatalysts, under dark and solar light irradiation at different time intervals are presented in Fig. 4a. There is a sharp reduction in MB concentration in first 5 min of contact which is due to the fast adsorption of MB at beginning. Almost 100% degradation of MB was observed during 5 and 60 min for TPG, AmTF and AnTF, respectively. The results of photocatalysts reusability showed that under identical condition TPG can be reused 5 times without any reduction in efficiency and AmTF and AnTF can be reused about 20 cycles without significant reduction in efficiency. Fig.4b shows AmTF and AnTF photocatalyst after MB removal after 20 cycles.

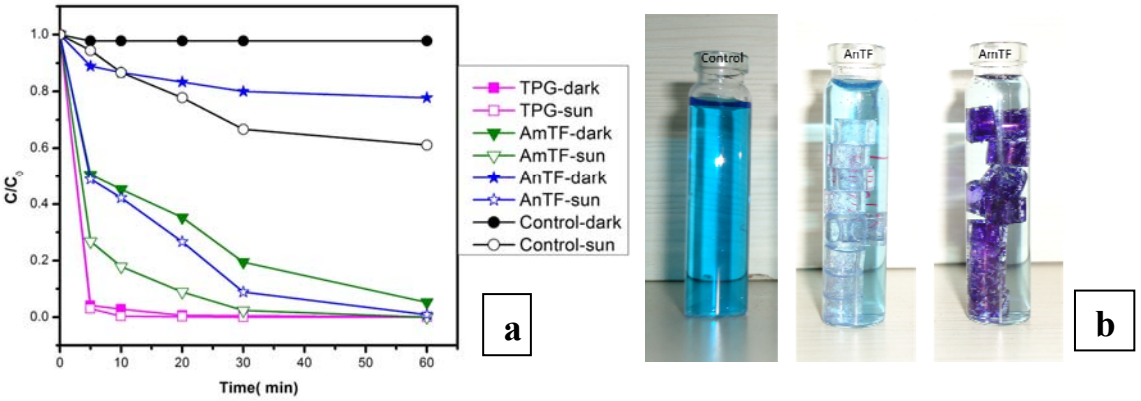

Fig. 4. MB removal using different photocatalyst in two different condition (a) and photocatalyst after 20 cycles

4. Conclusion

Three types of titanate based photocatalysts were synthesized using a simple sol-gel method. Their adsorption and photocatalytic activity were evaluated for MB removal. TPG was prepared without any thermal treatment. The results illustrated that the MB removal process could be completed in 5 min using TPG independent of sunlight, however it regenerates faster under sunlight irradiation. Removal efficiency and stability of TPG was found to be greatly affected by zeta potential. It can be regenerated and reused for 5 times without significant reduction in photocatalytic activity. The obtained gel has great potential in practical use in the area where the sun irradiation is limited.

AmTF was also prepared at ambient temperature. XRD and FTIR analysis of AmTF shows that the film consisted of different oxides of titanium. The band gap energy of this film was calculated to be about 2.8 eV indicating that there is band gap narrowing comparing to commercial TiO_2. This amorphous film found to be active for adsorption and degradation of MB, indicating the potential of this photocatalyst for the treatment of the dye house and textile wastewater.

AnTF with high durability was prepared under thermal treatment up to 500°C. This thin film also was found to be active for photocatalytic degradation of methylene blue under solar light. XRD analysis of AnTF shows that the TiO_2 anatase is the main crystalline phase. The band gap energy of the TiO_2 thin films was calculated to be about 2.91 eV for powder and 3.1 eV for the films heated up to 500°C, indicating band gap narrowing.

Among the catalysts investigated the TPG gel were the most active and AnTF, films calcined up to 500°C were found to be most durable catalyst for degradation of methylene blue. Finally, the most important observation is the long life of these films which can be used for number of cycles. There is no need for separation or filtration of photocatalyst and most importantly it is reusable. The use of sunlight as a source of light adds to the economy of process.

From the results of the present work it can be concluded that these photocatalysts can contribute to the photocatalytic treatment of the water/wastewater in different part of the world based on climate and this can lead to a breakthrough for application of a climate-efficient titanate based photocatalyst.

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