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Photodegradation of Congo red under sunlight catalysed by nanorod rutile TiO_2

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Abstract

Nanorod titanium oxide was obtained at room temperature and normal pressure using a simple method of preparation. The dilute titanium(III) chloride solution was stirred at room temperature for several hours, and then ammonium hydroxide was added. A white gel $TiO_2 \cdot xH_2O$ was obtained with nanorod shape and rutile crystalline structure. When Congo red solution was mixed with the wet gel; adsorption of Congo red took place in few seconds. The Congo red adsorbed on titanium oxide particles was easily decomposed under sunlight. Powder $TiO_2 \cdot 0.6H_2O$, obtained by drying the gel at room temperature, was also active under sunlight; although it showed slower adsorption compared to the wet gel $TiO_2 \cdot xH_2O$.

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Keywords: Soft chemistry preparation; Rutile titanium oxide; Congo red photodegradation

1. Introduction

Photodegradation of pollutants in textile wastewater is important to environmental issue. The most studied photocatalyst material is titanium oxide TiO_2 [1–3]. It shows great photodegradation activity toward many pollutants like organic dyes. The UV irradiation found to be necessary to achieve such decomposition. Many researches are carried out to improve the catalyst in order to substitute the UV irradiation by visible light. Doped titania with various metals as well as non-metals were found to be active in visible light [4–6]. In general, TiO_2 activity depends on many factors. (1) Crystalline phase: anatase phase was found to be photocatalytically active over the two other form rutile and brookite [1,7]. (2) The purity of the phase: commercialized mixture of anatase and rutile (Degussa P25) exhibited much superior photocatalytic activity compared to pure-anatase and rutile [8,9]. (3) The size of the particles: very fine particles (few nanometers) showed decrease in photocatalytic activity although the surface area was higher; this is explained by recombination of e^-/h^+ (electron–hole pairs), which could be high in extremely small particles [10]. (4) The shape of titanium oxide particles: for instance, nanorod shape anatase was found to be less active for Congo red photodegradation than dot shape anatase [11].

In general, titanium oxide, TiO_2, can be prepared by several methods. Many of them require special apparatus, or they are using highly costly starting materials, which could limit commercialization. A simple soft chemistry technique is required especially if it leads to a reactive materials. In this paper, a simple low cost method at room temperature and normal pressure was used to obtain nanorod rutile that shows excellent photodegradation of Congo red under sunlight.

2. Experimental

$TiCl_3$ solution (30%, w/v $TiCl_3$ BDH Laboratory, England) was diluted with distilled water and stirred for 65 h at room temperature. The solution which was purple dark presently turn to white colloidal solution with an acidic pH 0.8. Then ammonium hydroxide 10% NH_4OH was added. A white gel appears immediately; solution pH was 9.2. The gel at the bottom of the beaker was easily separated from the solution by decantation; it was then washed with distilled water. After each washing, the mixture was allowed to settle in order to allow the separation of the gel from the solution by decantation. The product was prepared

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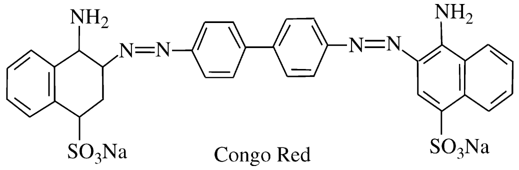
according to the following chemical reaction:

$$\underset{(20\,\text{mL})}{\text{TiCl}_3(\text{aq})} + \underset{(180\,\text{mL})}{\text{H}_2\text{O(l)}} \xrightarrow{\text{stirring for 65 h}} \text{white colloidal solution}$$

$$\xrightarrow{+10\%\ \text{NH}_4\text{OH}} \text{TiO}_2 \cdot x\text{H}_2\text{O(white gel)}$$

The wet gel obtained can be dried at room temperature and used for purity and particles size analysis. Congo red is water soluble; yielding a red solution with high absorption bond in UV spectrum located around 500 nm. It has the following chemical structure.



Congo Red

The Congo red solution was prepared by dissolving Congo red powder ($C_{32}H_{24}N_6O_6S_2$ from BDH Chemical Ltd. Poole England) in distilled water to obtain a solution 2.5×10^{-5} M concentration. The photocatalysis experiments were carried out in 100 mL beaker containing about 70 mL of Congo red aqueous solution (0.025 mM) and about 90 mg of TiO_2 as wet gel $TiO_2{\cdot}xH_2O$ or as powder $TiO_2{\cdot}0.6H_2O$. The photodegradation experiments were carried out under sunlight. These experiments were followed by different spectroscopic techniques as powder X-ray diffraction (Philips 1710, diffractometer), Thermal analyses (TG and DTA, 2960 Universal TA Instruments, under nitrogen gas and with heating rate 10 °C min^{-1}), UV spectroscopy (UV spectrometer Cary 50 Conc) and transmission electron microscope (Jeol 1234).

3. Results and discussion

Fig. 1 shows the X-ray diffraction pattern of the powder obtained from drying the titanium oxide gel $TiO_2{\cdot}xH_2O$ at room temperature. It shows a pure crystalline phase with all diffraction peaks identified to TiO_2 rutile structure.

The as-prepared product was analyzed by thermal analysis TGA and DTA, Fig. 2(a and b).

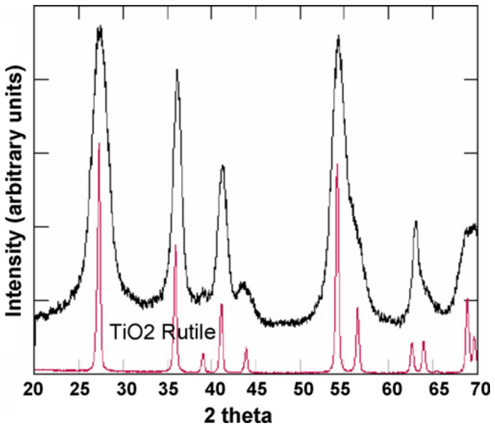


Fig. 1. Powder X-ray diffraction pattern of the gel dried at room temperature (for comparison, pure rutile TiO_2 XRD pattern is included).

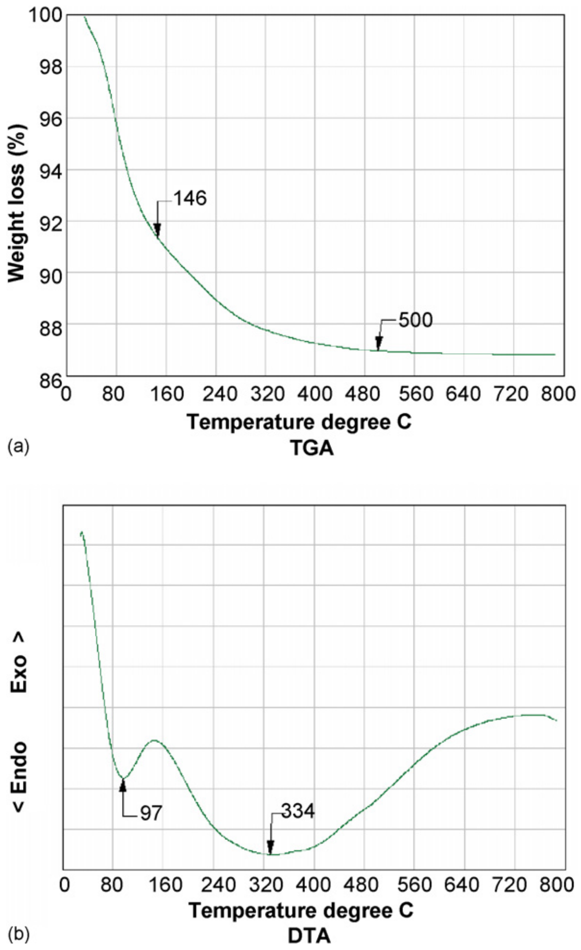


Fig. 2. (a) TGA and (b) DTA curves of $TiO_2{\cdot}0.6H_2O$.

DTA curve shows two endothermic peaks; the first one is centered at 97 °C and ended at about 146 °C (about 8.6% lost on TG curve). It will correspond to the lost of adsorbed water. The second endothermic peak is centered at 334 °C. From TG curve the lost of water ended at around 500 °C (about 4.4% lost on TG curve). It will correspond to the lost of chemically bonded water. DTA curve does not show any exothermic peak, which indicates that the product is pure crystalline phase without any other amorphous phase. The thermal behavior of as-prepared titanium oxide gel can be summarized as follows:

$$\underset{\text{rutile (wet gel)}}{\text{TiO}_2 \cdot x\text{H}_2\text{O}} \xrightarrow{25\,^\circ\text{C}} \underset{\text{rutile (powder)}}{\text{TiO}_2 \cdot 0.6\text{H}_2\text{O}}$$

$$\xrightarrow{146\,^\circ\text{C}} \underset{\text{rutile (powder)}}{\text{TiO}_2 \cdot 0.2\text{H}_2\text{O}} \xrightarrow{500\,^\circ\text{C}} \underset{\text{rutile (powder)}}{\text{TiO}_2}$$

The X-ray diffraction peaks in Fig. 1 are broad, which probably indicates small particles size. TEM micrograph, Fig. 3, shows agglomeration of nanorod particles of average size 35 nm of length and 3 nm of width.

In a recent study [12,13], we show that the wet tin oxide gel $SnO_2{\cdot}xH_2O$ particles was less agglomerate than the powder particles obtained after drying the gel at room temperature. Thus, tin oxide gel was found to be more reactive in photodegradation of Congo red rather than powder. In the present study, the wet

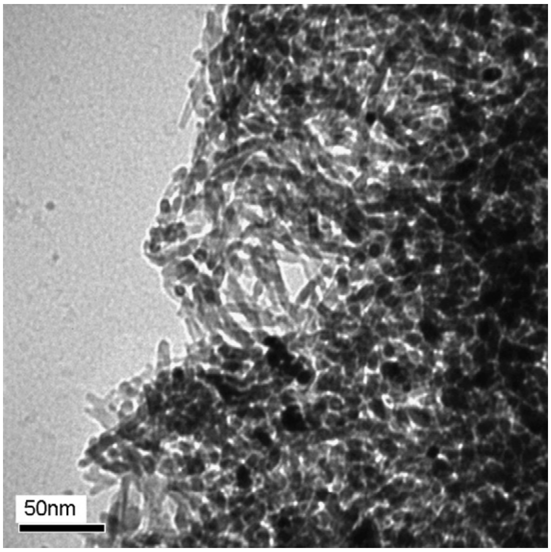


Fig. 3. TEM micrographs of powder $TiO_2·0.6H_2O$.

titanium oxide gel $TiO_2·xH_2O$ also shows less agglomerated particles (Fig. 4) compared to powder $TiO_2·0.6H_2O$. The difference between the gel and the powder is the amount of water. Titanium oxide powder contains only $0.6H_2O$; in contrast the gel contains a high number of water molecules. Probably, because of interaction between water and titanium oxide, these particles could not strongly agglomerate like in powder sample. Less agglomerated particles in such application are needed because catalyst reaction usually takes place on the surface.

Photodegradtion of Congo red solution was carried out at room temperature by using the wet titanium oxide gel as catalyst and sunlight as light source. A fresh $TiO_2·xH_2O$ gel at the bottom of the beaker was easily separated from distilled water by decantation. Then, Congo red solution was added. After only few seconds all Congo red was adsorbed on titanium oxide particles and a colorless solution was obtained (see Supplementary data). This mixture was stirred for 45 min under sunlight between 11:00 and 12:00 a.m. The temperature under sunlight was 28 °C. With reaction time running, the red color intensity of titanium oxide gel decreases until disappearance. This indicates decomposition of Congo red on titanium oxide particles surface. The same experiment was carried out in the dark, after 45 min of stirring the red color on titanium oxide gel remains, which indicates that Congo red adsorbed was not decomposed. Another experiment was carried out under sunlight with the same gel used for the first experiment. The reused gel shows the same capabilities for adsorption and decomposition of Congo red as the fresh gel. Fig. 5 shows the UV spectra. All curves are similar, even for the experiment carried out in the dark. Because in the first seconds of the experiment, in all three cases, both under sunlight or in dark, Congo red was completely removed from the solution by adsorption on titanium oxide particles. Sunlight was not necessary for adsorption; however the Congo red adsorbed on titanium oxide particles surface decomposes only on sunlight presence (see Supplementary data).

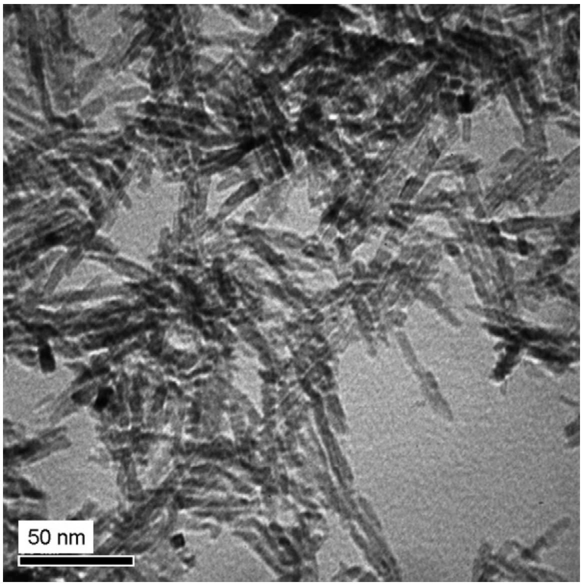


Fig. 4. TEM micrograph of wet titanium oxide gel $TiO_2·xH_2O$.

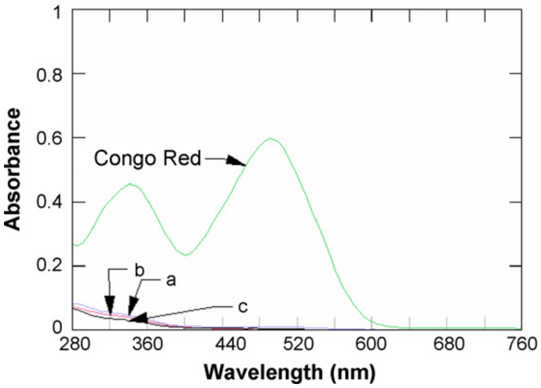


Fig. 5. UV spectra: (a) Congo red solution with $TiO_2·xH_2O$ gel under sunlight (45 min); (b) Congo red solution with $TiO_2·xH_2O$ gel in dark (45 min); (c) Congo red solution with reused $TiO_2·xH_2O$ gel under sunlight (45 min).

A comparison of adsorption of Congo red in the dark between titanium oxide gel and powder was carried out (Fig. 6). Although the powder shows a good adsorption of Congo red after 15 min of stirring, the gel adsorption still better after only few seconds

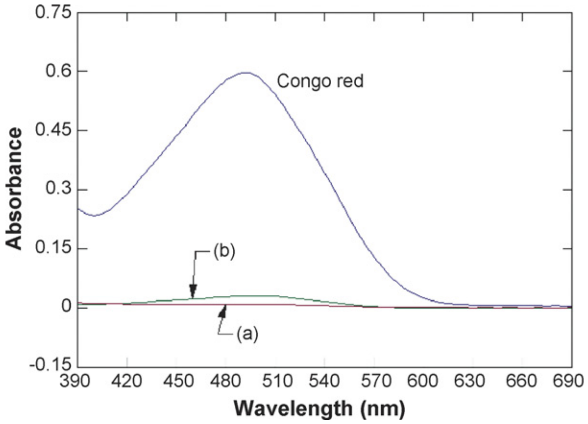


Fig. 6. UV spectra: (a) Congo red solution with $TiO_2·xH_2O$ gel in dark (few seconds); (b) Congo red solution with $TiO_2·0.6H_2O$ powder in dark (15 min).

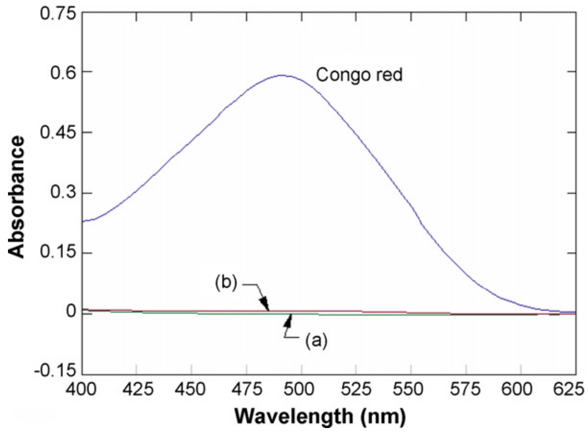


Fig. 7. UV spectra: (a) Congo red solution with $TiO_2 \cdot xH_2O$ gel under sunlight (45 min); (b) Congo red solution with $TiO_2 \cdot 0.6H_2O$ powder under sunlight (45 min).

of stirring. This is probably the consequence of less agglomerated particles that can provide more surface area for Congo red adsorption in a very short time. It is important to indicate that if chlorine ions were not removed from the wet gel, by washing it with distilled water several times until the $AgNO_3$ test indicated the absence of chloride ions in the decanted solution, adsorption decreases dramatically. The chlorine ions seem to be poisonous to the surface area of titanium oxide.

When the two solutions are exposed to sunlight, in both experiments the decomposition of adsorbed Congo red takes place and the red color disappear from both catalysts. Fig. 7 depicts the UV spectra. Titanium oxide powder presents the same performance as the gel. The difference seems to be in adsorption step where Congo red is adsorbed on $TiO_2 \cdot xH_2O$ gel quickly compared to $TiO_2 \cdot 0.6H_2O$ powder.

It is worth noting that when anatase is prepared with nanorod shape it shows less activity compared to dot shape anatase [11]. Also it is known that the anatase TiO_2 is a more efficient photocatalyst than the rutile TiO_2 [1,7]. In The present work nanorod rutile phase has excellent photodegradation under sunlight better than both dot and rod anatase under UV irradiation [11]. This excellent photodegradation of Congo red under sunlight probably can be explained by the presence in the same time of all favorable parameters: particle size, shape of the particles and crystalline phase. It was reported that rutile with nanodot shape was found to be less active for Congo red degradation compared to anatase phase [11]. It seems that the catalyst will not only depend on the crystalline structure (anatase, rutile and brookite) but will also depend strongly on other parameters as the particle size and shape. When all these favorable parameters are found together, like in the present work, pure rutile phase was found to be active under sunlight. The same thing can be said for anatase phase. If appropriate size and shape are present; anatase could be also active under sunlight as the rutile phase or better. If nanorod shape with the present size is favorable for rutile, the same shape and size probably could not be favorable for anatase because the two phases present different crystalline structure. It seems that for each titanium oxide phase some optimum size and shape exist where each phase will present high photocatalytic activity.

4. Conclusion

With a simple method, it was easy to prepare a nanorod rutile phase at room temperature. Soft chemistry or *chimie douce* is powerfull technique for preparing new materials or improving some chemical and physical properties of materials. Pure rutile nanorod shows excellent photodegradation of Congo red under sunlight. It seems that the present particles have favorable size and shape for such reaction. Although both pure rutile gel and powder show active photodegradation of Congo red under sunlight, the adsorption step is more active with the gel owing to the less agglomeration of particles. This study shows that the size and the shape of the particles have also an effect on the catalyst along with the crystalline structure.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.photochem.2006.05.004.

References

[1] R.J. Gonzalez, R. Zallen, H. Berger, Phys. Rev. B 55 (1997) 7014.
[2] A. Pottier, C. Chance, E. Tronc, L. Mazerroles, J. Jolivet, J. Mater. Chem. 11 (2001) 1116.
[3] H. Lachheb, E. Puzenat, A. Houas, M. Ksibi, E. Elaloui, C. Guillard, J.M. Hermann, Appl. Catal. B: Environ. 39 (2002) 75.
[4] W. Choi, A. Termin, M.R. Hoffmann, J. Phys. Chem. 98 (1994) 13669.
[5] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 293 (2001) 269.
[6] A.R. Gandhe, J.B. Fernandes, J. Solid State Chem. 178 (2005) 2953.
[7] H. Kominami, S.Y. Murakami, J.I. Kato, B. Ohtani, J. Phys. Chem. B 106 (2002) 10501.
[8] T. Ohno, K. Tokieda, S. Higashida, M. Matsumura, Appl. Catal. A: Gen. 244 (2003) 383.
[9] B. Sun, P.G. Smirniotis, Catal. Today 88 (2003) 49.
[10] C.B. Almquist, P. Biswas, J. Catal. 212 (2002) 145.
[11] R.K. Wahi, W.W. Yu, Y. Liu, M.L. Mejia, J.C. Falkner, W. Nolte, V.L. Colvin, J. Mol. Catal. A: Chem. 242 (2005) 48.
[12] K. Melghit, A.K. Mohammed, I. Al-Amri, J. Mater. Sci. Eng. B 117 (2005) 302.
[13] K. Melghit, M.S. Al-Rubaei, I. Al-Amri, J. Photochem. Photobiol. A: Chem., in press.