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Chimie douce preparation, characterization and photocatalytic activity of nanocrystalline SnO_2

Khaled Melghit[a,*], Abdul Kabir Mohammed[a,1], Issa Al-Amri[b]

[a] *Chemistry Department, College of Science, Sultan Qaboos University, P.O. Box 36, Al Khoudh 123, Oman*
[b] *Electron Microscopy Unit, College of Medicine and Health Sciences, Sultan Qaboos University, P.O. Box 36, Al Khoudh 123, Oman*

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Abstract

Nanosize particles SnO_2 gel was prepared by mixing $SnCl_2{\cdot}2H_2O$ powder with distilled water and stirring at room temperature for 2 days. The solid phase of the gel obtained was characterized by X-ray diffraction, thermogravimetric analysis, transmission electron microscopy and FT-IR spectrocopy. The gel obtained was investigated for photocatalytic activity for the degradation of Congo Red aqueous solution and compared with the gel dried at room temperature for 2 days and the gel heated at 600 °C for 1 day, The results obtained indicates that the wet gel that has not been dried or heated shows higher photocatalytic activity. This highly photoactive wet gel shows less agglomeration of the nanosize particles (2–3 nm) of SnO_2.

Keywords: Tin oxide; Nanostructures; Photocatalysis

1. Introduction

Tin dioxide (SnO_2) is an important material with many technological applications such as photovoltaic devices [1], photosensors [2], transparent conductive electrodes [3], catalysis [4], and recently in Lithium rechargeable battery [5]. The synthesis of nanosize particle materials has attracted the interest of many researchers worldwide in recent years. Due to their high active surface area, nanosize particle materials are more active compared to the same materials with larger particle sizes. For example, in Li-ions battery, electrodes composed of nanocrystalline particles exhibit high capacity and better cyclability [6]; in sensor devices, the sensitivity of SnO_2 to both CO and H_2 increases as grain size is reduced [7]. High surface area SnO_2 was recently used as a support for Pd catalysts, it is found to be highly active for the reduction of NO to N_2 at relatively low temperature [8]. Also, various nanosize semiconducting materials (such as oxides) find applications in heterogeneous photocatalysis for air and water purification treatment. Among these oxides, TiO_2 (Degussa P25) has attracted most attention mainly because of its high photocatalytic activity [9]. Recently, a mixture of SnO_2 with TiO_2 was found to show higher photocatalytic activity than Degussa P25 [10]. Nanosize particles of tin dioxide have been prepared by different techniques such as the sol–gel processes [11–13]. Generally, these techniques involve more than one step and some of the methods involve the use of expensive starting materials. Finding a simple and low-cost method of preparation is desirable because this will reduce the time required for preparation and also make it more practical. This paper will show that nanocrystalline particles of SnO_2 can be prepared in aqueous solution by a simple one-step synthetic method; it will also discuss the effect of tin dioxide particle size and degree of agglomeration on the photocatalytic degradation of Congo Red solution.

* Corresponding author. Tel.: +968 513 333x2599; fax: +968 513 415.
E-mail address: melghit@squ.edu.om (K. Melghit).
[1] Visiting Fulbright Scholar at Sultan Qaboos University, 2003–2004. Permanent address: Department of Chemistry, North Carolina Agricultural & Technical State University, 1601 E. Market Street, Greensboro, NC 27411, USA.

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2. Experiments

The method of preparation consists only of mixing tin(II) dichloride ($SnCl_2{\cdot}2H_2O$) with distilled water at room temperature:

$$SnCl_2 \cdot 2H_2O\,(\text{powder}) + H_2O\,(\text{distilled water}) \xrightarrow[2\,\text{days}]{\text{stirring}} \text{gel}$$

Thus 5 g of $SnCl_2{\cdot}2H_2O$ (BDH, England) was mixed with 800 mL of distilled water. This mixture was maintained under stirring for 2 days. During this period, the solution remained cloudy and white. The pH of the solution decreased rapidly after a few minutes of stirring to reach pH 2 and it remained almost constant. After 2 days, the stirring was stopped and the mixture was allowed to settle. The gel at the bottom of the beaker was easily separated from the solution by decantation, it was then washed several times 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 washings were stopped after the $AgNO_3$ test indicated the absence of chloride ions in the decanted solution. The gel obtained can be used for thin film preparation or it can be dried at room temperature to yield a white powder.

The solid phase of the gel was characterized by X-ray powder diffraction (Philips 1710), thermogravimetric analysis (Perkin-Elmer TGA 7 under nitrogen atmosphere and with a heating rate of 10 °C/min), FTIR spectrometer Nicolet Impact 400D (transmittance spectra acquired between 400 cm^{-1} and 4000 cm^{-1}, the sample powder was dilute with KBr), UV spectrometer Cary 50 Conc (spectra acquired between 300 cm^{-1} and 800 cm^{-1}), and transmission electron microscope JEOL 1234.

The photocatalysis experiments were carried out in 100 mL beaker containing 0.01 mM of Congo Red (BDH, England) aqueous solution and 4.3 g/L of the SnO_2 catalyst. The irradiation was done with an 80-W UV lamp (OSRAM) which was placed close to the beaker.

3. Results and discussion

After the gel has been dried at room temperature, it was analyzed by X-ray diffraction (Fig. 1). The X-ray pattern shows broad peaks characteristic of tetragonal cassiterite (JCPDS No 41-1445).

Fig. 2(a and b) shows the infrared spectra of tin(II) chloride $SnCl_2{\cdot}2H_2O$ (a) and the gel after drying at room temperature (b). Cassiterite SnO_2, with rutile structure, presents four vibrations active in infrared with frequencies observed for single crystals (243 cm^{-1}, 284 cm^{-1}, 465 cm^{-1}, and 605 cm^{-1}) [14]. Fig. 2(b) is characteristic of typical infrared spectrum of tin dioxide [15]; the spectrum starts with a broad and intense peak centered at 3747 cm^{-1} associated with the stretching vibration of H-bonded hydroxyls followed by a peak with lower intensity at 1626 cm^{-1} associated with water physisorbed on the surface of the gel. This is due to presence of water in the sample. Thermogravimetric analysis indicates that the gel dried at room temperature contains about 1.7 molecules H_2O. A broad intense peak centered at 588 cm^{-1} can be seen in the spectrum, which is characteristic of SnO_2 network vibration [13]. The $SnCl_2{\cdot}2H_2O$ infrared spectrum (Fig. 2a) shows other vibration peaks (as 2332 cm^{-1}, 1533 cm^{-1}, 1452 cm^{-1}, 1394 cm^{-1}, and 1302 cm^{-1}), which are not present in the spectrum of the gel dried at room temperature. This confirms the result of the X-ray diffraction, which indicates the formation of tin dioxide.

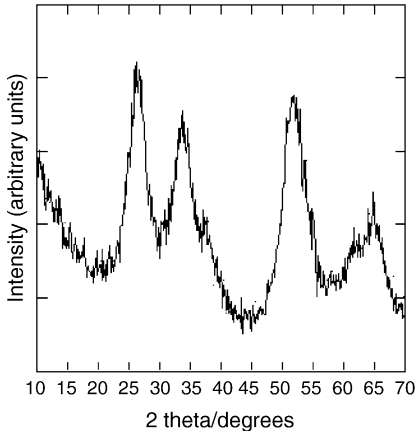

Fig. 1. X-ray diffraction of the gel dried at room temperature.

Thus, in a one-step procedure of only mixing tin dichloride with distilled water, gel of tin dioxide can be obtained in good yield. This method is similar to other sol–gel methods. It seems that the formation of SnO_2 gel passes through tin hydroxide, which is probably the reason why the pH of the water decreases quickly after the addition of $SnCl_2{\cdot}2H_2O$ indicating that more $H^+_{(aq)}$ are present in the solution than $OH^-_{(aq)}$. Structural changes induced by heat treatment were also investigated. Fig. 3 depicts the X-ray diffraction of the gel heated at 600 °C for 1 day. This pattern is similar to the X-ray pattern of the gel dried at room temperature; the only difference is that the diffraction peaks are narrower and more

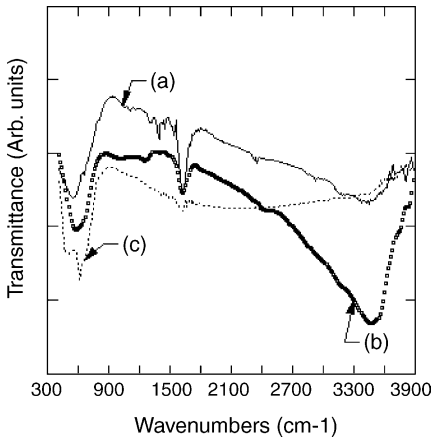

Fig. 2. FTIR spectra of (a) $SnCl_2{\cdot}2H_2O$, (b) the gel dried at room temperature, and (c) the gel heated at 600 °C.

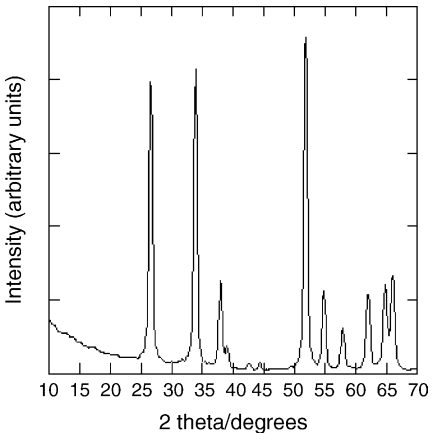

Fig. 3. X-ray diffraction of the gel heated at 600 °C for 1 day.

intense which indicates better crystallinity for the gel dried at 600 °C. This pattern is characteristic of pure SnO_2 (no other crystal phase could be detected). The infrared spectra of the gel heated at 600 °C for 1 day is reported in Fig. 2(c). It shows that the broad peak at 3747 cm^{-1}, characteristic of hydroxyl vibration, has disappeared; a weak broad peak can be seen at 1626 cm^{-1} associated with physisorbed water. Two intense peaks can be seen at 607 cm^{-1} and 503 cm^{-1}, associated with SnO_2 network vibration. Compared to the gel dried only at room temperature, it can be concluded that after heating, the water present has evaporated (the peaks associated with water vibration disappear) and the peaks associated with SnO_2 network vibration are more resolved which probably is the consequence of better crystallinity of SnO_2.

Three types of tin dioxide: wet tin dioxide gel, the gel dried at room temperature and the gel dried at 600 °C were investigated for their photocatalytic activity based upon the degradation of Congo Red aqueous solution (0.01 mM). The experiments were carried out in three 100 mL beakers. To get the same concentration of catalyst (SnO_2) in all experiments, the same concentration of $SnCl_2{\cdot}2H_2O$ (0.625 g/100 mL) were used. The gels were obtained as described above. After washing, three white gels were obtained. In the first beaker, contaning the wet gel, was added Congo Red solution (75 mL) immediately after the sythesis. The gel in the second beaker was dried at room temperature for 2 days, which produced a white powder. It was then mixed with Congo Red solution (75 mL). The third gel was dried at room temperature for 2 days and heated at 600 °C for 1 day, which produced a white-yellowish powder, which was then mixed with Congo Red solution (75 mL). The three beakers containing Congo Red solution and the catalyst were subjected to the same photocatalysis condition (each mixture was exposed to UV light for 3 h with stirring). The mixtures were centrifuged to separate the solution from the solid phase and the solutions were analyzed by UV–vis spectroscopy. Fig. 4 shows the UV–vis spectra obtained. The Congo Red solution, exposed to UV light without catalyst (Fig. 4a), shows some decomposition (the absorption peaks are less intense compared to Congo

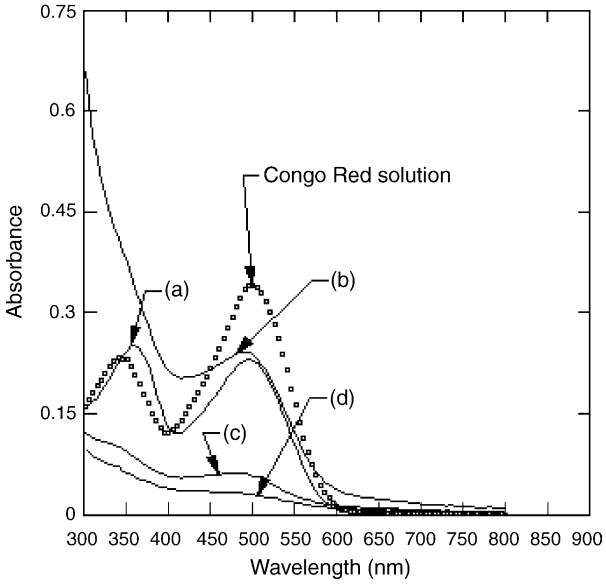

Fig. 4. UV–vis spectra of Congo Red solution irradiated with UV light for 3 h: (a) without catalyst, (b) with the gel heated at 600 °C, (c) with the gel dried at room temperature, and (d) with the wet gel.

Red solution); however, when a catalyst was added, the rate of degradation increased appreciably. Fig. 4 shows that the wet gel that has not been dried or heated produced the highest photocatalytic activity (Fig. 4d) and the tin dioxide obtained after heating at 600 °C shows the lowest activity (Fig. 4b).

In order to gain a better understanding of these results, transmission electron microcopic analyses of the three samples (wet gel, gel dried at room temperature and gel heated at 600 °C) were carried out. A small amount of each sample was first mixed with ethanol solution. Copper grids coated with *Formvor* film were placed on drops of each sample for 15 s, the samples were dried and then viewed under 120 kV. The wet gel (Fig. 5a) shows dispersed spherical nanosize particles (with average size 2–3 nm); the gel dried at room temperature (Fig. 5b) showed strongly agglomerated particles although the size remains 2–3 nm. It is known that the particles size increase with the firing temperature due to continued grain growth. The transmission electron micrograph of the gel heated at 600 °C for 1 day (Fig. 5c) shows spherical particles with average size of about 25–30 nm. Although the heating was done at a relatively high temperature, the particle size was still in the nanosize range. However, they remain strongly agglomerated.

From these results, it seems that the reactivity of SnO_2 catalyst gel is related to its particle size and degree of agglomeration. As the particle size increases, the photocatalytic activity decreases. Particles of the same size with lower agglomeration will show higher activity compared to particles with higher agglomeration. In a recent study, it was also reported that higher surface hydroxyl groups and water molecules increase the photocatalytic activity [16]. In this experiment, it is clear that the amounts of adsorbed water or surface hydroxyl groups are much higher in the wet gel, used before drying,

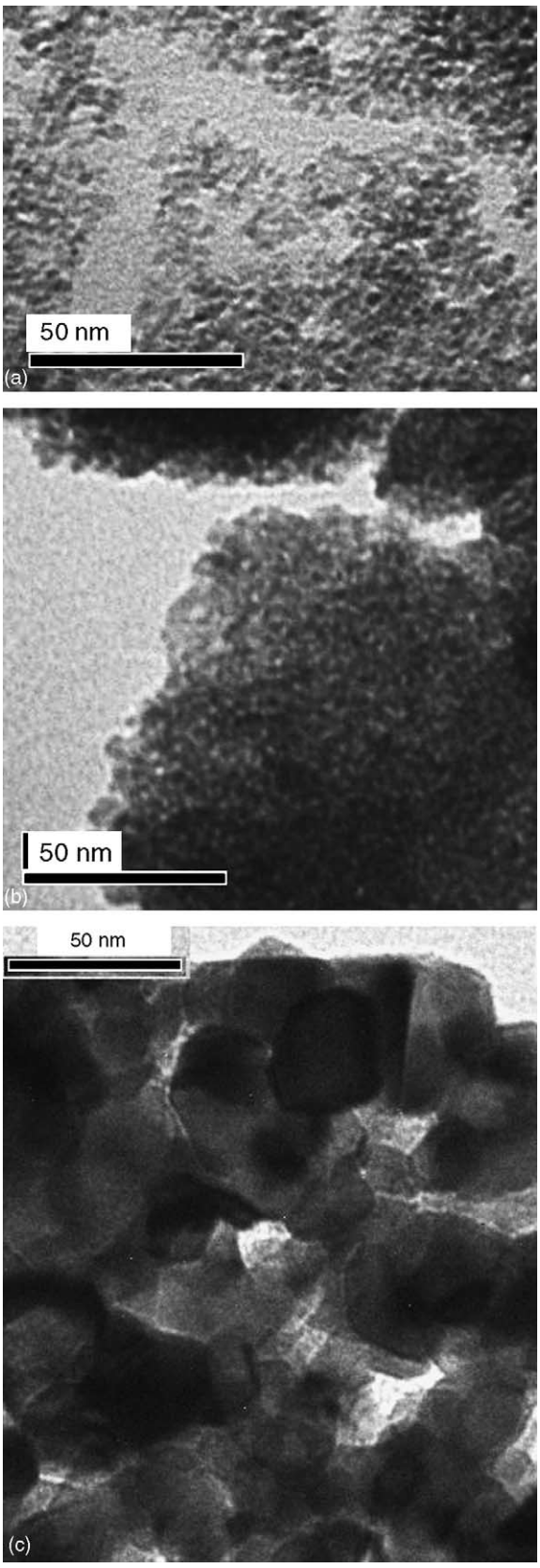

Fig. 5. TEM migrographs of (a) wet gel, (b) the gel dried at room temperature, and (c) the gel heated at 600 °C.

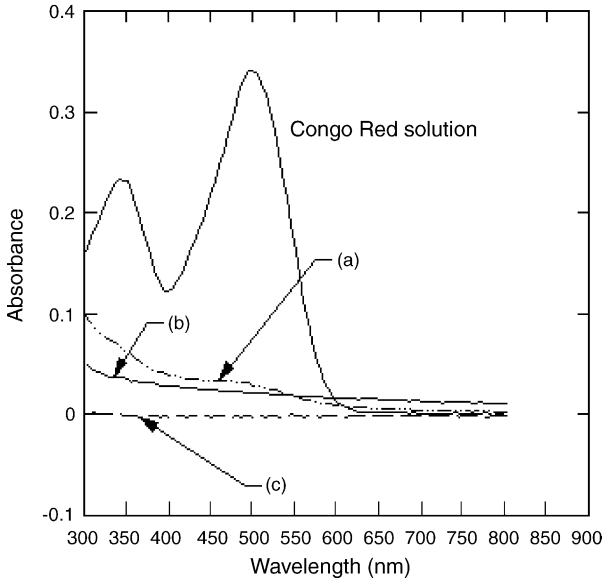

Fig. 6. UV–vis spectra of Congo Red solution irradiated with UV light: (a) with fresh gel (3 h reaction), (b) with reused gel (3 h reaction), and (c) with reused gel (6 h reaction).

than in the gel dried at room temperature or the gel heated at 600 °C. The gel obtained can be reused for photocatalytic degradation and it was found to be more reactive (Fig. 6a and b). The intensity of absorption peaks decreases as the gel is used for the second time, and with more reaction time (6 h), a complete decomposition of Congo Red solution was obtained (Fig. 6c).

4. Conclusions

The simple preparation method described in this article shows the possibility of preparing nanosize particles of SnO_2 by using only a one-step aqueous method. A good yield of about 80% was obtained and the average particle size is around 2–3 nm; even after heating the gel at 600 °C for 1 day, the particles remain in the nanosize range, about 25–30 nm. However, the wet gel that has not been dried contained less agglomerated particles and had higher photocatalytic activity for the degradation of Congo Red solution.

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