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Synthesis and characterization of Fe^{3+} doped TiO_2 nanoparticles and films and their performance for photocurrent response under UV illumination

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ABSTRACT

Undoped TiO_2 and Fe^{3+} doped (0.1, 0.3, 0.6 and 1 wt.%) TiO_2 nanoparticles have been synthesized by the acid-catalyzed sol–gel method. Iron cations are introduced in the initial solution, before gelification, what promotes their lattice localization. The Fe^{3+} doped TiO_2 films have been fabricated using a dip-coating technique. The effect of iron content on the crystalline structure, phase transformation and grain growth were determined by X-ray diffraction (XRD), Raman spectroscopy, UV–visible diffused reflectance spectroscopy (DRS) and Electron paramagnetic resonance (EPR) spectroscopy. It has demonstrated that all catalysts are composed of mixed-phase crystals of anatase and brookite with anatase as dominant phase. The crystallinity of the brookite and anatase phases decreased with increasing the iron content. The analysis of EPR result further confirms that Fe^{3+} ion are successfully doped in the TiO_2 lattice by substituting Ti^{4+}. It was demonstrated that Fe^{3+} ion in the TiO_2 films plays a role as the intermediate for the efficient separation of photogenerated hole–electron pairs and increases the photocurrent response of the film under UV light irradiation. The maximum photocurrent is obtained on the Fe^{3+} doped TiO_2 film with 0.1% Fe, which is 1.46 times that achieved on undoped TiO_2 film.

1. Introduction

A great deal of effort has been devoted in recent years to develop heterogeneous photocatalysts with good optical-electronic properties. However, TiO_2 catalysts inevitably encounter a serious limit in the following two aspects. A first disadvantage of titania is its high band gap value (3.2 eV) which selectively limits its photoactivity to wavelength lower than 387 nm. A second limiting factor of the TiO_2 performance is the fast recombination of photogenerated electron–hole pairs. Metal doping is a popular method to improve the photo reactivity of TiO_2 semiconductors under UV–Vis illumination [1,2]. Amongst a variety of metals, iron has been considered an appropriate candidate for incorporation in TiO_2 structure due to the similarity of the ionic radius of Fe^{3+} (0.64 Å) with that of octahedraly coordinated Ti^{4+} (0.68 Å) [3]. It was been also proposed that Fe doping directly influences the intrinsic properties of TiO_2, such as particle size and photocurrent responses under UV light irradiation. The beneficial effect consists in the fact that Fe^{3+} plays a role as intermediate for the efficient separation of photogenerated hole–electron pairs. Fe^{3+} traps photogenerated electrons due to the energy level for Fe^{3+}/Fe^{2+} below the conduction band edge of TiO_2. Simultaneously, Fe^{3+} can trap photogenerated holes due to the energy level for Fe^{4+}/Fe^{3+} above the valence band edge of TiO_2 [4,5].

The number of papers on Fe^{3+} doped TiO_2 (iron doped TiO_2) is undergoing an exponential increase. As often occurs in the case of an explosively growing subject, a certain degree of confusion due to conflicting evidence and interpretations is present in the literature. This is mainly due to the variety of synthetic methods adopted to prepare the catalyst [6–11]. Some authors reported the beneficial effect of Fe^{3+} in enhancing electron/hole separation thus increasing the photocatalytic activity [12–14]. As opposite other authors suggested a detrimental effect of Fe^{3+} due to an increase of the rate of charge recombination [15]. To put this controversy into a more realistic and practical catalytic perspective, one study reported that Fe^{3+} doped TiO_2 powder with optimal doping concentration exhibited a greatly enhanced photocatalytic activity in the degradation of isopropanol [16]. Zhu et al. [17] have indicated that iron doping of TiO_2 improves photocatalytic activity up to a doping level 0.09% of Fe^{3+}. The concentration of the dopant seems to be the essential factor to determine the potoactivity. In particular the optimum photocatalytic activities can be achieved upon doping at a relatively weak level.

It is well known that titania has three polymorphs in nature: rutile, anatase, and brookite. The two latter phases are metastable at all temperatures and transform commonly to rutile when they are heated. The coexistence of phases in TiO_2 has been suggested to be

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a factor which reduces the recombination rate of the e^-/h^+ pair [18,19]. As a consequence, an increase in photoactivity seems to be correlated to the coexistence of anatase and brookite phases in TiO_2 [19,20]. Therefore, it is important to understand the effect of the distribution and content of the dopant on phase composition of TiO_2.

The present work aims at complementing such investigations comparing undoped TiO_2 and Fe^{3+} doped TiO_2 nanoparticles and films which are synthesized by the acid-catalyzed sol–gel method. An advantage of the acidic catalysis is that it is possible to enhance simultaneously the crystallization of anatase phase and growth of brookite at low temperature. The influence of Fe^{3+} doping content on both anatase and brookite TiO_2 nanoparticles and the anatase–rutile transformation in the presence of brookite was evaluated. In addition, the photocurrent responses and stability of the Fe^{3+} doped TiO_2 films under a UV–Vis illumination were investigated by amperometric measurement in 0.1 M of NaOH aqueous solution. Our results indicate that Fe^{3+} doped TiO_2 photocatalysts could be an optimal structure for highly sensitive optoelectronic sensors.

2. Materials and methods

2.1. Preparation of Fe^{3+} doped TiO_2 powders

Fe^{3+} doped anatase/brookite TiO_2 powders were synthesized by acid catalyzed sol–gel route. In a typical procedure, a precursor of acidic aqueous solution was prepared by mixing a certain amount of nitric acid with 90 mL of distilled water (pH = 2.5) (solution A). 14.8 ml of Titanium tetraisopropoxide ($Ti(OC_3H_7)_4$, Sigma–Aldrich, 97%) were diluted in 80 ml of isopropanol. To this solution, different amounts (1, 0.6, 0.3 and 0.1%) of $Fe(NO_3)_3 \cdot 9H_2O$ (Sigma–Aldrich, 99.99%) were added according to the required Fe/Ti atom ratio (solution B). Solution A is added drop wise to solution B with constant and vigorous stirring for 24 h. The resulting mixture was undergone aging for 12 h, filtered and washed several times with deionised water. The final product was dried at 50 °C during 24 h. The resulting powders were calcined in air at various temperatures for 2 h. For comparison, undoped TiO_2 was also prepared by the same procedure without the addition of iron precursor. The Fe^{3+} doped TiO_2 calcined powders are labeled according to their iron content and calcination temperature: $TFe1_t$, $TFe0.6_t$, $TFe0.3_t$, $TFe0.1_t$ and undoped TiO_2 $TFe0_t$, where t means the calcination temperature. For example, $TFe0.6_{500}$ represents the Fe^{3+} doped TiO_2 with Fe/Ti = 0.6% calcined at 500 °C.

2.2. Preparation of Fe^{3+} doped TiO_2 films

The as-prepared powders were used to prepare Fe^{3+} doped anatase/brookite TiO_2 films using a dip-coating technique. TiO_2 films were deposited on a conductive glass plate (area, 4 cm^2). A well-dispersed suspension (0.4 wt.%) of Fe^{3+} doped TiO_2 powders was prepared in distilled water and stirred for 24 h. A substrate glass plate was coated with TiO_2 by dipping in the TiO_2 suspension, drying under air, and then heating at 120 °C for 30 min. The dip-coating procedure was repeated four times until a thick film of TiO_2 was obtained. The TiO_2 films were then calcined at a rate of 1 °C min^{-1} up to 400 °C and sintered at this temperature for 30 min.

2.3. Physical–chemical characterization of synthesized solids

The powder X-ray diffraction patterns were recorded at room temperature (using advanced D8, Bruker, Germany): X-ray tube operating at 40 kV and 40 mA, 0.6 mm fixed divergence slits, diffracted beam curved graphite monochromator (Cu Kα + 1 radiation, λ_1 = 1.540600 Å, λ_2 = 1.544390 Å) and 0.1 mm fixed slit in front of the scintillation detector. The data were collected in the 2θ range 2–70° with a step size of 0.02° and a counting time of 5 s/step. All peak data measured by XRD analysis were assigned by comparing with those of PCD database. TGA/DTA analysis data were recorded using TG/DTA instrument (Model Pyres Diamond TG/DTA, Perkin Elmer instrument). The temperature ranged from room temperature to 1000 °C in order to obtain crystallization and phase-transformation data. All analyses were performed in a flowing air atmosphere of 30 min^{-1} with the heating rate of 20 °C min^{-1}. Raman spectra were recorded with a LABRAM HR800 Raman Spectrometer equipped with a He-Ne ion laser emitting at a wavelength of (633 nm). UV–Vis diffuse reflectance (DR UV–Vis) spectra were recorded by a Varian Cary 5000/UV–Vis–N.I.R. spectrometer. Electron Paramagnetic Resonance (EPR) spectra were run using a X-band CW-EPR Bruker EMX spectrometer equipped with a cylindrical cavity operating at 100 kHz field modulation. The measurements were carried out in cells that can be connected to a conventional high-vacuum apparatus (residual pressure <10^{-6} kPa).

The iron content of the samples was determined using Atomic absorption flame emission spectroscopy AAS (ICE 3000 series). Prior to analyse, fifty milligrams of samples Fe^{3+} doped TiO_2 was transferred into Teflon flask and then completely dissolved in HF-HNO_3 solution (30/70% in volume). After dissolution, the mixture was diluted with 100 mL of deionized water and analyzed by (AAS).

2.4. Photo-electrochemical characterization

Photocurrent characterization was performed using a VoltaLab 40 PGZ301 potentiostat (Radiometer Analytical) and VoltaMaster 4.0 software for data acquisition. A 100 ml cell made of quartz was used as photoelectrochemical cell with the Fe^{3+} doped anatase/brookite TiO_2 films as working electrode, a Pt counter electrode and a saturated calomel reference electrode (SCE). All potentials are quoted versus SCE. The geometric surface of the working electrode was 4 cm^2. The electrolyte was an air-saturated aqueous solution with 0.1 M of NaOH. A 150 W Xenon lamp was employed as a UV excitation source (λ = 380 nm).

3. Results and discussion

3.1. Determination of iron content

The actual content of Fe^{3+} in different samples was determined by atomic absorption flame emission spectroscopy (AAS). The results are listed in Table 1. It is shown that the actual content of Fe^{3+} measured by AAS is quite close to the theoretical value, indicating that most of Fe^{3+} is inserted in the framework of TiO_2.

3.2. X-ray diffraction patterns of undoped TiO_2 and Fe^{3+} doped TiO_2

Figure ure1 shows the evolution of the titania XRD powder spectra as function of the iron loading (calcination T = 500 °C). The whole pattern is due to the presence of a mixed phase anatase (Pearson's Crystal Data PCD # 1003622) and brookite ($2\theta \sim 30.8°$) (PCD # 1906427) present in all samples including $TFe0_{500}$ with a preponderance of the anatase phase (Table 2). Diffraction peaks due to iron are completely absent in the XRD pattern of the doped iron TiO_2 powder. The absence of peaks due to metal may be attributed to fine dispersion of metal particles on TiO_2 or due to very small metal content [21].

The examination of the diffractograms of the prepared samples indicates that, with increasing iron doping, there is a parallel decrease of intensity of the anatase (1 0 1) and brookite (1 2 1) peaks. This phenomenon, more evident for TFe0.6 and TFe1 samples, could arise from the increased surface disorder and/or for the presence of defect sites induced by the iron ions doping [22].

Fig. 2a shows the XRD patterns of TFe1 calcined at different temperatures. It can be observed that acid catalysis enhances the anatase and brookite crystallinity of TiO_2 xerogel dried at 200 °C. Anatase and brookite are a metastables TiO_2 polymorphs [23], which are commonly formed at low temperatures in/from solutions. These results are similar to those observed by Yu et al. [24], who synthesized by sol–gel TiO_2 catalysts using acidic (HNO_3) and basic (NH_4OH) catalysis. These Authors claim that the presence of an acidic catalyst enhances the phase transformation of the TiO_2 powders from amorphous to anatase and the growth of brookite phase at 100 °C with weight fractions of 65.2 and 34.8%, respectively. In contrast, the NH_4OH not only retards the phase transformation of the TiO_2 powders from amorphous

Table 1
Iron content in Fe^{3+} doped TiO_2 samples obtained from (AAS).

Sample	Calculated Fe content (%)	(AAS) Fe content (%)
TFe1	1	0.82
TFe0.6	0.6	0.47
TFe0.3	0.3	0.26
TFe0.1	0.1	0.098
TFe0	n.d	n.d