JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 8, August 2007, p. 2648 - 2652

Synthesis of iron-doped anatase -TiO_2 powders by a particulate sol-gel route

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TiO_2 anatase doped with 0.5 at%Fe powders were prepared by sol-gel technique. Titanium (IV) butoxide and iron (III) acetylacetonate were used as starting precursors, n-butanol as solvent, acetylacetone is added as a chelating agent and acetic acid to decrease the kinetics of the hydrolysis and condensation of $Ti(O\text{-}Bu^n)_4$. The evolution of the network bonds and the structural characterization of the gel were studied by thermogravimetric analysis (TG), differential thermal analysis (DTA) , differential thermogravimetric analysis (DTG), Fourier transform infrared spectroscopy(FTIR) scanning electron microscopy (SEM) , transmission electron microscopy (TEM) and X-ray diffraction (XRD) techniques, respectively. A gel-precusor nanopowder with the mean grain size of about 15-20 nm was obtained. In order to prepare a Fe-doped TiO_2 material with the structure of the anatase, a thermal treatment at 450°C, 3 h in air, was fund enough.

(Received June 7, 2007; accepted July 10, 2007)

Keywords: Anatase-TiO_2, Sol-gel, Powder gel characterization

1. Introduction

TiO_2 is considered the most common photo catalyst employed in oxidation studies of organics in both the aqueous and gas phase [1-6]. Efforts have also been made to improve the photocatalytic activity of the TiO_2 itself considering the relationship between chemical, crystallographic and morphologic properties of the TiO_2 and its photocatalytic activity [7]. Investigations were conducted to improve the photocatalytic activity by adding dopants to TiO_2. This latter research can be divided into two categories: one is associated with shifting the absorption band gap edge to the red in order to enhance activity in visible portion of the spectra [8]. Some researchers have pursued doping TiO_2 with transition metals as a way to shift the absorption edge to larger wavelengths. For example, Anpo [9] claimed to have successfully shifted the absorption edge of TiO_2 to the red by doping TiO_2 with Cr(III) ions. The second category of research has been to increase the photocatalytic activity of TiO_2 in the near UV (e.g. TiO_2–ZrO_2, TiO_2–SiO_2) [10]. In this aim to improve photocatalytic activity, the recombination of holes and electrons in activated TiO_2 has also been a subject of intense interest [11, 12]. The most common method proposed to lower charge recombination rates has been to dope TiO_2 with transition metals [12-15]. Special efforts have been dedicated to doping TiO_2 with Fe (III) [12, 14, 16]. This interest is based on the idea that Fe (III) ions act as shallow charge traps in the TiO_2 lattice [17-19]. Ranjit and Viswanathan [12] have indicated that Fe (III)-doped TiO_2 improves photocatalytic activity up to a certain doping level (1.8 wt. %) of Fe (III). Other authors have concluded that the doping technique seems to be one of the most important factors for controlling the reactivity of Fe (III)-doped titanium dioxide [14, 20]. This paper describes a sol gel technique for preparing TiO_2 doped with 0.5 at% Fe powders, crystallized on the anatase lattice of TiO_2.

2. Experimental

Titanium (IV) butoxide, 97%, (Aldrich) and iron (III) acetylacetonate, 99.9+% (Aldrich) were used as starting precursors and n-butanol as a solvent to prepare TiO_2 anatase doped with 0.5 at%Fe. Acetic acid was used on the place of water to decrease the kinetics of the hydrolysis and polycondensation of $Ti(O\text{-}Bu^n)_4$ and iron (III) acetylacetonate ($Fe(acac)_3$). As titanium alkoxide is among the most reactive, the speed of hydrolisis and condensation is very high, therefore, it is difficult to form a stable sol. Acetylacetone is added as a chelating agent to decrease the reactivity of titanium butoxide and stabilize the sol. As shows the flow sheet of Fe doped TiO_2 synthesis by sol-gel method (Fig.1), the sol obtained from $Ti(O\text{-}Bu^n)_4$, $Fe(acac)_3$, n-butanol and acetylacetone was kept under reflux with strong magnetic agitation at 75°C for 2 hours.

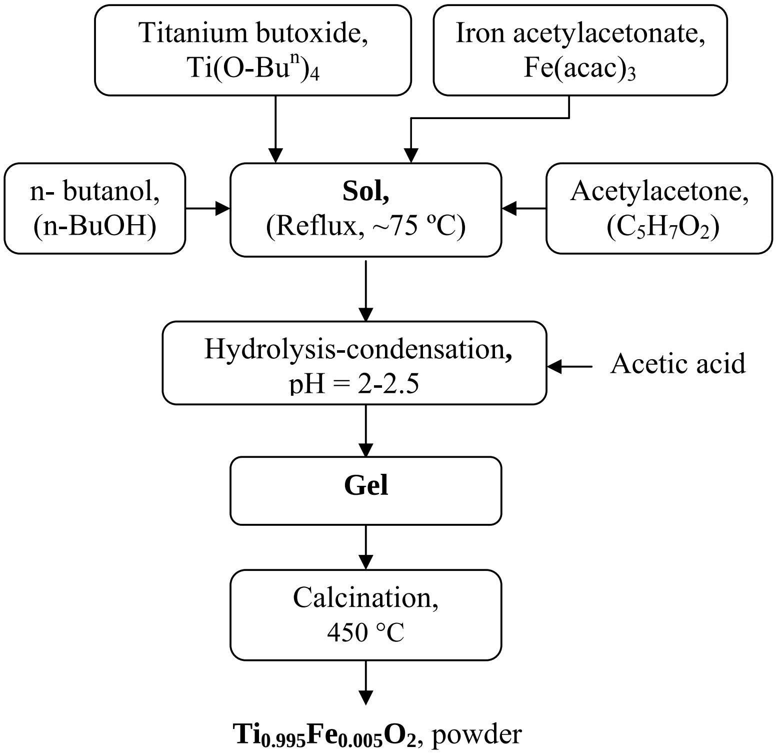


Fig. 1. Flow sheet of Fe doped TiO_2 synthesis by sol-gel method.

Acetic acid is added gradually to the sol. Acetic acid initiates hydrolysis via an esterification reaction as follows:

$$R\text{-}OH + R'\text{-}COOH \leftrightarrow H_2O + RCOOR' \text{ , [21]}$$
$$C_4H_9\text{-}OH + CH_3\text{-}COOH \leftrightarrow C_4H_9COOCH_3 + H_2O$$

Moreover, it has been shown that acetic acid induces the modification of the molecular structure of the precursor [22]. Titanium alkoxides reacts directly with glacial acetic acid or acetylacetone at a molecular level:

$$M(OR)_4 + H\text{-}(OAc) \rightarrow M(OR)_3(OAc) + R\text{-}OH$$
$$M(OR)_4 + acac\text{-}H \rightarrow M(OR)_3(acac) + R\text{-}OH,$$

where, M = metal cation, OA = acetate, OR= alkoxy, acac-H = acetylacetone and OH = hydroxyl groups. The molecularly modified precursor's hydrolysis and polycondensation reactions are slowed down considerably since on exposure to water although the alkoxy groups hydrolyze rapidly, the modifying groups are quite stable towards such reactions and remain unhydrolyzed even on addition of large excess of water:

$$M(OR)_3(OAc) + H\text{-}OH \rightarrow M(OR)_2(OH)(OAc)$$

$$M(OR)_3(acac) + H\text{-}OH \rightarrow M(OR)_2(OH)(acac)$$

The molar ratios $n_{acid\ acetic}/(n_{Ti} + n_{Fe)}$ and $n_{acac}/(n_{Ti} + n_{Fe)}$ used were 0.2 and 0.3 respectively. The proper amount of n-butanol to obtain a stable sol with pH=2-2.5 and a concentration of 2.6 M was used. The as obtained sol was maintained at reflux with magnetic agitation, for 4h, to achieve the gelification process. The solvents were evaporated from the gel by drying at 100 °C. By heating of the gel at 450 °C, a Fe doped-TiO_2 (anatase) powder was obtained.

The gel powder was characterized by thermogravimetric analysis (TG), differential thermal analysis (DTA) and differential thermogravimetric analysis (DTG) using a TGA Instrument, model Pyris Diamond, Perkin Elmer Instruments, at temperatures from 25 to 800 °C with a heating rate of 20 °C/min, in air. A mixture of the gel powder and KBr powder was used for infrared spectroscopy studies. A Fourier transform infrared spectrometer (FTIR) (Model Spectrum BX, Perkin Elmer Instruments) was used for IR measurements. The microstructure of the powders was investigated using a Hitachi S-2600N Scanning Electron Microscope and a Jeol TEMSCAN 200CX transmission electron microscope. The structure of the powder was characterized by the XRD technique using an X-ray diffractometer (Model DEBYEFLEX 2002 "MZ III" Seifert). For powder diffraction, CuKα1 radiation, (wavelength 1.5406 Å), a LiF crystal monochromator and Bragg-Brentano diffraction geometry were used. The data were acquired at

25 °C with a step-scan interval of 0.020 ° and a step time of 10 s.

3. Results and discussion

3.1. Thermal analysis

Thermal analysis results of Fe doped TiO_2 precursor gel are presented in Fig. 2.

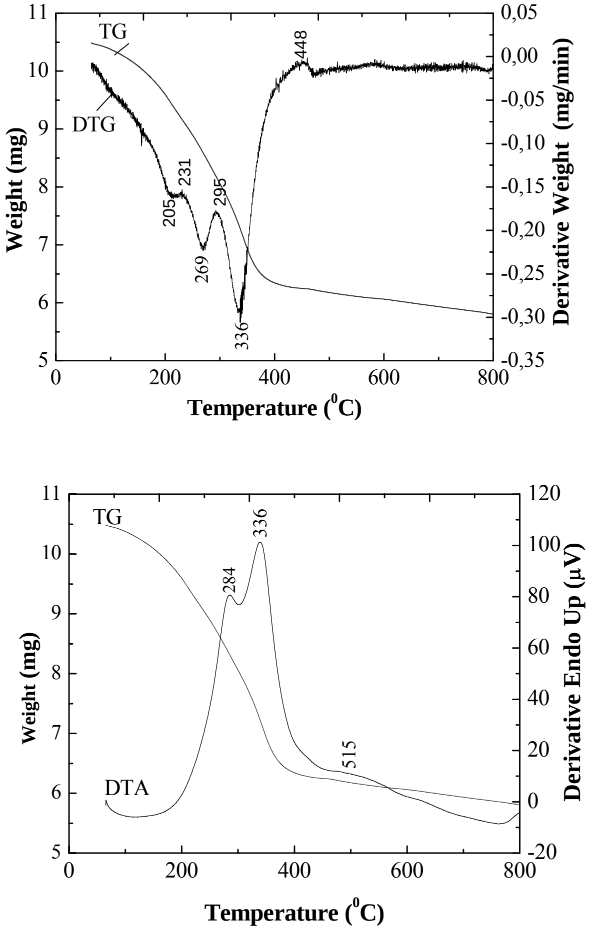


Fig. 2. Thermal analysis results of Fe doped TiO_2 precursor gel.

Two steps of the mass loss are detected on the TG curve. Up to ~ 400ºC, a mass loss (35.68%) occurs due to loss of the organic part from the gel. More precisely, three sub steps can be distinguished, corresponding to: 25-231ºC, 231-295ºC and 295-448ºC. The thermal effects (endothermic peaks) that accompany the mass loss due to the volatilisation of the solvents: acetic acid, n-butanol and acetylacetone, and the pyrolysis of the organic groups bonded to titanium and iron, are centred at 284º and 336ºC. The second step occurs between 400º and 800ºC. On the TG curve, a continuous mass loss (4.8%) is observed. The mass loss is due to OH groups bonded to Ti. The -Ti-OH groups are derived from the environment humidity which hydrolyzes the titanium alkoxide. Up to 800ºC, these groups loss water by a condensation reaction as follows:

$$2\,(\text{-Ti-OH}) \rightarrow \text{-Ti-O-Ti-} + H_2O\uparrow$$

On the DTA curve, one peak (at 515ºC) due to crystallization of TiO_2 as rutile is indicated.

3.2. FTIR Spectroscopy

FTIR spectra recorded for the precursor gel of Fe doped TiO_2, heated at 100° and 450°C are shown in Fig.3.

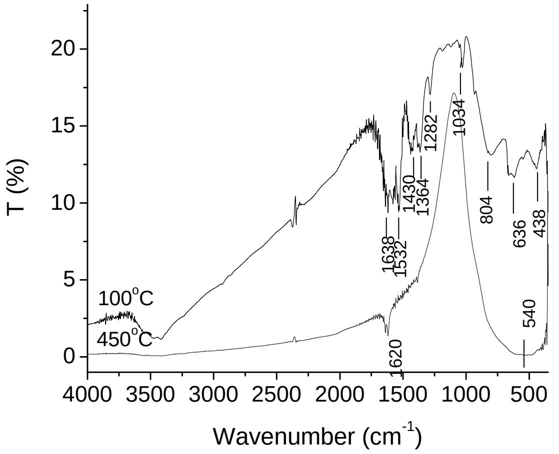
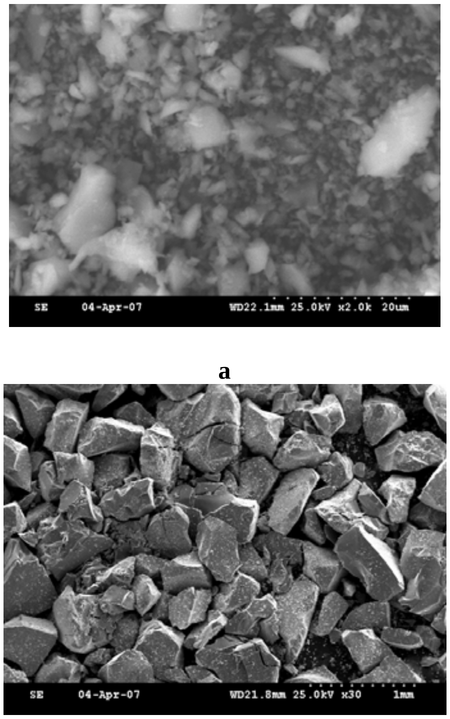


Fig. 3. FTIR spectra of Fe doped-TiO_2 gel heated at 100° and 450°C.

FTIR spectrum of the gel dried at 100°C shows transmission bands at about 3360, 1638, 1532, 1430, 1364, 1282, 1034, 804, 636 and 438 cm^{-1}. In general, lattice water absorbs at 3550-3200 cm^{-1} (antisymmetric and symmetric OH stretching) and at 1630-1600 cm^{-1} (HOH bending) [23, 24]. The bands at 1532, 1430 and 1364 cm^{-1} are due to organic groups (acetylacetonate and acetate) bonded to titanium and iron. The metal-OH bands are placed at about 1200 cm^{-1}. The low-frequency region of the spectrum (below 900 cm^{-1}) shows bands attributed to stretching metal-oxygen-organic radical (Ti-O, Ti-O-Ti and, Ti-O-Bu^n) [25, 26]. For the gel calcined at 450°C, these last bands are replaced by the band centred at 540 cm^{-1} due to metal-oxygen bonds (Ti-O, Fe-O) of the (Ti, Fe)O_2 solid solution. The bands corresponding to organic groups bonded to titanium (1650-1000 cm^{-1} region) are replaced by the band at 1620 cm^{-1}, probably due to residual OH groups.

3.3. SEM and TEM results

The SEM micrographs of Fe doped-TiO_2 gel, heated at 100° and 450°C are presented in Fig.4. Iron doped TiO_2 precursor gel, dried at 100ºC (Fig.4(a)) show a microstructure consisting of grains with average size of 400-500 nm which form aggregates with various sizes (>2 µm).



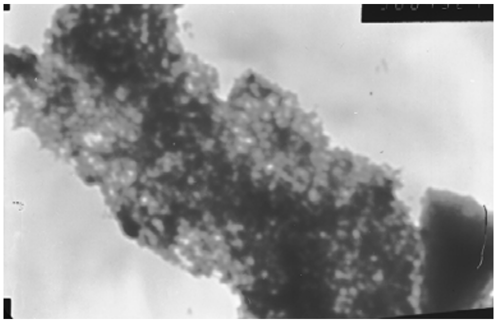
a

b

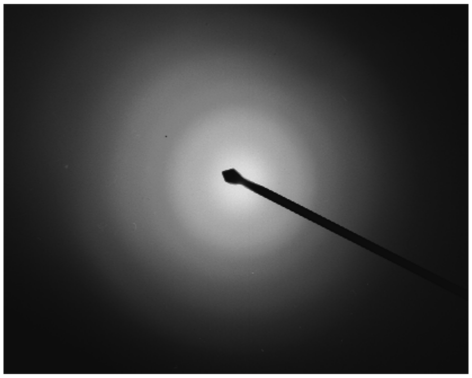
Fig. 4. SEM micrographs of Fe doped-TiO_2 gel, heated at 100°C (a) and 450°C (b).

The gel heated at 450ºC shows a more homogeneous morphology with very large grains of about 400-500 µm (Fig.4 (b)).

The amorphous structure of Fe doped-TiO_2 gel, heated at 100°C and the well crystallized structure (anatase) of the gel, heated at 450°C, are presented in TEM micrographs (Fig.5 and Fig.6). Fig.6(a) shows the fine granular structure of agglomerated powder (the mean grain size of about 15-20 nm) and in the associated selected area electron diffraction pattern (Fig.6(b)) the main difraction rings (101), (004)/(112), (105)/(211) and (204) belonging to anatase phase can be easily identified.

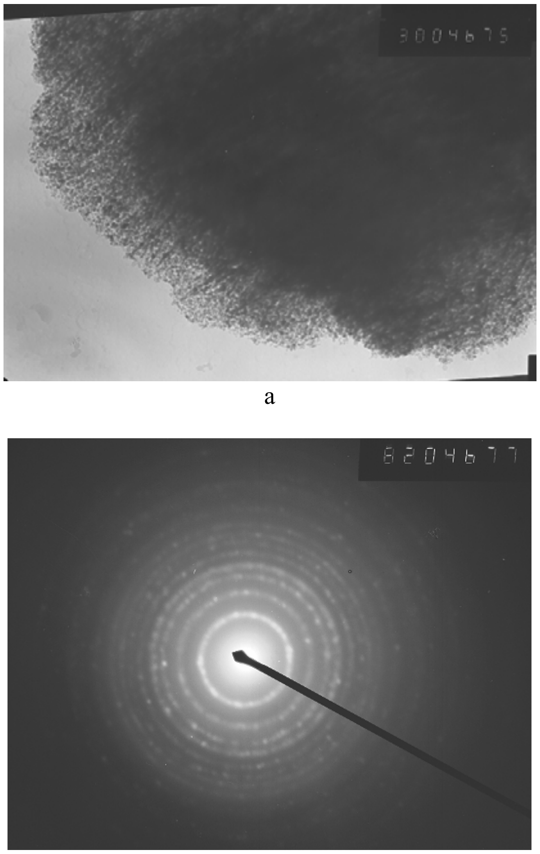


a



b

Fig.5. TEM micrographs of Fe doped-TiO_2 gel, heated at 100°C.



a

b

Fig. 6. TEM micrographs of Fe doped-TiO_2 gel, heated at 450°C.

3.4. X-ray diffraction analysis

The XRD pattern of the gel dried at 100°C shown an amorphous structure. In Fig.7, is shown the XRD pattern of Fe doped-TiO_2 gel, heated at 450°C, 3 h in air.

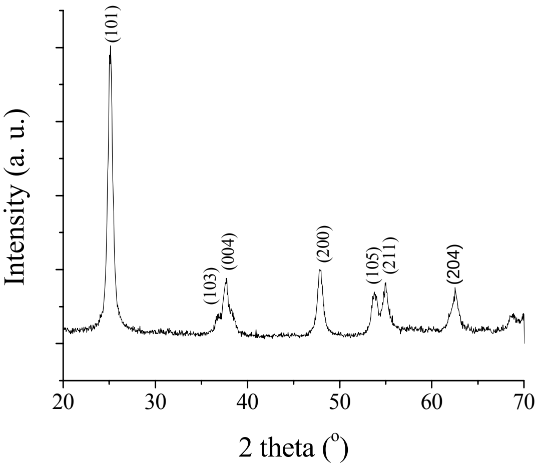


Fig. 7. XRD pattern of Fe doped-TiO$_2$ gel, heated at 450°C..

All the diffraction peaks can be indexed according to the anatase structure of TiO$_2$, the peak positions being in good agreement with previously reported data [27]. The missing of the main rutile peaks suggests that the gel precursor of TiO$_2$ doped with 0.5 at%Fe, heated at 450ºC, corresponds to a single phase (TiO$_2$ anatase) without the presence of secondary phases.

4. Conclusions

$Ti_{0.995}Fe_{0.005}O_2$ powder with a structure characteristic to anatase has been prepared by a particulate sol-gel technique from precursor type alkoxide modified molecular with acetic acid and acetyl acetone. Acetic acid was used for the hydrolysis and polycondensation of Ti(O-Bu^n)$_4$ and iron (III) acetylacetonate (Fe(acac)$_3$). A gel-precusor nanopowder with the mean grain size of about 15-20 nm was obtained. The FTIR and thermal analysis showed a gel structure comprising organic groups which are completely evolved at temperature of around 450°C. The amorphous structure of Fe doped-TiO$_2$ gel, heated at 100°C and, the anatase structure of the gel, heated at 450°C are revealed by XRD and TEM analysis. Such prepared powders can be used in many applications in areas from photo catalysts to gas sensors [28].

Acknowledgements

This work was partially supported by the Romanian National Research Program "CEEX"- Contract No. 23/2005

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