

# Synthesis and Characterization of Rutile TiO<sub>2</sub> Nanopowders Doped with Iron Ions

Nadica D. Abazović · Luciana Mirengi ·  
Ivana A. Janković · Nataša Bibić · Daniela V. Šojić ·  
Biljana F. Abramović · Mirjana I. Čomor

Received: 8 December 2008 / Accepted: 8 February 2009 / Published online: 28 February 2009  
© to the authors 2009

**Abstract** Titanium dioxide nanopowders doped with different amounts of Fe ions were prepared by coprecipitation method. Obtained materials were characterized by structural (XRD), morphological (TEM and SEM), optical (UV/vis reflection and photoluminescence, and Raman), and analytical techniques (XPS and ICP-OES). XRD analysis revealed rutile crystalline phase for doped and undoped titanium dioxide obtained in the same manner. Diameter of the particles was 5–7 nm. The presence of iron ions was confirmed by XPS and ICP-OES. Doping process moved absorption threshold of TiO<sub>2</sub> into visible spectrum range. Photocatalytic activity was also checked. Doped nanopowders showed normal and up-converted photoluminescence.

**Keywords** Titanium dioxide · Rutile · Doping · Characterization

## Introduction

Since its commercial production in the early 20th century, titanium dioxide (TiO<sub>2</sub>) has been widely used as a pigment

[1] and in sunscreens [2, 3], paints [4], ointments, toothpaste [5], etc. In 1972, Fujishima and Honda [6–8] discovered the phenomenon of photocatalytic splitting of water on a TiO<sub>2</sub> electrode under ultraviolet (UV) light. Since then, enormous efforts have been devoted to the research of TiO<sub>2</sub> material, which has led to many promising applications in areas ranging from photovoltaics and photocatalysis to photo/electrochromics and sensors [9–12]. These applications can be roughly divided into “energy” and “environmental” categories, many of which depend not only on the properties of the TiO<sub>2</sub> material itself but also on the modifications of the TiO<sub>2</sub> material host (e.g., with inorganic and organic dyes) and on the interactions of TiO<sub>2</sub> materials with the environment [13].

An exponential growth of research activities has been seen in nanoscience and nanotechnology in the past decades [14–18]. New physical and chemical properties emerge when the size of the material becomes smaller and smaller, and down to the nanometer scale. Among the unique properties of nanomaterials, the movement of electrons and holes in semiconductor nanomaterials is primarily governed by the well-known quantum confinement and the transport properties related to phonons and photons are largely affected by the size and geometry of the materials [14–17]. The specific surface area and surface-to-volume ratio increases dramatically as the size of a material decreases [14, 19]. The high surface area brought about by the small particle size is beneficial to many TiO<sub>2</sub>-based devices, as it facilitates reaction/interaction between the devices and the interacting media, which mainly occurs on the surface or at the interface and strongly depends on the surface area of the material. Thus, the performance of TiO<sub>2</sub>-based devices is largely influenced by the sizes of the TiO<sub>2</sub> building units, apparently at the nanometer scale.

N. D. Abazović · I. A. Janković · N. Bibić · M. I. Čomor (✉)  
Vinča Institute of Nuclear Sciences, P.O. Box 522,  
Belgrade 11000, Serbia  
e-mail: mirjanac@vinca.rs; mirjanac@vin.bg.ac.yu

L. Mirengi  
ENEA, UTS MAT, Brindisi Research Centre, S.S.7 Appia,  
Brindisi 72100, Italy

D. V. Šojić · B. F. Abramović  
Department of Chemistry, Faculty of Sciences, University  
of Novi Sad, Trg D. Obradovića 3, Novi Sad 21000, Serbia

Titanium dioxide can be obtained in three crystalline phases: anatase, rutile, and brookite. The most stable phase is rutile and it is usually obtained after annealing at temperature above 500 °C [20]. TiO<sub>2</sub> is transparent normally in the visible light region; its band gap is 3.0 eV for rutile and 3.2 eV for anatase crystalline phase. By doping or sensitization, it is possible to improve the optical activity of TiO<sub>2</sub> and to move its absorption threshold into the visible light region.

The subject of this work is the synthesis by low temperature coprecipitation method of Fe-doped TiO<sub>2</sub> nanopowders and their characterization. Several concentrations of Fe ions were implied. Detailed characterization was conducted and photodegradation of mecoprop was chosen as a probe reaction for evaluation of photocatalytic activity of prepared samples. The relationship between optical properties (PL) and photoactivity of samples is discussed.

## Experimental Section

All chemicals used were of p.a. purity and were used without further purification. Triply distilled water was used for aqueous solutions.

Fe-doped TiO<sub>2</sub> powders were prepared by a modified synthetic procedure of Abazović et al. [21]. An appropriate amount of FeCl<sub>3</sub> (Aldrich) was dissolved in 200 mL of triply distilled water. Then, 5 mL of TiCl<sub>4</sub> (Fluka) pre-chilled to −20 °C was added dropwise into solution containing FeCl<sub>3</sub> under stirring. After 2 h of stirring at room temperature, the obtained dispersions were heated and kept at 50 °C for 16 h with constant stirring. The resulting precipitates were dialyzed against water until test reaction for Cl<sup>−</sup> ions was negative and subsequently dried in vacuum at 40 °C. Pure TiO<sub>2</sub> powder was synthesized in the same manner, without FeCl<sub>3</sub> in the reaction solution.

The obtained powders were characterized by several techniques. For UV/vis spectrometry a Perkin–Elmer λ-35 spectrophotometer, equipped with reflectance accessory and referenced with BaSO<sub>4</sub>, was used. Photoluminescence was measured using a Perkin–Elmer LS-3b instrument. Raman spectra were obtained using a Raman system R-2001<sup>TM</sup>.

The X-ray diffraction measurements of the powders were performed on a Philips PW1710 diffractometer.

Microstructural characterization of the iron ions doped TiO<sub>2</sub> nanopowders was carried out on a Philips EM-400 transmission electron microscope operated at 100 kV and on a Cambridge 250MKIII scanning electron microscope. Samples for TEM analysis were dispersed in methanol, ultrasonicated for 1 h and deposited on C-coated Cu grids. Samples for SEM were deposited on carbon tapes.

The X-ray photoelectron spectroscopy (XPS) measurements were carried out on a VG Scientific ESCALAB 210 spectrometer using non-monochromatic MgK<sub>α</sub> radiation. The calibration of peak position was made using the Ag 3d<sub>5/2</sub> line at 368.26 eV of a standard silver foil, used as a reference sample. It was in situ sputtered with argon ions in order to remove the surface oxide and acquire a clean reference spectrum. We used C1s to calibrate the peak positions after experimental acquisitions, because on the surface region carbon was well detected and unequivocally associated to adventitious carbon (for air exposure of the samples) expected at 285 eV of binding energy [22].

Chemical quantitative analysis was performed by inductively coupled plasma optical emission spectroscopy (Spectroflame ICP, 2.5 kW, 27 MHz). ICP-OES analysis was performed by measuring the intensity of radiation of the specific wavelengths emitted by each element. The samples dispersed in liquid were introduced into the plasma as aerosol, where they were vaporized, atomized, and excited.

Photocatalytic degradation was carried out in a cell made of Pyrex glass (total volume of ca. 40 mL, liquid layer thickness 35 mm), with a plain window on which the light beam was focused, equipped with a magnetic stirring bar and a water circulating jacket. A 125 W medium-pressure mercury lamp (Philips, HPL-N, emission bands in the UV region at 304, 314, 335, and 366 nm, with maximum emission at 366 nm), together with an appropriate concave mirror, was used as the radiation source.

Experiments were carried out using 20 mL of the solution of mecoprop (2.7 mmol dm<sup>−3</sup>) and 40 mg of catalyst. Herbicide mecoprop (RS-2-(4-chloro-otolyloxy) propionic acid, C<sub>10</sub>H<sub>11</sub>ClO<sub>3</sub>) was chosen as a model compound of a photodegradable organic waste substance in water because of its worldwide use for the selective control of many annual and some perennial weeds and because it is the herbicide most often found in drinking water [23, 24]. The aqueous suspensions were sonicated in the dark for 15 min before illumination, to make the photocatalyst particles uniform and attain adsorption equilibrium. The suspensions thus obtained were thermostated at 40 ± 0.5 °C, in a stream of O<sub>2</sub> and then irradiated. During the irradiation, the mixtures were stirred at a constant speed.

Photocatalytic activity was checked on a spectrophotometer (Secomam anthelie Advanced 2). Namely, 0.25 cm<sup>3</sup> aliquots of the samples were taken at different illumination times and diluted to 10.00 cm<sup>3</sup> with double distilled water. The suspensions containing photocatalyst were filtered through Millipore (Millex-GV, 0.22 μm) membrane filters and spectra were recorded on a spectrophotometer. Kinetics of the aromatic ring degradation was monitored at 228 nm.

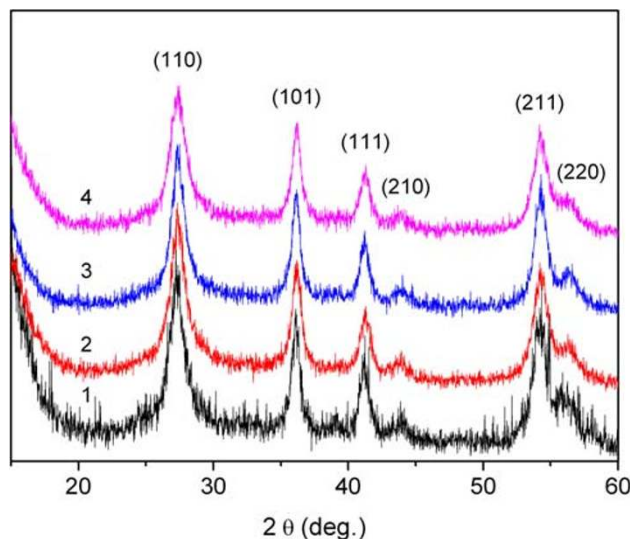
## Results and Discussion

The crystal phase of the prepared powders was rutile as can be seen in Fig. 1. All XRD peaks ((110), (101), (111), (210), (211), and (220)) correspond to rutile crystal structure [25]. The diameter of the particles was calculated using the Scherrer diffraction formula, relating the diffraction angular width ( $\beta$ ) at the half height of the (101) diffraction peak, to the domain size:

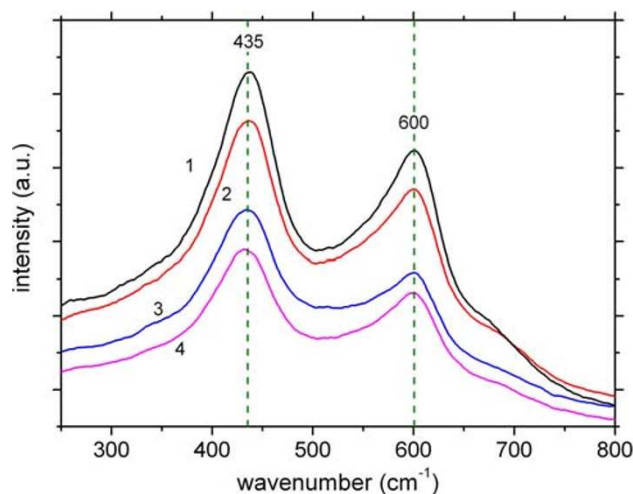
$$D = \frac{k\lambda}{\beta \cos \theta} \quad (1)$$

where  $k$  is a geometrical factor taken to be 0.89,  $\lambda = 1.541 \text{ \AA}$  is the X-ray wavelength, and  $\theta$  is the diffraction angle of the most prominent peak for rutile structure ( $2\theta \sim 27.4^\circ$ ). We found that Fe-doped  $\text{TiO}_2$  crystal domains are in the range from 5 to 7 nm in diameter. X-ray structural analysis of doped samples showed that the samples had typical peaks of rutile structure without any detectable dopant related peaks. The dopant ions may have been moved either into interstitial positions or substitutional sites of the  $\text{TiO}_2$  nanocrystal structure, or their concentration was too low to be detected.

Raman spectra of our samples are consistent with XRD data and suggested pure rutile structure as can be seen in Fig. 2. According to literature data, rutile features in the Raman spectra are bands at 241, 444, and  $607 \text{ cm}^{-1}$  [26]. Our pure  $\text{TiO}_2$  and doped  $\text{TiO}_2$  powders have bands at 435 and  $600 \text{ cm}^{-1}$ . Band at  $241 \text{ cm}^{-1}$  is not visible in our spectra, due to technical limitations of the Raman device. The Raman peak broadening and



**Fig. 1** XRD pattern of pure and Fe-doped  $\text{TiO}_2$  nanopowders with atomic percent (stoichiometric concentration) of dopant ions: 1.0%; 2.5%; 3.10%; and 4.20%



**Fig. 2** Raman spectra of pure and Fe-doped  $\text{TiO}_2$  nanopowders with atomic percent (stoichiometric concentration) of dopant ions: 1.0%; 2.5%; 3.10%; and 4.20%

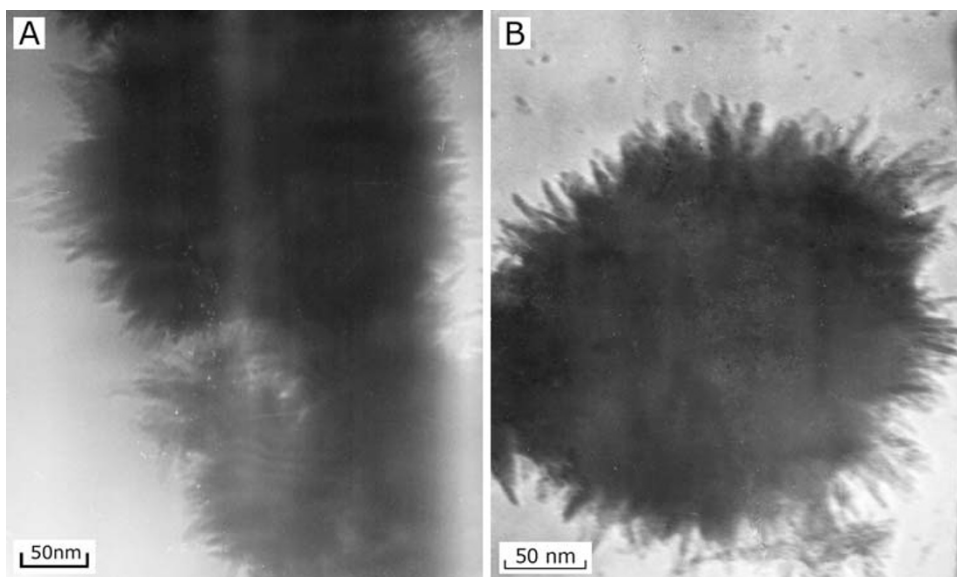
small frequency blue-shifting compared to literature [26] might be attributed to variation of particle sizes or the stoichiometry in the samples (oxygen vacancies) [27, 28].

In Fig. 3 a typical TEM images of pure (A) and Fe-doped (B)  $\text{TiO}_2$  powder nanoparticles can be seen. For both materials flower-like agglomerates with diameters in the size range from 100 to 150 nm can be observed. Flower-like agglomerates consist of nanorods with 5–10 nm diameters. Similar morphology was observed after prolonged aging at room temperature of titania particles prepared by acidic hydrolysis of titanium tetrabutoxide in reverse micelles [25]. In Fig. 3b spherical nanoparticles with 5–10 nm diameters can also be seen. The formation of well-defined  $\text{TiO}_2$  nanorods most likely can be explained by the prolonged aging at elevated temperature. This is in agreement with literature data concerning hydrothermal synthesis of  $\text{TiO}_2$  rods [21, 29, 30].

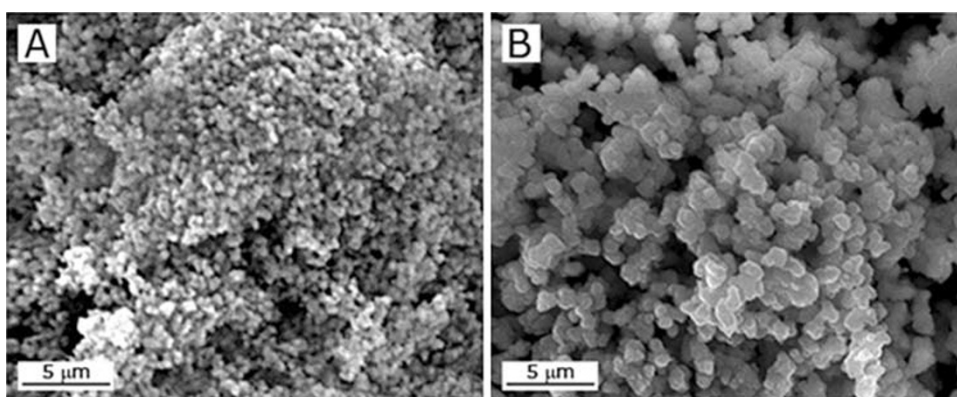
Diameters are in good agreement with the diameters obtained from XRD measurements using the Scherrer diffraction formula. Similar  $\text{TiO}_2$  morphology was observed for all dopant concentrations.

SEM images of the Fe-doped  $\text{TiO}_2$  agglomerates are presented in Fig. 4. The sizes of agglomerates were of broad distribution and could not be determined exactly from the SEM images. It is obvious that the particles agglomerated during synthesis and drying, but they could be re-dispersed in appropriate solvent using an ultrasonic bath. Samples for SEM were prepared by direct deposition of powder on carbon tapes so agglomerates were observable. Agglomerates of  $\text{TiO}_2$  particles doped with 10 at.% of Fe have smaller sizes (Fig. 4a) than agglomerates of  $\text{TiO}_2$  particles doped with 20 at.% of Fe, but their size distribution was narrower (Fig. 4b).

**Fig. 3** Typical TEM images of pure TiO<sub>2</sub> (a) and 10 at.% Fe–TiO<sub>2</sub> (b)



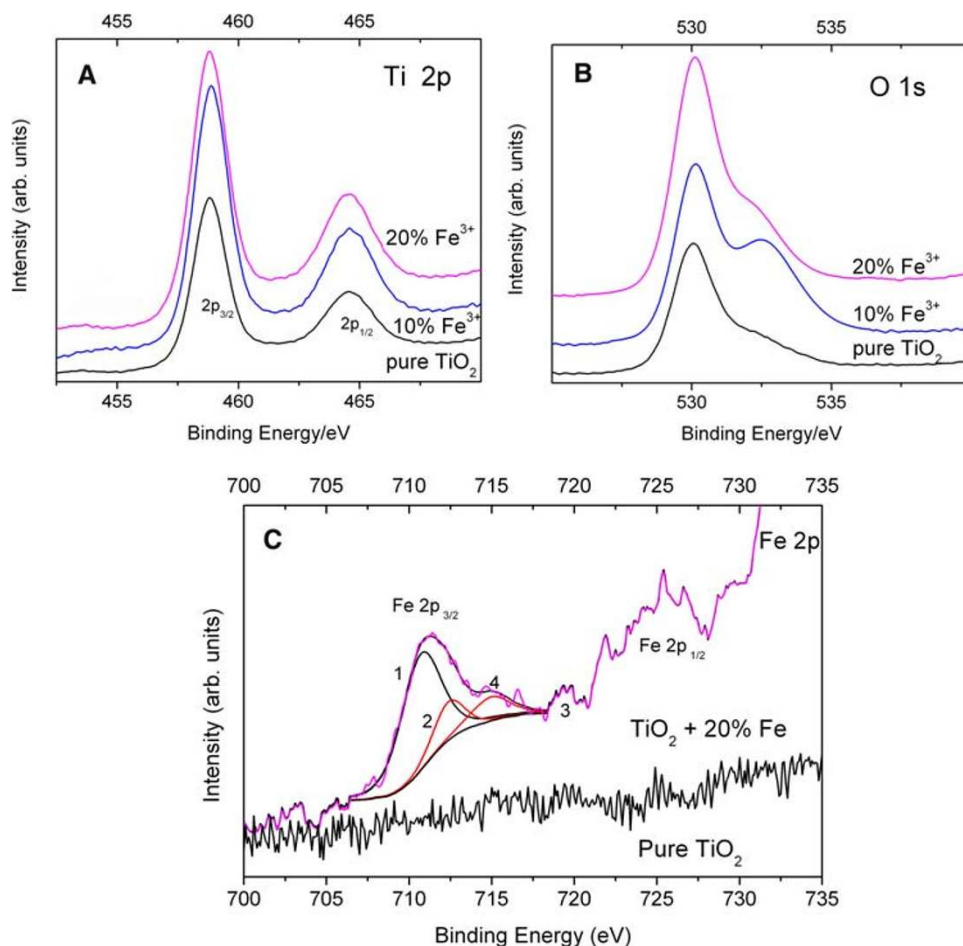
**Fig. 4** Typical SEM images of TiO<sub>2</sub> powders doped with 10 at.% Fe (a) and 20 at.% Fe (b)



In order to reveal the presence of iron ions in our samples, which was not confirmed by XRD measurements, and to define oxidation state of Fe ions, we have examined three areas of the XPS spectrum of our samples: the Ti 2p region between 455 and 470 eV (Fig. 5a), the O 1s region between 525 and 535 eV (Fig. 5b) and the Fe 2p<sub>3/2</sub> region near 710 eV (Fig. 5c). It must be noted that in all spectra peak at around 284.6 eV was found (not presented in Fig. 5a), corresponding to carbon impurities, arising probably from the background of XPS test or the residual precursors. The Ti 2p<sub>1/2</sub> and Ti 2p<sub>3/2</sub> spin-orbital splitting photoelectrons for all samples are located at binding energies of 464.6 and 458.9 eV, respectively, as can be seen in Fig. 5a. These data are in excellent agreement with data obtained by Zhu et al. [31]. It seems that these energies are not affected by doping with iron ions. Although, due to the low concentration of iron, the shift of Ti 2p peaks could have been below the detection limit. No Ti<sup>3+</sup> species were observed in XPS. The absence of peak broadening of Ti 2p<sub>3/2</sub> signals (FWHM was about 1.4 eV for all samples) may also indicate the presence of Ti<sup>4+</sup>

species only [32], and good crystallization for all samples [33]. Figure 5b shows the O 1s core level spectra of pure and doped TiO<sub>2</sub>. The peak at 530.1 eV for all samples is due to O<sup>2-</sup> ion in the TiO<sub>2</sub> lattice. In all spectra at higher binding energy a shoulder is observed (the spectrum of 10% Fe–TiO<sub>2</sub> shows a second peak located at a binding energy of 532.6 eV), which can be attributed to the surface hydroxyl groups of chemisorbed water molecules on the titania [33, 34] or this is the way in which presence of Fe ions influences the TiO<sub>2</sub> matrix. The atomic weight ratio of O to Ti in samples increases with doping: from pure TiO<sub>2</sub>: 1.955; 10% Fe–TiO<sub>2</sub>: 2.3; to 20% Fe–TiO<sub>2</sub>: 3. The XPS spectrum of Fe is very weak (Fig. 5c) due to the low doping level. The presence of Fe ions was detected only in 20% Fe–TiO<sub>2</sub> sample, estimated concentration being about 0.2%. The Fe ions could not be detected in 10% Fe–TiO<sub>2</sub> due to detection limit of instrument, but their presence can be indirectly assumed from O/Ti ratio (2.3), as mentioned before. The binding energies from 711.0 to 711.8 eV and from 725.4 to 726.0 eV should be assigned to 2p<sub>3/2</sub> and 2p<sub>1/2</sub> of Fe<sup>3+</sup>, respectively. These data exhibit a small shift

**Fig. 5** XPS spectra of pure and doped TiO<sub>2</sub> samples: Ti 2p energy region (a), O 1s energy region (b), and Fe 2p energy region together with deconvolution of the Fe 2p<sub>3/2</sub> (c)



compared to those in Fe<sub>2</sub>O<sub>3</sub> (711.3 eV for 2p<sub>3/2</sub>) probably indicative of more positively charged surface due to diffusion of the Fe<sup>3+</sup> in TiO<sub>2</sub> lattice and possible formation of the Fe–O–Ti bond in the sample [35]. Also it can be seen in Fig. 5c that Fe 2p<sub>3/2</sub> peak can be decomposed in several contributions corresponding to different oxidation states of iron. The main contribution can be attributed to Fe<sup>3+</sup> ions (peak 1, binding energy at 710.9 eV) and the other to Fe<sup>2+</sup> ions (peak 2, binding energy at 712.8 eV). These statements can be supported with the presence of characteristic satellite peaks at ~720 eV for Fe<sup>3+</sup> (peak 3) and at ~716 eV for Fe<sup>2+</sup> (peak 4), well established for Fe 2p spectra for Fe<sub>2</sub>O<sub>3</sub> and FeO, respectively [36].

Concentration of Fe ions in TiO<sub>2</sub> matrix was also checked by emission spectroscopy using ICP instrument. Measurements confirmed that real concentration of Fe in TiO<sub>2</sub> matrix is much lower compared to stoichiometric values, as can be seen in Table 1.

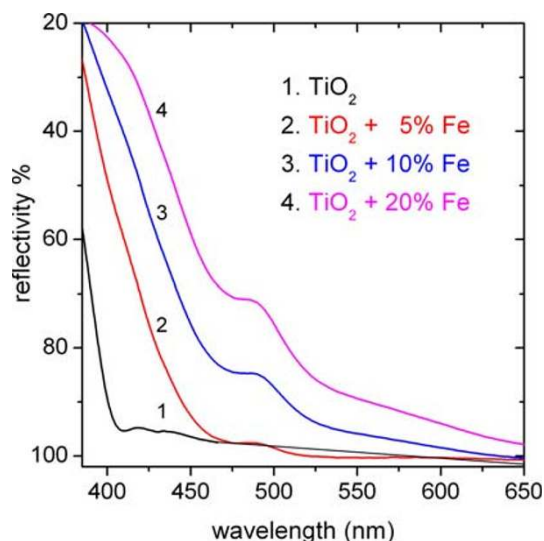
Influence of doping on UV/Vis spectral properties of TiO<sub>2</sub> is clearly evident in Fig. 6, and it is manifested by change of the color of doped powders from light to dark yellow. Reflection spectra of all doped samples contain shoulder at 500 nm, with intensity increasing with Fe<sup>3+</sup>

**Table 1** Concentration of Fe in doped TiO<sub>2</sub> powders, determined by ICP-OES

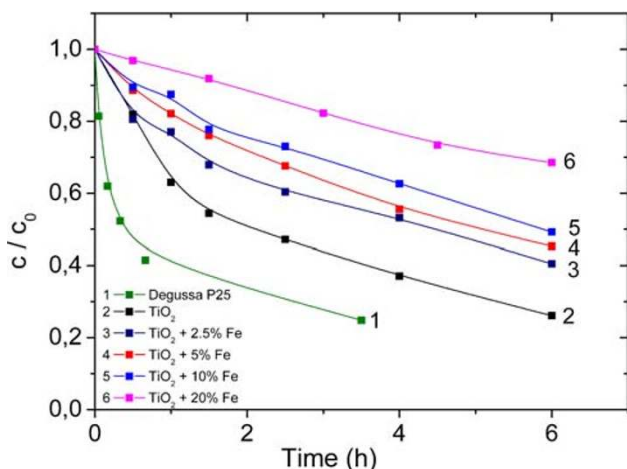
Sample (% Fe–TiO <sub>2</sub> )	Fe at. %
0.0	0.03
2.5	0.20
5.0	0.43
10.0	1.00
20.0	1.70

concentration [31]. Pure TiO<sub>2</sub> has sharp decrease of reflection around 420 nm which corresponds to rutile band gap of ~3.0 eV. The band gap energy of doped TiO<sub>2</sub> samples decrease with increasing Fe concentration—from 3 eV for pure TiO<sub>2</sub> to ~2.3 eV for 20 at.% Fe–TiO<sub>2</sub>. This indicates that photocatalytic activity of TiO<sub>2</sub> could be probably influenced by Fe-doping.

The influence of Fe-doping on intrinsic TiO<sub>2</sub> photocatalytic activity was studied using photocatalytic degradation of mecoprop, under UV light irradiation. The results are presented in Fig. 7 together with results obtained using commercially available Degussa P25 TiO<sub>2</sub>. Iron ions can act in different ways with photogenerated charges [37], as

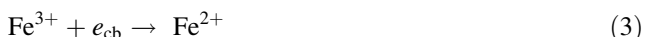


**Fig. 6** UV/vis reflectance spectra of pure TiO<sub>2</sub> and TiO<sub>2</sub> doped with different at.% of Fe ions, indicated in the figure



**Fig. 7** Kinetics of mecoprop degradation (2.7 mmol dm<sup>-3</sup>) under UV irradiation monitored by spectrophotometry, in the presence of Fe–TiO<sub>2</sub> with various amounts of Fe ions, pure TiO<sub>2</sub> and Degussa P25. Catalyst amounts: 2 mg cm<sup>-3</sup>

recombination centre or as charge transfer centre, according to reactions (Eqs. 2–6):



As can be seen in Fig. 7, doping with Fe<sup>3+</sup> ions reduces photocatalytic activity of degradation of mecoprop. All doped samples showed reduced photocatalytic activity compared to pure rutile and P25 (Table 2). Literature data

**Table 2** Effect of at.% Fe in catalysts on mecoprop photocatalytic degradation rate with UV light

Sample (% Fe–TiO <sub>2</sub> )	10 <sup>3</sup> k' (min <sup>-1</sup> ) <sup>a</sup>	r <sup>b</sup>
Degussa P25	0.58	0.855
0.0	0.42	0.995
2.5	0.24	0.966
5.0	0.18	0.993
10.0	0.15	0.973
20.0	0.06	0.999

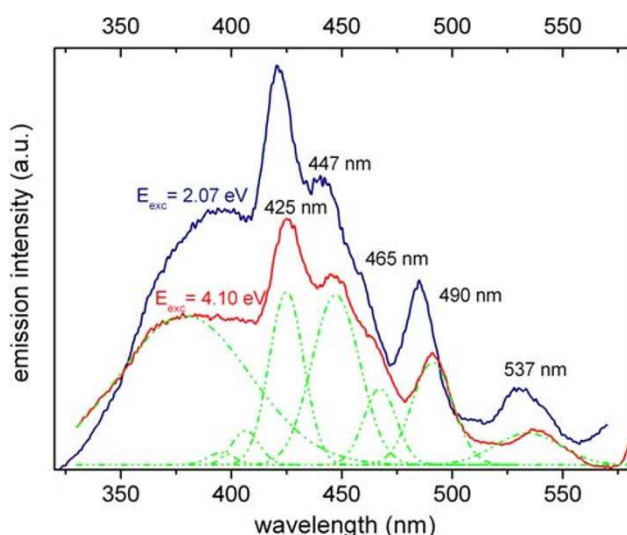
<sup>a</sup> Pseudo first-order rate constant determined for the first 90 min of irradiation

<sup>b</sup> Linear regression coefficient

concerning influence of Fe doping on TiO<sub>2</sub> photocatalytic activity, showed critical dependence on the method of preparation and choice of compound whose degradation was followed [38–40]. In the case of high doping concentrations, iron ions act mainly as recombination centers for photogenerated electrons (e<sub>cb</sub>) and holes (h<sub>vb</sub>) (Eqs. 3–6), the species essential for the production of radicals responsible for mecoprop degradation [24]. As usual, Degussa P25 TiO<sub>2</sub>, showed the best photocatalytic activity due to its mixed anatase/rutile phase composition which significantly reduces recombination probability [41].

Doping of TiO<sub>2</sub> with iron ions is also beneficial for introducing oxygen vacancies in/on the crystal lattice or surface of TiO<sub>2</sub> [42]. When oxygen vacancies are on or near the particle surface, they can favor adsorption of water and the formation of surface hydroxyl groups (we have many hydroxyl groups on the surface of samples observed by XPS), which can promote photocatalytic activity. Since it did not happen in our experiments we assumed that oxygen vacancies are mainly inside the nanoparticles. We checked their existence by PL spectra measurements. A typical PL spectra of Fe-doped TiO<sub>2</sub> dispersions (2.5 at.% of Fe), with two different excitation energies, are presented in Fig. 8. One excitation energy is higher than the band gap energy of TiO<sub>2</sub> (4.1 eV) and the other is lower (2.07 eV). In the later case, the observed phenomenon is so called up-conversion (UC)—the observation of an emission at energies higher than the excitation energy [21, 30]. It can be noticed that UC spectra have the same position of peaks/shoulders and similar intensities compared to the normal PL spectrum. Broad emission in the spectral range from 325 to 400 nm was observed as well as the presence of well-resolved peaks/shoulders at 425, 447, 465, 490, and 537 nm.

High energy peaks can be assigned to band edge luminescence of the TiO<sub>2</sub> particles, while lower energy peaks/shoulders are induced by the presence of the oxygen vacancies [21, 30]. Among the other facts, it seems that radiative recombination of photogenerated charge carriers



**Fig. 8** Typical PL and UCPL spectra and deconvolution of PL spectrum of the rutile 2.5% Fe-TiO<sub>2</sub> nanoparticles

through oxygen vacancy-cascade can also be considered as the process which can decrease the photocatalytic activity of iron doped TiO<sub>2</sub>.

## Conclusion

TiO<sub>2</sub> nanopowders doped with different concentration of Fe ions were synthesized by coprecipitation method. Applied synthetic procedure induced formation of pure rutile crystalline structure. TEM measurements revealed formation of flower-like agglomerates with diameters in the size range from 100 to 150 nm. XPS measurements showed that Fe ions are mainly in Fe<sup>3+</sup> oxidation state and that concentrations of incorporated iron ions are much lower than stoichiometric. Doping with Fe ions has great influence on optical characteristics of the host material. Reflection measurements showed that doping of TiO<sub>2</sub> with Fe<sup>3+</sup> causes shift of the absorption threshold toward visible spectral region. No increase of TiO<sub>2</sub> photocatalytic activity after doping, was observed. The induced photoluminescence as well as the decrease of photocatalytic activity is probably the consequence of the introduction of oxygen vacancies through doping procedure. For higher dopant concentrations (>5%, stoichiometric concentration) also recombination of photogenerated charge carriers occurs with higher probability.

**Acknowledgments** The authors are grateful to Dr Amelia Montone for help in performing SEM measurements. Financial support for this study was granted by the Ministry of Science and Technological Development of the Republic of Serbia (Project No. 142066 and 142029).

## References

- G. Pfaff, P. Reynders, *Chem. Rev.* **99**, 1963 (1999). doi:10.1021/cr970075u
- A. Salvador, M.C. Pascual-Marti, J.R. Adell, A. Requeni, J.G. March, *J. Pharm. Biomed. Anal.* **22**, 301 (2000). doi:10.1016/S0731-7085(99)00286-1
- R. Zallen, M.P. Moret, *Solid State Commun.* **137**, 154 (2006)
- J.H. Braun, A. Baidins, R.E. Marganski, *Prog. Org. Coat.* **20**, 105 (1992). doi:10.1016/0033-0655(92)80001-D
- S.A. Yuan, W.H. Chen, S.S. Hu, *Mater. Sci. Eng. C* **25**, 479 (2005). doi:10.1016/j.msec.2004.12.004
- A. Fujishima, K. Honda, *Nature* **37**, 238 (1972)
- A. Fujishima, T.N. Rao, D.A. Tryk, *J. Photochem. Photobiol. Chem.* **1**, 1 (2000). doi:10.1016/S1389-5567(00)00002-2
- D.A. Tryk, A. Fujishima, K. Honda, *Electrochim. Acta* **45**, 2363 (2000). doi:10.1016/S0013-4686(00)00337-6
- M. Grätzel, *Nature* **414**, 338 (2001). doi:10.1038/35104607
- A. Hagfeldt, M. Grätzel, *Chem. Rev.* **95**, 49 (1995). doi:10.1021/cr00033a003
- A.L. Linsebigler, G. Lu, J.T. Yates Jr, *Chem. Rev.* **95**, 735 (1995). doi:10.1021/cr00035a013
- A. Millis, S. Le Hunte, *J. Photochem. Photobiol. A* **108**, 1 (1997). doi:10.1016/S1010-6030(97)00118-4
- X. Chen, S.S. Mao, *Chem. Rev.* **107**, 2891 (2007). doi:10.1021/cr0500535
- A.P. Alivisatos, *J. Phys. Chem.* **100**, 13226 (1996). doi:10.1021/jp9535506
- A.P. Alivisatos, *Science* **271**, 933 (1996). doi:10.1126/science.271.5251.933
- C. Burda, X. Chen, R. Narayanan, M.A. El-Sayed, *Chem. Rev.* **105**, 1025 (2005). doi:10.1021/cr030063a
- C.B. Murray, C.R. Kagan, M.G. Bawendi, *Annu. Rev. Mater. Sci.* **30**, 545 (2000). doi:10.1146/annurev.matsci.30.1.545
- Y. Yin, A.P. Alivisatos, *Nature* **437**, 664 (2005). doi:10.1038/nature04165
- X. Chen, Y. Lou, S. Dayal, X. Qiu, R. Krolicki, C. Burda, C. Zhao, J. Becker, *J. Nanosci. Nanotechnol.* **5**, 1408 (2005)
- U. Diebold, *Surf. Sci. Rep.* **48**, 53 (2003). doi:10.1016/S0167-5729(02)00100-0
- N.D. Abazović, M.I. Čomor, M.D. Dramićanin, D.J. Jovanović, S.P. Ahrenkiel, J.M. Nedeljković, *J. Phys. Chem. B* **110**, 25366 (2006). doi:10.1021/jp064454f
- Y. Lei, K. Ng, L. Weng, C. Chan, L. Li, *Surf. Interface. Anal.* **35**, 852 (2003). doi:10.1002/sia.1615
- A.S. Topalov, D.V. Šojić, D.A. Molnár-Gábor, B.F. Abramović, M.I. Čomor, *Appl. Catal. B Environ.* **54**, 125 (2004). doi:10.1016/j.apcatb.2004.06.012
- A. Topalov, D.M. Molnar-Gabor, K.B. Abramovic, *Water Res.* **34**, 1473 (2000). doi:10.1016/S0043-1354(99)00304-8
- D. Zhang, L. Qi, J. Ma, H. Cheng, *J. Mater. Chem.* **12**, 3677 (2002). doi:10.1039/b206996b
- J. Yang, S. Mei, J.M.F. Ferreira, P. Norby, S. Quaresmã, *J. Colloid Interface Sci.* **283**, 102 (2005). doi:10.1016/j.jcis.2004.08.109
- R. Alexandrescu, F. Dumitrache, I. Morjan, I. Sandu, M. Savoiu, I. Voicu, C. Fleaca, R. Piticescu, *Nanotechnology* **15**, 537 (2004). doi:10.1088/0957-4484/15/5/023
- H. Liu, W. Yang, Y. Ma, Y. Cao, J. Yao, J. Zhang, T. Hu, *Langmuir* **19**, 3001 (2003). doi:10.1021/la026600o
- L. Miao, S. Tanemura, S. Toh, K. Kaneko, M. Tanemura, *Appl. Surf. Sci.* **238**, 175 (2004). doi:10.1016/j.apsusc.2004.05.201
- N.D. Abazović, I.A. Ruvarac-Bugarčić, M.I. Čomor, N. Bibić, S.P. Ahrenkiel, J.M. Nedeljković, *Opt. Mater.* **30**, 1139 (2008). doi:10.1016/j.optmat.2007.05.038

31. J. Zhu, F. Chen, J. Zhang, H. Chen, M. Anpo, J. Photochem. Photobiol. Chem. **180**, 196 (2006). doi:[10.1016/j.jphotochem.2005.10.017](https://doi.org/10.1016/j.jphotochem.2005.10.017)
32. W. Zhang, Y. Li, S. Zhu, F. Wang, Chem. Phys. Lett. **373**, 333 (2003). doi:[10.1016/S0009-2614\(03\)00618-3](https://doi.org/10.1016/S0009-2614(03)00618-3)
33. K. Nagaveni, M.S. Hegde, N. Ravishankar, G.N. Subbanna, G. Madras, Langmuir **20**, 2900 (2004). doi:[10.1021/la035777v](https://doi.org/10.1021/la035777v)
34. B. Erdem, R.A. Hunsicker, G.W. Simmons, E.D. Sudol, V.L. Dimonie, M.S. El-Aasser, Langmuir **17**, 2664 (2001). doi:[10.1021/la0015213](https://doi.org/10.1021/la0015213)
35. A. Glisenti, J. Mol. Catal. A Chem. **153**, 169 (2000). doi:[10.1016/S1381-1169\(99\)00344-1](https://doi.org/10.1016/S1381-1169(99)00344-1)
36. P. Graat, M.A.J. Somers, Appl. Surf. Sci. **100\101**, 36 (1996). doi:[10.1016/0169-4332\(96\)00252-8](https://doi.org/10.1016/0169-4332(96)00252-8)
37. D. Beydoun, R. Amal, G. Low, S. McEvoy, J. Nanopart. Res. **1**, 439 (1999). doi:[10.1023/A:1010044830871](https://doi.org/10.1023/A:1010044830871)
38. C. Wang, C. Böttcher, D.W. Bahnemann, J.K. Dohrmann, J. Mater. Chem. **13**, 2322 (2003). doi:[10.1039/b303716a](https://doi.org/10.1039/b303716a)
39. E.P. Reddy, B. Sun, P.G. Smirniotis, J. Phys. Chem. **108**, 17198 (2004). doi:[10.1021/jp047419m](https://doi.org/10.1021/jp047419m)
40. W.Y. Teoh, R. Amal, L. Mädler, S.E. Pratsinis, Catal. Today **120**, 203 (2007). doi:[10.1016/j.cattod.2006.07.049](https://doi.org/10.1016/j.cattod.2006.07.049)
41. D.C. Hurum, K.A. Gray, T. Rajh, M.C. Thurnauer, J. Phys. Chem. B **109**, 977 (2005). doi:[10.1021/jp045395d](https://doi.org/10.1021/jp045395d)
42. N. Serpone, J. Phys. Chem. B **110**, 24287 (2006). doi:[10.1021/jp065659r](https://doi.org/10.1021/jp065659r)