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Polymorphic phase study on Nitrogen-doped TiO$_2$ nanoparticles: Effect on oxygen site occupancy, dye sensitized solar cells efficiency and hydrogen production

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In this work we show that phase formation and oxygen substitution can be controlled by the source of nitrogen used during the synthesis of TiO$_2$ nanoparticles. By performing a thorough study on the structure of the nanoparticles, the use of NH$_4^+$ or NO$_3^-$ was found to influence not only the N-doping level but also the formation of the polymorphic phase. Structural and microstructural refinement obtained by XRD spectra and data processing performed by the Rietveld refinement revealed that TiO$_2$ obtained with HNO$_3$ present ca. 98 % of anatase and ca. 2% for rutile. Meanwhile TiO$_2$ nanoparticles synthesized with NH$_4$F and NH$_4$Cl present a single anatase phase with ca. 70 % and 4.4 % of Nitrogen substitutional Oxygen sites, respectively. The local structure of N-doped TiO$_2$ around Ti atoms was investigated by X-ray absorption spectroscopy. The XANES spectra show that N-doped TiO$_2$ possesses a characteristic pre-edge of single anatase structure. The coordination number decreased and the shrinking Ti-O bond distances are due to the N-doping in the TiO$_2$ structure. The most efficient Dye Sensitized solar cell and the higher hydrogen production was obtained from the TiO$_2$/NH$_4$Cl, which was obtained as single anatase phase with intermediary concentration of N substitutional oxygen sites.

**Introduction**

Within the last two decades many research groups have devoted their efforts to the development of efficient and clean ways to produce and store clean energy.$^{1-7}$ Solar Cells and hydrogen production by water splitting, comes to light as very promising alternatives to efficiently contribute to the world energetic matrix. In 1972, Fujishima and Honda presented to the world the possibility hydrogen production by water splitting$^1$ and in the last 40 years numerous researches have been conducted in order to boost the hydrogen generation efficiency and reduce the external applied potential.

About 25 years has passed since the work reported by O'Regan and Grätzel in 1991,$^8$ in this mean time many research groups have focused their efforts to the study of new electrolytes,$^9-11$ sensitizers$^{12-14}$ and semiconductors,$^{15-17}$ resulting in efficiencies of ca. 12%.$^{18}$ All this effort has made dye sensitized solar cells (DSSC) a promising candidate to efficiently contribute to the world energy matrix. In DSSC, in order to generate high photocurrent, upon photoexcitation the charge transfer from the highest occupied molecular orbital (LUMO) of the dye to the conduction band of TiO$_2$ must be faster than charge recombination between the photoexcited electron and the hole in the dye. Also the reduction of the oxidized lowest unoccupied molecular orbital (HOMO) by redox species in the electrolyte must be faster than the charge recombination reaction between the oxidized dye and injected photoexcited electrons in the semiconductor. Although different materials such as p-NiO, p-CuInSe$_2$, ZnO and SnO$_2$ have been studied, until now, TiO$_2$ photoanodes have resulted in the most efficient devices, allowing the fastest charge transfer rates.[$^{16-19}$] In fact, due to the wide range of application, TiO$_2$ is the most extensively studied metal oxide. In order to obtain TiO$_2$ nanostructures presenting ideal properties for different applications, many works have been conducted on the effect of dopants, structural defects, sample preparation and thermal treatment on the TiO$_2$ properties. The results have shown that TiO$_2$ properties are directly related to the crystalline phase, crystal size, chemical structure and doping level.$^{20-24}$ For both photocatalyst, hydrogen production and DSSC application, the anatase phase results in more efficient systems,$^{25-27}$ due to improved catalytic activity and electron mobility; therefore the control of phase formation during the synthesis and the solid-solid phase transformation during thermal treatment is a concern. A major drawback is the wide band gap of TiO$_2$, presenting absorption mostly only within the ultraviolet range. In order to overcome this issue,
band gap narrowing has been obtained by doping TiO$_2$ with metals such as Cu, Co, Ni, Mo, Fe, Ru, Au and Ag.\textsuperscript{21,28–30} Although resulting in a wider absorption spectrum, studies have shown that metal impurities result in thermal instability. Another approach been explored is the doping by non-metallic elements.\textsuperscript{22,31–33} Among the studied elements, nitrogen has been widely explored and many reports have shown different ways to dope TiO$_2$ with nitrogen and the effects on photocatalytic properties resulting in materials presenting high thermal stability, low carrier-recombination rates and higher ability to absorb light in the visible range.\textsuperscript{34–39}

Although many works have been published on this subject, a wide experimental study on the effects of different nitrogen sources on the structural and microstructural properties of TiO$_2$, therefore on its optical and electronic properties is warranted to contribute to a better control of this material. Herein, we synthesized N-doped TiO$_2$ nanoparticles obtained using three different nitrogen sources, HNO$_3$, NH$_4$Cl and NH$_4$F. The materials were characterized in detail by UV-Vis spectroscopy, XRD, Rietveld refinement, XANES, EXAFS and have been applied to assemble dye sensitized solar cells and to produce hydrogen by photolysis.

**Experimental part**

**Synthesis of N-doped TiO$_2$ nanoparticles.** Three samples of TiO$_2$ nanoparticles were obtained: i) through a well-known synthetic route using HNO$_3$ labelled as TiO$_2$/HNO$_3$\textsuperscript{16} ii) using NH$_4$F labelled as TiO$_2$/NH$_4$F and iii) using NH$_4$Cl labelled as TiO$_2$/NH$_4$Cl. The synthetic approach used to obtain TiO$_2$/NH$_4$F and TiO$_2$/NH$_4$Cl is also based on Grätzel work where 0.05M of acetic acid was added to 0.05M of titanium isopropoxide at room temperature. The solution was stirred for 15 min and poured into 72.5 mL of deionized water. The mixture was maintained under constant stirring for one hour at room temperature, to complete the hydrolysis. 0.025M of nitric acid 63\% (NH$_4$F or NH$_4$Cl) was added. The mixture was stirred for 8 h at 80 °C. After adding 95 mL of distilled water the solution was kept in autoclave and heated at 230 °C for 12 h. Finally, all samples were rinsed with anhydrous ethanol, to remove residual H$^+$ and water.

**Microscopy Analysis.** The morphology of the synthesized TiO$_2$ nanoparticles was obtained by Transmission Electron Microscopy (TEM) performed using a Libra Zeiss 120. For TEM, a small amount of sample was dispersed in isopropyl alcohol using a 450 W ultrasound horn and then depositing them onto a carbon-coated copper grid.

**Absorption Spectra.** Diffuse reflectance was performed using a Shimadzu UV-2450PC spectrophotometer with integrating sphere ISR-2200, at room temperature.

**Specific Surface Area.** N$_2$ adsorption–desorption isotherms were determined at liquid nitrogen boiling point, using a micrometrics TriStar II equipped with krypton accessory. The samples were previously degassed at 140 °C under vacuum, during 6 hours. The specific surface areas were determined by BET multipoint method.

**X-ray photoelectron spectroscopy**. XPS experiments were carried out at beamline 5XS of the Brazilian Synchrotron Light Laboratory. The operating pressure in the ultrahigh vacuum chamber (UHV) during the analysis was 1 × 10$^{-9}$ Pa. The XPS spectra were collected using incident photon energy of 1840 eV. Energy steps were of 20 eV with 0.1 eV step energy and 200 ms per point acquisition time. The component of the C 1s peak of adventitious carbon was fixed at 285 eV to set the binding energy scale.

**Crystalline Structure.** X-ray powder diffraction (XRD) patterns were obtained using a Siemens D5000 diffractometer with Cu-Ka ($\lambda$ = 1.5418 Å) in a 2θ range from 10 to 90° with a step size of 0.05° and time of 1 s per step. Rietveld refinements of the structure were carried out for all samples. The structural refinements were performed from X-ray diffraction patterns for the scale factor, atomic positions, anisotropic temperature factors and peak parameters (peak widths, cell dimensions, zero point, background, point interpolation, etc.) were also varied. The instrument resolution function of the diffractometer was obtained from well-crystallized standard LaB$_6$ and taken into account in separated input files. Rietveld refinements were performed using the atomic position set and the space group of the Anatase structure $I4_1/amd$ No. 141. The unit cell is defined by the lattice vectors $a$ and $c$ and contains two TiO$_2$ units with Ti ions at 4b Wyckoff positions (0,1/4,3/8), (0,3/4,5/8) and O ions at 8e Wyckoff positions (0,1/4,a), (0,3/4,1/4+a), (1/2,1/4,1/2), (1/2,3/4,1/4-a) and Rutile structure $P4_2/mnm$, N° 136 the unit cell is defined by the lattice vectors $a$ and $c$ and contains two TiO$_2$ unit with Ti ions at 2a Wyckoff positions (0,0,0), (1/2,3/4,1/4-a), (1/2,1/4,1/2) and O ions at 4f Wyckoff positions $\pm(a,a,0)$ and $\pm(0,0,1/2)$ and $\pm(1/2,1/2,1/2)$. The unit-cell parameters have been determined using x-ray diffraction and Rietveld refinement by means of the software FullProf. The pseudo-Voigt profile function of Thompson, Cox and Hastings\textsuperscript{41} was used with asymmetry correction at low angle. Corrections to the preferred orientation were performed using the Modified March’s function. The anisotropic size broadening effects, related to the coherence volume of diffraction, were simulated using a model of spherical harmonics.

**Electron distribution density.** The electron density on a point (x; y; z) of the crystallite cell with volume $V$ was calculated by Fourier series using the structural factors $F$ (hkl) obtained from Rietveld refinement.\textsuperscript{45}

**X-ray absorption spectroscopy (XAS) and data analysis.** XAS spectra were measured on the K-edges of titanium (4966 eV) in transmission mode at room temperature using a channel-cut S (111) crystal and three ionization chambers in the Brazilian Synchrotron Light Laboratory (LNLS, Campinas, Brazil) at the XAFS1 beamline. To calibrate the measurements, a Ti foil was used as reference sample. The powder samples were diluted with boron nitride and mounted on a tape. X-ray absorption near edge structure (XANES) data was measured from 80 eV below to 100 eV above the main absorption edge with energy step of 0.4 eV around the edge with 2s of acquisition per step. XAS data were analysed in accordance with the standard procedure for data reduction, using
The EXAFS signal $\chi(k)$ was extracted and Fourier transformed (FT) using a Kaiser–Bessel window with a k-range from 2.2 to 11.2 Å⁻¹.

**Dye-sensitized Solar Cells Assembly.** The TiO₂ pastes was screenprinted on the transparent conductive substrate (fluorine-doped tin oxide – FTO) previously soaked in 40 mM TiCl₄ aqueous solution at 60 °C for 30 minutes. The substrate was heated on a hot plate at 125 °C for 20 min and at 450°C for 30 min in a tubular oven. The mesoporous TiO₂ electrode was immersed in 0.5 mM cis-bis(isothiocyanato) ruthenium(II)N≡N-719 solution of acetonitrile/tertbutyl alcohol (1:1 v/v) and kept at room temperature 24 h. The counter-electrodes were prepared by coating the FTO surface with a 30 µL of 1 mM hexachloroplatinic acid and heated at 500°C. The mediator, responsible for the regeneration of the dye was placed in between the dye sensitized photoanode and the counter-electrode. The device was sealed using a polymeric film of low melting temperature (Meltonix). The electrolyte was a 0.6 M BMII, 0.03 M I$_3$, 0.10 M guanidinium thiocyanate and 0.5 M 4-tertbutylpyridine in a mixture of acetonitrile and valeronitrile.

**Impedance spectra of DSSCs.** Impedance spectra of DSSCs were recorded at open circuit potential, under 100 mW cm⁻² bias illumination over a frequency range of 100 kHz – 10 mHz at signal amplitude of 10 mV using Autolab, PGSTAT100. Circuit fitting was complied by NOVA software.

**Characterization of the Solar Cells.** The performance of the DSSCs was evaluated by current versus potential measurements, carried out using a 300 W Xenon arc lamp and an AM1.5 filter. The power of the simulated light was calibrated to 100 mW/cm² and recorded by a picoamperimeter Keithley, model 2400.

**Hydrogen production by photolysis.** 10 mg of the photocatalyst: TiO₂/HNO₃, TiO₂/NH₄F or TiO₂/NH₄Cl was dispersed in a mixture of 7.5 mL of water and 2.5 mL of ethanol, kept in ultrasonic bath during 20 minutes and purged in argon. The samples were irradiated in a quartz cell by using a 240 W Xe lamp. The temperature was maintained constant at 25 °C using a cooling system. Hydrogen evolution was analysed with a gas chromatograph Shimadzu 2014 equipped with a molecular column Sieve 5 in a TCD detector using argon carrier. 50 µL aliquots were collected every 30 minutes and analysed.

**Results and Discussion**

The size and morphology of the TiO₂ NPs were investigated by TEM. Fig. 1 shows the images of the nanoparticles as synthesized (before thermal treatment). One can observe that all samples present the same shape and nearly the same size and size distribution of around 20 nm in diameter. Hence, the morphological properties are found not dependent on the source of nitrogen used during the synthesis.

The samples present similar energy band gaps with absorption edge at ca. 400 nm, towards the ultraviolet range (Fig. 2). The inset shows that nanoparticles obtained using NH₄Cl and NH₄F present a weak absorption band from ca. 400 to ca. 500 nm. Nitrogen have unpaired electrons which can easily bind to Ti4+ through acid-base reaction.\(^{36,37}\) The absorption band observed from ca. 400 to ca. 500 nm is related to the interaction of mixed wave functions of nitrogen 2p with O 2p states, resulting in intermediary energy levels slightly above the top of the O 2p valence band of TiO₂.\(^{38-40}\) Once the cations NH$_4^+$ are hydrolyzed to NH$_3$ and H$_2$O, the NH$_3$ seems to result in a slight higher doping level than NO$_3^-$. By considering the motion of NH$_3$ and NO$_3^-$ within TiO$_2$: NH$_3$ has larger mobility once NO$_3^-$ undergoes electrostatic interaction with the TiO$_2$ lattice. The expected larger diffusion of NH$_3$ would result in a larger degree of doping, after thermal treatment. Studies on bulk diffusion of nitrogen doped TiO$_2$ by NH$_3$ at high temperatures have suggested the presence of substitutional and interstitial nitrogen.\(^{38,47}\) In addition, EPR studies has shown that calcination of NO$_3^-$ results in NO$_2^-$ species, meanwhile calcination of NH$_3$ results in NO.\(^{58}\) Smaller molecules shall diffuse easily through the TiO₂ nanoparticles. The SEM images show that after thermal treatment, size and size distribution of the nanoparticles were maintained in the mesoporous film; however TiO₂/NH₄F seems to result in a more homogenous film.

Considering the formation of intermediary energy levels upon doping, a redshift of the absorption edge is expected along with an increase in doping. In this work the redshift was only observed for TiO₂/NH₄F, which also presented a slight more intense absorption band from 400 to 500 nm than TiO₂/NH₄Cl. Previous reports have shown that improved photocatalytic activity have been obtained for co-doping TiO₂ with both Nitrogen and Fluorine. The improved activity was attributed to a synergistic effect of the co-doping where fluorine atoms improved visible-light absorption.\(^{49,50}\) Based in these previous results, for TiO₂/NH₄F, we should account for the presence of Fluorine atoms, however for refining the XRD data (discussed in next section) a good fitting was obtained by considering only nitrogen substitutional.
Fig. 2. Absorption spectra of N-doped TiO2 NPs synthesized using different sources of nitrogen, after thermal treatment at 500°C.

Fig. 3 shows the nitrogen adsorption-desorption isotherms of TiO2/HNO3, TiO2/NH4F and TiO2/NH4Cl as-synthesized and after thermal treatment at 500 °C. All samples show adsorption isotherms with a hysteresis type IV, characteristic of mesoporous material. The samples also present a small contribution of isotherms of the type I, characteristic of micropores. All of the isotherms present low nitrogen adsorption at P/P0 smaller than 0.4 values, and high nitrogen volume adsorption at high values of P/P0, above 0.8. After calcination the most significant change was observed from TiO2/NH4F, where a higher decrease on amount of nitrogen desorption results from a decrease in surface area.51,52

Fig. 3. N2 adsorption–desorption isotherms of the N-doped TiO2 NPs prepared using different sources of nitrogen. (left) as-synthesized and (right) thermally treated at 500 °C.

Figure 4 shows the N 1s XPS spectra of TiO2/HNO3, TiO2/NH4F and TiO2/NH4Cl. One can observe a broad N 1s peak with maximum at 400 eV is observed in the spectra of N-doped samples. These values fit well with the binding energy for N-doped TiO2 reported in the literature. Xiao et al showed that the binding energy peak of N 1s, related to N-doped TiO2 is a broad peak ranging from 397.4 eV to 403.7 eV. The discussion on interstitial and substitutional doping is rather difficult and the XPS assignment for interstitial or substitutional sites in N-doped TiO2 has been the subject of a constant debate; as stated by Asahi et al, it is subject of controversial hypothesis.54 XPS peaks within 399-400 eV have been attributed to Ti-O-N and Ti-N-O55,57, to NH3 adsorbed on the TiO2 surface55,57 and to either interstitial or substitutional nitrogen.55,64

By refining the XRD data, the best fitting was obtained by considering substitutional nitrogen. For the sake of comparison, we have used the best possible fitting with statistically improved agreement factors, to evaluate the presence of Nitrogen in the TiO2 lattice. Therefore from the XPS and the XRD analyses it is reasonable to suggest that interstitial sites are preferentially formed at the surface while in the bulk substitutional nitrogen is observed, albeit very small.

Fig. 4. N1S XPS spectra of TiO2/HNO3, TiO2/NH4F and TiO2/NH4Cl.

For the sake of comparison, we have used the best possible fitting with statistically improved agreement factors, to evaluate the presence of Nitrogen in the TiO2 lattice. Therefore from the XPS and the XRD analyses it is reasonable to suggest that interstitial sites are preferentially formed at the surface while in the bulk substitutional nitrogen is observed, albeit very small.

Fig. 5 shows the XRD patterns and Rietveld refinement fitting results for all samples. TiO2/HNO3 presents diffraction peaks corresponding to the anatase phase (JCPDS # 84-1286) and small additional peaks related to the rutile phase (JCPDS # 76-0649). The percentages of anatase and rutile phases from TiO2/HNO3 were 98.21 ± 0.70 and 1.97 ± 0.01, respectively. In both anatase and rutile structures of TiO2, each Ti4+ is surrounded by six species O2-, resulting in an octahedral structure. The difference between the two polymorphic phases is related to different orthorhombic distortions of each octahedron and by the assembling of the octahedral resulting in the crystalline structure. For TiO2/HNO3, structural and microstructural refinement revealed that the phase of anatase was a tetragonal structure with an I41/amd space group, with lattice parameters: a=b=3.7856 Å, c=9.5068 Å, α=β=γ= 90°, an average grain size of 16.40 ± 1.53 nm and micro-strain of 15.22 ± 0.0039 (%). In addition, the secondary phase associated to rutile was found a tetragonal structure with a P42mm space group, with lattice parameters: a=b=4.5982 Å, c=2.9579 Å, α=β=γ= 90°, an average grain size of 48.82 ± 0.08 nm and a micro-strain (%), of 10.61 ± 0.0031. This difference in microstrain from anatase to rutile is mainly related to the dimension of the crystals.
As observed by XPS, TiO$_2$/HNO$_3$ is also doped by Nitrogen. In fact, using the approach we have used to synthesize TiO$_2$, nitrogen doping is process intrinsic to the synthesis. We considered TiO$_2$/HNO$_3$ as a standard sample to compare how other nitrogen sources would affect the structure and the optical properties of the materials. For N-doped TiO$_2$ the refinement proceeded by allowing a simultaneous presence of N and O at the 8e Wyckoff position. The atomic coordinates of N atoms were constrained to be the same as those of O. In order to study the influence of nitrogen incorporation on the stoichiometry of the materials, the occupancies factors were left to vary free. On the basis of chemical analysis, the rest of the positions were fixed to the theoretical occupancies factors. The occupancy factors are normalized in such a way as to represent the number of atoms in a formula unit.

Previous reports have shown that pH has a strong influence on the anatase and rutile phase formation in TiO$_2$. In very acidic media the rutile phase has been found favoured over the anatase, meanwhile at intermediary pHs a single anatase phase can be obtained. Considering the previous studies suggesting that phase transformation from anatase to rutile is more difficult as the pH increases, a smaller concentration of H$^+$ resulting from the hydrolysis of NH$_4^+$ when compared to H$^+$ from HNO$_3$ is probably favoring the single anatase phase formation in TiO$_2$/NH$_4$F and TiO$_2$/NH$_4$Cl. In addition, in the conditions studied in this work we have observed that the presence both F$^-$ and Cl$^-$ either favours the formation of anatase phase or do not contribute significantly against it. This result is interesting once previous work in the literature shows that F$^-$ and SO$_4^{2-}$ contributes to the formation of anatase, while Cl$^-$ favours the formation of the rutile phase. Considering the anatase phase of TiO$_2$/NH$_4$F a tetragonal structure was found with an I4$_{1}$/amd space group, lattice parameters: $a=b=3.7889$ Å, $c=9.5059$ Å, and an average grain size of 14.19 ± 0.98 nm and a micro-strain (%, 10$^{-3}$) of 10.38 ± 0.0039. In addition a 0.14% of Ti vacancies and 4.43% of nitrogen substitutions in the oxygen sites were calculated. This result corroborates the absorption spectra (Fig. 2) showing that TiO$_2$/NH$_4$F presents a slight higher doping level than TiO$_2$/NH$_4$Cl and TiO$_2$/HNO$_3$. The average size for all of the samples and the shape of the grains were calculated using the modified Scherrer equation, using a model of spherical harmonics. \[ \beta_h = \frac{\lambda}{D_h \cos \theta} \frac{\lambda}{\cos \theta} \sum_{i=0}^{n} Y_i \theta_i (\theta_h, \phi_h) \]

Fig. 5 shows the shape of the crystallites calculated by Rietveld refinement using the XRD diffraction patterns. The image of the grains were projected on the x, y and z directions. The grain presents the same growth feature on the x/y plane, however a different anisotropic growth is observed on the y/z and x/y planes. In addition a more spherical shape is expected for TiO$_2$/NH$_4$Cl.

These results are very interesting, once Fig. 2 shows that TiO$_2$/NH$_4$F presents a larger concentration of defects than TiO$_2$/HNO$_3$ and TiO$_2$/NH$_4$Cl presents similar optical spectra. Therefore by considering the results observed in Fig. 6 we suggest a relation between shape and concentration defects, where a more regular structure presents smaller defects concentration. The good agreement between the structure factors from the experimental data simulated by Rietveld Refinement, allowed us to obtain a Fourier electron density map, showing a two-dimensional mapping of the atoms inserted in the unit cell (Fig. 7).
octahedrons, meanwhile in anatase each octahedron is surrounded by eight neighbours. This difference in structure can result in different mass densities and electronic band structures. In order to study the local structure around Ti atoms, we have carried out the XAS experiments at Ti K-edge.

The Ti K-edge XANES spectra for TiO$_2$/HNO$_3$, TiO$_2$/NH$_4$Cl and TiO$_2$/NH$_4$F is displayed in Fig. 8. The XANES pre-edge region was used to identify the local Ti coordination of the samples. All spectra have a very similar overall shape in the pre-edge and post edge regions. The pre-edge region of the samples shows a sharp peak that can be attributed to 1s to 3d transitions and the three pre-peaks in the same energy position in 4968.9, 4971.7 and 4974.1 eV that originates from the first and second coordination shells of Ti neighbours that gives evidence of the majority presence of TiO$_2$ anatase-type structure. The post-edge XANES spectra (region II) are similar to each other. However, the TiO$_2$/HNO$_3$ present slight changes in the spectral range from 4990 to 4995 eV (see arrows in Fig 8), with peaks features indicating the presence of the rutile phase. Therefore, TiO$_2$/HNO$_3$ present a mixture of majority TiO$_2$ anatase phase and small amount of rutile. Meanwhile the XANES spectra of TiO$_2$/NH$_4$Cl and TiO$_2$/NH$_4$F have the same single anatase crystalline structure, which corroborates the results obtained by XRD. 58

Fig. 7. Fourier electron density map for TiO$_2$/HNO$_3$, TiO$_2$/NH$_4$Cl and TiO$_2$/NH$_4$F.

**Fig. 8.** Ti K-edge XANES for TiO$_2$/HNO$_3$, TiO$_2$/NH$_4$Cl and TiO$_2$/NH$_4$F.

**Fig. 9** (a, c, e) and (b, d, f) shows k$^3$-weighted Ti K-edge EXAFS spectra and the corresponding Fourier Transforms (FT), respectively, for TiO$_2$/HNO$_3$, TiO$_2$/NH$_4$Cl and TiO$_2$/NH$_4$F. The k$^3$-weighted EXAFS spectra of TiO$_2$/NH$_4$Cl and TiO$_2$/NH$_4$F (Figs 9 c, d) are very similar to each other, but different from the standard TiO$_2$ (Fig. 9a), that exhibit broad peak around at 4.5Å-1. This result indicates that the local environment around Ti atoms in TiO$_2$/NH$_4$Cl and TiO$_2$/NH$_4$F seems to resemble that in anatase crystalline structure, corroborating the previous discussion.

**Fig. 9.** (a, c, e) k$^3$-weighted Ti K-edge EXAFS signal and (b, d, f) the corresponding Fourier transform magnitude. Red lines represent the best fits obtained.

**Fig. 9** (b, d and f) displays Ti K-edge FTs of EXAFS spectra corresponding to the shells of the Ti-O, Ti-Ti and O-Ti-O scattering path for the TiO$_2$. It can be seen that the FT features of all samples are look quite similar. The fitting results are summarized in Table 1. The best fitting results of the EXAFS spectra showed that the first peak at 1.96, 1.93 and 1.93 Å for TiO$_2$/HNO$_3$, TiO$_2$/NH$_4$Cl and d...
TiO$_2$/NH$_4$F, respectively, are due to the single-scattering path from first coordination shells of Ti-O bond by oxygen octahedron nearest neighbors around the Ti atom. Both N-doped TiO$_2$ NPs have Ti-O bond distances less than TiO$_2$/HNO$_3$ material. Table 1 show that all coordination numbers (N) for single Ti-O first shells are near to 6 that are close with theoretical value. Considering the uncertainties of EXAFS fittings, the N-doped TiO$_2$ samples prepared in NH$_4$F and NH$_4$Cl possess the same coordination number. The smaller bond distances of the nearest Ti-O with respect to the TiO$_2$/HNO$_3$ sample suggests the presence of nitrogen doping in the structure of TiO$_2$ NPs. The peaks appearing at 3.05, 3.04 and 3.04 Å are due to Ti-Ti bond distances at second shell. The shrinking Ti-Ti second shell coordination and increasing of Debye-Waller factor is an indication of increasing in disorder in TiO$_2$ structure probably due to the N doping.

<table>
<thead>
<tr>
<th>Sample</th>
<th>R (Å)</th>
<th>N</th>
<th>σ$_2$(Å$^2$)</th>
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<tr>
<td>TiO$_2$/HNO$_3$</td>
<td>Ti-O</td>
<td>1.96 ±0.02</td>
<td>6.39 ±0.16</td>
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<td></td>
<td>Ti-Ti</td>
<td>3.05 ±0.01</td>
<td>3.30 ±0.10</td>
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<tr>
<td>TiO$_2$/NH$_4$Cl</td>
<td>Ti-O</td>
<td>1.93 ±0.062</td>
<td>5.70 ±0.74</td>
</tr>
<tr>
<td></td>
<td>Ti-Ti</td>
<td>3.04 ±0.076</td>
<td>3.74 ±0.85</td>
</tr>
<tr>
<td>TiO$_2$/NH$_4$F</td>
<td>Ti-O</td>
<td>1.93 ±0.004</td>
<td>5.85 ±0.76</td>
</tr>
<tr>
<td></td>
<td>Ti-Ti</td>
<td>3.04 ±0.010</td>
<td>3.98 ±0.92</td>
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</table>

From the current versus potential curves (Fig. 10), we have obtained the short-circuit current (Isc), open circuit voltage (Voc), Fill Factor (FF) and efficiency ($\eta$) from the devices assembled with the three TiO$_2$ samples (Table 2). The device assembled with TiO$_2$/NH$_4$Cl presents improved FF. Considering the data obtained from XRD, Rietveld refinement, XANES and EXAFS we can relate this result to the presence of a single phase anatase and to a lower concentration of defects (0.14% of Ti vacancies in and 4.43% of nitrogen substitutions in the oxygen sites). These properties result in improved electron mobility by hoping from one nanoparticle to another, in order to reach the charge collecting electrode.

Fig. 11 shows the results obtained from hydrogen production performed by photolysis in ethanol/water solution. The lowest efficiency was obtained from TiO$_2$/HNO$_3$ presenting hydrogen production rate of 0.15 mmol.g$^{-1}$h$^{-1}$ while TiO$_2$/NH$_4$Cl present a two fold increase, resulting in hydrogen production rate of 0.3 mmol.g$^{-1}$h$^{-1}$. The literature shows many works where Nitrogen doped TiO$_2$ and bare TiO$_2$ present similar photocatalytic activity under UV light but improved photocatalytic activity under visible light is obtained by N-doped TiO$_2$. Some works correlate the enhancement in photocatalytic activity on the intensity of the peaks at 400–404 eV.

These results corroborate the DSSC measurements, showing that the intermediary doping combined to the single anatase phase, which results in higher photocurrent and lower recombination rate favours both photolysis and solar cell efficiency.
Table 3. EIS Parameters of the Three Devices Determined by Fitting the Data According to the Equivalent Circuit Model (See Fig. 12).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$R_0$ (Ω)</th>
<th>$R_1$ (Ω)</th>
<th>$R_{1/2}$ (Ω)</th>
<th>$R_{total}$ (Ω)</th>
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<tr>
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<tr>
<td>TiO$_2}$/NH$_4$F</td>
<td>11.39</td>
<td>53.20</td>
<td>97.91</td>
<td>162.50</td>
</tr>
<tr>
<td>TiO$_2$/NH$_4$Cl</td>
<td>12.14</td>
<td>55.26</td>
<td>103.41</td>
<td>170.81</td>
</tr>
</tbody>
</table>

Conclusions

In this work we show that single anatase phase TiO$_2$ nanoparticles can be obtained by tuning the nitrogen source used during the synthesis. The use of NH$_4^+$ which is hydrolyzed to NH$_3$ leads to the formation of a single anatase phase, meanwhile NO$_3^-$ was found to result in a mixed anatase/rutile lattice. In addition, we have observed a dependence of the amount of nitrogen on the source of nitrogen, hence effecting doping level and electronic properties of the nanoparticles. Although only a small change in the optical spectra was detected, the changes observed by XRD, XANES and EXAFS show that the efficiency of Dye sensitized solar cells and hydrogen production are deeply dependent on the N-doping of the semiconductor.

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Notes and references


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