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Effect of Nd^{3+} doping on structure, microstructure, lattice distortion and electronic properties of TiO_2 nanoparticles

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Abstract: Doped and undoped TiO_2 nanoparticles were prepared by Stöber method and thermally treated at 600 ºC. The effect of Nd^{3+} ion on the structure and microstructure of anatase-phase TiO_2 nanocrystals was studied by Rietveld refinement method using X-ray powder diffraction data. Bond lengths, bond angles, and edges distances were analyzed. The phase formation was confirmed by high-resolution transmission electron microscopy. The adjustment of Ti–O bond length induced by the addition of Nd^{3+} ions, reduced the octahedral distortion and altered the octahedral array in the anatase-phase TiO_2 nanocrystal. The changes of structure and microstructure were mainly observed for TiO_2 nanoparticles doped with 0.1 at.% of Nd^{3+} ions and attributed to the cationic substitution of Ti^{4+} ions which promoted changes in the density of states and gap band of TiO_2. The dopant insertion resulted in a better structural stability of the nanocrystals that enhanced their charge transference and photocatalytic efficiency.

Keywords: neodymium; TiO_2 nanoparticles; microstructure; lattice distortion; photocatalytic activity; optical properties; Rietveld refinement; rare earths

Titania nanoparticles doped with rare earth (RE) elements have applications in the degradation of persistent contaminants and dye-sensitized solar cells (DSSC). Several changes are attributed to the RE dopant in the nanocrystal, e.g., size, microstrain, specific surface area, and band gap. The modifications involve complex interactions between the RE dopant and their surrounds in the TiO_2 lattice like charge, orbital ordering, and distortions. Where, the analysis of microstructural and structural parameters is essential for the understanding of the charge transference in the photocatalytic activity or the photovoltaic performance.

The anatase-phase TiO_2 structure shows an array of empty and full octahedrons. The addition of RE^{3+} ions changes the octahedral array in the matrix of Ti^{4+} ions. It may happen in two routes: (i) the occupation of a cationic interstitial site, which is an empty octahedron generated from the arrangement of six occupied octahedrons or (ii) the cationic substitution in body-centered (BC) or face-centered (FC) positions[1]. In both substitutions, an REO_6 octahedron replaces a TiO_6 octahedron if the coordination number is six like Ti^{4+}.

For trivalent Nd (effective ionic radius of 6-coordinate Nd^{3+} is 0.098 nm), the difference in bond length between the axial Ti–O bond and the Nd–O bond is approximately 0.04 nm from their effective ionic radii[2,3] or taking the experimental value reported in perovskites structures[4,5]. Therefore, the insertion of NdO_6 octahedron may cause structural deformations that adjust Ti–O bond lengths, O–Ti–O bond angles and O–O distances in the unit cell altering Ti–O–Ti bond angles and Ti–Ti distances between adjacent octahedrons in the anatase-phase TiO_2 lattice.

In polyhedral structures, the distortion of octahedrons can be measured using the bond angles variance $\sigma^2_{\theta(\mathrm{oct})}$ and the mean quadratic elongation $\langle\lambda_{(\mathrm{oct})}\rangle$[6]. For polymorphs TiO_2, Meagher and Lager reported both parameters showing that the anatase phase is the most distorted among TiO_2 phases because it is sharing the higher number of edges[7]. The addition of the Nd^{3+} ion can adjust the structural distortion in the polyhedral array of the anatase phase TiO_2. The understanding of this evidence can contribute to explaining modifications in the microstructure of doped TiO_2 nanoparticles.

Furthermore, the effect of RE^{3+} ions on the microstructure of nanocrystalline anatase-phase TiO_2 samples has been reported in detail[8–11]. However, the structural distortion due to RE^{3+} such as Nd^{3+} is yet being studied in details. The role of RE^{3+} ions in the improvement of electronic transport properties of these

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samples has been reported by several authors[10,12–18]. Among all RE-TiO_2, the system based on Nd^{3+} ions is of interest because this coordination improved the trapping-to-recombination rate ratio of photogenerated electrons and holes. However, the structural characterization and study of the doping effect on octahedral distortion were not addressed previously.

We studied nanocrystalline anatase-phase TiO_2 nanoparticles doped with Nd^{3+} ions to investigate changes in the structure of the unit cell, also their effect on the electronic properties and the photocatalytic activity. In this research several characterization techniques were used like Rietveld refinement, high-resolution transmission electron microscopy (HRTEM) and UV diffuse reflectance (DRS) resulting in aspects as detailed crystal structures and measures of lattice distortions clarifying the effect of Nd^{3+} ions on the microstructure, charge transference and photocatalytic efficiency of anatase-phase TiO_2 nanoparticles.

1 Materials and methods

All chemicals were used as received without further purification and were purchased from Sigma-Aldrich. ammonium hydroxide (NH_4OH), Congo red dye ($C_{32}H_{22}N_6Na_2O_6S_2$), neodymium nitrate hexahydrate ($Nd(NO_3)_3·6H_2O$), titanium tetrachloride ($TiCl_4$), acetonitrile (CH_3CN), ethanol (C_2H_6O), 2-propanol (C_3H_8O), and nanocrystalline commercial anatase TiO_2 powders as the reference material (RM-TiO_2).

The synthesis of TiO_2 nanoparticles doped with Nd^{3+} ions was carried out by Stöber method. For 100 mL of absolute ethanol, 4 mL of $TiCl_4$ was added at 0 ºC with constant magnetic stirring for 30 min, then $Nd(NO_3)_3·6H_2O$ was added, dissolved in 5 mL water and then reacted for 30 min more. The amounts of Nd^{3+} ions were calculated in order to substitute 0.0, 0.1 at.%, 0.2 at.%, 0.3 at.% and 0.4 at.% Ti^{4+} ions and were labeled as 0.0, 0.1 at.%, 0.2 at.%, 0.3 at.% and 0.4 at.%, respectively. After this time, 10 mL of NH_4OH at 0.33 mol/L was added to the hydrolysis reaction mixture with constant stirring forming a sol-gel system. The resulting suspension was preserved at 0 ºC for 30 min. The obtained material was separated by filtration, dried in an oven at 100 ºC for 24 h. It was thermally treated at 600 ºC for 6 h. All dissolutions were prepared using deionized water.

X-ray spectra were acquired using a diffractometer (XPert-Pro MPD, Panalytical), operated at 40 kV and 35 mA, equipped with a Cu Kα source at 0.154060 nm and a PW3011/20 detector. The intensity data were collected with 2θ ranging from 20º–85º with step size 0.017 and step time 12 s. Previously, the instrumental resolution function (IRF) was acquired using a silicon sample (Si SMR640 NIST) for broadening effects according to the Bragg angle; and the peaks profile was fitted using the Pseudo-Voigt function[19] and processed in the WinPlotr software[20].

For the profile of peaks, Rietveld refinements were done with the Full Prof software[21]. The initial value was acquired from the anatase and rutile phases described by Howard et al.[22]. The background was fitted using a linear interpolation between set background points with refinable heights. The Kα_1 was corrected removing the intensity Kα_2 (ratio Kα_1/Kα_2=0.5) and the preferred orientation was corrected. Any treatment of smoothing or filtering was carried out on the spectra acquired. All phases reflections were considered that are ranging from 20º to 85º of 2θ (º) and taken into account for data refinement, but the results of the rutile-phase TiO_2 were excluded from the results and discussion section.

The least squares refinement was used to minimize the difference between the observed and calculated profile. The weighed profile residual (R_{wp}) and expected error (R_{exp}) were used like quality standard between the measured peaks and the shape of the fitting function, also, the value of goodness of fit (GoF) is reported. The line profile model was the pseudo-Voigt profile function proposed by Thompson-Cox-Hastings with the treatment of axial divergence. Parameters of microstrain (U, X) and size (Y, I^2G) were refined using a physical model[23]. The specific surface area (SSA) was estimated using the Sauter equation[24]. The lattice parameters and atomic coordinates were used to generate 3D polyhedral coordination structures of refined samples in the VESTA software (V.3.0)[25]. We measured the bond lengths, bond angles, and edge distances of single polyhedrons, also calculated the volume polyhedral, the bond average $\langle$cation-anion$\rangle$ and distortion measures[26].

Microstructure details were characterized by high-resolution transmission electron microscopy (JEOL, JEM-2011) operated at 200 kV. The elemental composition was determined by an energy dispersive spectroscope (EDS) using a silicon detector Quantax (Bruker, Nano GmbH) operating a scanning electron microscopy (Tescan, Vega) and acquired from several nanocrystalline agglomerate particles. UV-Vis diffuse reflectance spectra were acquired using a UV-Vis spectrophotometer (Varian, Cary 100) with an integrating sphere attachment DRA-CA-30I, which was calibrated with a Spectralon standard (Labs phere SRS-99-010, 99% reflectance). All spectra were recorded in the range from 250 to 1000 nm with a step size of 1.0 at room temperature. The UV-Vis reflectance spectra were analyzed using the Kubelka-Munk Theory and the expression proposed by Tauc, Davis, and Mott; and the band gap was calculated. The calculations of density functional theory were carried out using the CASTEP code (Accelrys Company). Anatase TiO_2 supercells (2x2x1 unit cell) were constructed with 16 Ti atoms and 32 O atoms and doped with Nd^{3+} ion obtaining the states partial densities.