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UV-induced reactions of Mg^{2+}-doped anatase nanocrystals with exposed {001} facets: An EPR study

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The photoinduced processes of pristine and Mg^{2+}-doped anatase nanopowders with the exposed {001} facets synthesized by a solvothermal method, using HF as the capping agent, were investigated by EPR spectroscopy. The adsorbed fluoride ions on the {001} facets of the as-prepared anatase samples have been removed by NaOH washing (washed samples) or calcination at 600 °C (calcined samples). EPR spectra monitored at 100 K for the as-prepared and washed anatase nanopowders characterized with high percentage of the exposed {001} facets, evidenced the presence of paramagnetic signals attributed to the intrinsic Ti^{3+} centers with narrow-line axially symmetric spectrum ($g_{\perp} = 1.988$, $g_{\parallel} = 1.956$) and holes (O^-) characterized with g-tensor $g_{\perp} = 2.006$, $g_{\parallel} = 2.003$ already before exposure. Upon *in situ* UV exposure under air, the intensity of EPR signals of Ti^{3+} and O^- increased significantly and two additional signals compatible with the photogenerated $O_2^{\cdot-}$ and $^{\cdot}O_2H$ were observed. A series of indirect EPR techniques, e.g., spin trapping using 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO), hindered amine oxidation, or reduction of radical cation of 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonate), were applied to follow the reactions in the irradiated TiO_2 dispersions. While in the irradiated aerated aqueous media all anatase samples revealed the generation of $^{\cdot}$DMPO-OH spin-adduct, upon UV exposure of the as-prepared samples in deaerated acetonitrile, the formation of a unique EPR spectrum attributed to $^{\cdot}$DMPO-F was found. The $^{\cdot}$DMPO-F spin-adduct is most probably produced by the inverted spin trapping mechanism *via* interaction of $DMPO^{\cdot+}$ with the surface fluorides.

1. Introduction

The unique properties of titanium dioxide polymorphs (anatase, rutile, brookite) have caused an exponential growth of different TiO_2 oriented studies over the past four decades [1–6]. Sufficient stability, low cost, relatively low toxicity and tunable photocatalytic activity predispose TiO_2 to a wide range of possible applications in various areas (pigments, gas sensors, photocatalysts, solar cells, thin film capacitors, etc.) [7–9]. Among the materials previously-studied as potentially useful for photocatalysis, titanium dioxide meets the criteria for large-scale industrial applications [5,6]. However, there are certain restrictions on the technological use of TiO_2 as a photocatalyst, in particular the recombination of photogenerated holes and electrons on the nanosecond timescale together with the band gap energy value limiting the use of visible light for photoexcitation [7]. Two main approaches can be recognized among the current efforts to expand the photocatalytic activity of titanium dioxide. The first one represents the modification of the electronic and optical properties of the photocatalyst by metal or non-metal doping or by combination with another semiconductor, which can improve the efficiency of the photocatalytic system [3,6,7]. The second approach focuses on the controlling of the microstructure and morphology of TiO_2,

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Abbreviations: ABTS, 2,2′-azino-bis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt; ACN, acetonitrile; DMPO, 5,5-dimethyl-1-pyrroline *N*-oxide; EPR, Electron Paramagnetic Resonance; RhB, Rhodamine B; ROS, reactive oxygen species; SW, magnetic field sweep width; TEM, transmission electron microscopy; Tempone, 4-oxo-2,2,6,6-tetramethylpiperidine *N*-oxyl; TMPO, 4-oxo-2,2,6,6-tetra methylpiperidine; Tempol, 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl; XRD, X-ray powder diffraction; XPS, X-ray photoelectron spectroscopy.

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since the photoinduced processes are significantly influenced by the crystal structure of the photocatalyst, particle size, their morphology and porosity [8–11]. Previously, it was demonstrated that the average surface energies for anatase crystal facets decrease in the range 0.90 J m^{-2} for {0 0 1} > 0.53 J m^{-2} for {1 0 0} > 0.44 J m^{-2} for (1 0 1) [12]. An intensive effort in the synthesis of anatase nanocrystals with controlled crystal facets was initiated by the Yang theoretical predictions in 2008 [13], which indicated that the fluoride ions have the potential to reduce the energy of {0 0 1} surfaces below the surface energy of thermodynamically stable {1 0 1} facets, thus allowing the synthesis of anatase crystals with exposed {0 0 1} facets. In addition, using hydrofluoric acid as the morphology controlling agent, Yang et al. succeeded also in the experimental production of uniform anatase single crystals with a high percentage of exposed {0 0 1} facets [13,14]. Subsequently, F$^-$-containing compounds were extensively applied as the capping agents in the synthesis of anatase structures containing high-energy surfaces [15,16]. The strategic methodologies for the preparation of such anatase TiO_2 materials, and their testing with respect to the potential applications have been reviewed recently [8,9,15,17,18]. The systematic characterization of anatase TiO_2 with the exposed {0 0 1} facets, synthesized in the presence of F$^-$ as the morphology controlling agents, by X-ray photoelectron spectroscopy (XPS) unambiguously demonstrated the presence of fluoride anions adsorbed on {0 0 1} surface. The incorporation of F$^-$ in the anatase crystal structure during the synthetic procedure (hydrothermal or sol–gel with subsequent fluorination) was excluded [19–21]. However, previous XPS investigations on the effect of F$^-$ doping and heat treatment (100–700 °C) on the titania nanopowders synthesized by sol–gel technique evidenced F 1s signals characteristic for the surface F$^-$ ions (~684 eV), along with those assigned to the substitutional F$^-$ in the TiO_2 lattice (~688 eV) [22]. Further XPS experiments confirmed that F$^-$ ions displaced not only the surface hydroxyls (signal at 684.6 eV removable by NaOH washing), but also some lattice oxygens (signal at 689.6 eV) [23]. Recent study of the mesoporous TiO_{2-x} photocatalyst with high fluorine dopant concentration supported on the mesocellular foam revealed the incorporation of fluorides on the surface (Ti^{4+}–F), as well as in the TiO_2 lattice (Ti^{3+}–F) [24]. The high degree of F-lattice doping has substantial impact on the visible light absorption of F-doped TiO_2 photocatalysts [24].

The presence of F$^-$ adsorbed on {0 0 1} facets can substantially affect the surface-mediated steps in the photoinduced transformations [8,15,25,26]. While the performance of photocatalytic reactions involving predominantly hydroxyl radicals is enhanced on the fluorinated surfaces due to the more effective generation of the free $^{\cdot}OH$ in solution [8,19,27], the oxidation *via* the photogenerated holes is often limited since the adsorption of a substrate is hindered [28,29]. On the other hand, different sub-units of a molecule may interact with the fluorinated and fluoride-free TiO_2 {0 0 1} surfaces as was shown previously for the photocatalytic degradation of Rhodamine B (RhB) [23]. Among the variety of post-synthetic methods applied for the removal of surface fluoride anions from the {0 0 1} facets, the treatment in NaOH solutions results in fluoride-free {0 0 1} facets without lowering the percentage of these surfaces [30,31]. Calcination at 600 °C as an alternative method to obtain F$^-$-free {0 0 1} facets [32,33], can cause the equilibrium shift of the anatase crystals toward the {1 0 1} facets [30]. Our previous studies on anatase nanoplates with exposed {0 0 1} facets confirmed that the dimensions of the as-prepared F$^-$-containing nanocrystals are comparable with F$^-$-free nanoparticles obtained by NaOH washing, but the calcined nanoplates became larger and their {1 0 1} facets expanded as the {0 0 1} facets shrunk [30].

Specific attention is oriented on the synthesis and characterization of doped anatase TiO_2 structures with exposed {0 0 1} facets, since the co-existence of metal ions or non-metal elements and high-energy surfaces is often coupled with enhanced photoactivity of TiO_2 upon UV and visible light excitation [9,34]. Previously, nitrogen-, sulfur- and carbon-doped anatase TiO_2 materials with exposed crystal facets were synthesized and their photoinduced activity upon visible light excitation was monitored mostly using dye degradation, e.g., methylene blue, methyl orange, RhB, or hydroxylation of terephthalic acid [9]. Recently, we synthesized and characterized a series of anatase nanoparticles with exposed {0 0 1} facets doped with Mn^{4+} or Mg^{2+} ions [35,36]. The determination of their UV-photoinduced activity in the oxidation of gaseous pollutants (NO and acetaldehyde) confirmed that the optimal content of doping ions (~2 at.%) enhances the photonic efficiency [35,36]. As the difference between the ionic radii of Mg^{2+} and Ti^{4+} is negligible, Mg^{2+} ions may easily enter into the anatase lattice, and substitute Ti^{4+} ions, forming doped anatase crystals with an increased hole density [36]. The presence of Mg^{2+} ions in the anatase crystal lattice is reflected in a slight decrease in the band gap energy [36].

The present work is oriented on the characterization of UV-induced processes of pristine and Mg^{2+}-doped anatase nanocrystals with exposed {0 0 1} facets using Electron Paramagnetic Resonance (EPR) spectroscopy. The photogenerated charge carriers in the solid matrix are monitored directly *in situ* at low temperatures while the indirect EPR techniques (spin trapping, hindered amine oxidation, $ABTS^{\cdot+}$ reduction) are applied to follow the reactions in the TiO_2 dispersions.

2. Experimental

2.1. Chemicals and reagents

Titanium(IV) isopropoxide ($Ti(C_3H_7O)_4$) purchased from Alfa Aesar Chemicals, absolute ethanol, hydrofluoric acid (HF 40%), sodium hydroxide, magnesium nitrate ($Mg(NO_3)_2{\cdot}6H_2O$, 99%) and silver nitrate ($AgNO_3$, extra pure) from Merck were used without additional purification. Spin trapping agent 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO) purchased from Sigma–Aldrich was distilled before application and stored at −18 °C. 2,2′-Azinobis(3-ethylbenzothiazoline-6-sulfonic acid) diammonium salt (ABTS), potassium persulfate ($K_2S_2O_8$), 4-oxo-2,2,6,6-tetramethylpiperidine *N*-oxyl (Tempone) and 4-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxyl (Tempol) were obtained from Sigma–Aldrich and used as supplied. The sterically hindered amine 4-oxo-2,2,6,6-tetramethylpiperidine (TMPO) from Merck-Schuchardt was applied. Deionized water or dried acetonitrile (ACN, SeccoSolv® Merck) was used for the preparation of solutions and suspensions. $K_2S_2O_8$ served as the oxidant in the oxidation of ABTS to the corresponding radical cation ($ABTS^{\cdot+}$) according to the previously reported procedure [37]. The precise concentration of $ABTS^{\cdot+}$ was determined by UV–Vis spectroscopy ($\varepsilon_{735nm} = 1.5 \times 10^4$ M^{-1} cm^{-1}) [37] using a UV–vis–NIR spectrophotometer Shimadzu UV3600.

2.2. Synthesis of undoped and Mg^{2+}-doped anatase nanocrystals

Titania nanoplates and Mg^{2+}-doped anatase nanocrystals with exposed {0 0 1} facets were synthesized by the solvothermal method described previously [36]. Titanium isopropoxide was dissolved in absolute ethanol at room temperature under intensive stirring, with addition of HF as capping agent to achieve the dominant formation of {0 0 1} facets. The solutions were autoclaved in a Teflon-lined apparatus at 180 °C for 24 h and synthesized powder products were separated by centrifugation [30,36]. To obtain Mg^{2+}-doped TiO_2 magnesium nitrate was added to the calculated amount of TiO_2 and samples with different dopant concentration