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Introduction of oxygen vacancies and fluorine into TiO_2 nanoparticles by co-milling with PTFE

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ABSTRACT

Solid-state processes of introducing oxygen vacancies and transference of fluorine to n-TiO_2 nanoparticles by co-milling with poly(tetrafluoroethylene) (PTFE) powder were examined by diffuse reflectance spectroscopy (DRS) of UV, visual, near- and mid-IR regions, thermal analyses (TG-DTA), energy-dispersive X-ray spectroscopy (EDXS), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM) and X-ray diffraction (XRD). The broad absorption peak at around 8800 cm^{-1} (1140 nm) was attributed to the change in the electronic states, viz. electrons trapped at the oxygen vacancies (Vo) and d–d transitions of titanium ions. Incorporation of fluorine into n-TiO_2 was concentrated at the near surface region and amounted to ca. 40 at% of the total fluorine in PTFE, after co-milling for 3 h, as confirmed by the F1s XPS spectrum. The overall atomic ratio, F/Ti, determined by EDXS was 0.294. By combining these analytical results, a mechanism of the present solid state processes at the boundary between PTFE and n-TiO_2 was proposed. The entire process is triggered by the partial oxidative decomposition of PTFE. This is accompanied by the abstraction of oxygen atoms from the n-TiO_2 lattices. Loss of the oxygen atoms results in the formation of the diverse states of locally distorted coordination units of titania, i.e. $TiO_{6-n}Vo_n$, located at the near surface region. This leads subsequent partial ligand exchange between F and O, to incorporate fluorine preferentially to the near surface region of n-TiO_2 particles, where local non-crystalline states predominate.

1. Introduction

Anion substitution in TiO_2 has been extensively studied, mainly in the interests of visible light responsive photocatalysts [1–7]. One of the possible routes for anion substitution is milling titania with some organic crystalline species (OCs) as anion sources [8–15]. In contrast to the synthetic processes in a vapor or liquid phase, co-milling oxide nanoparticles with OCs is a solvent free solid state process and carried out at room temperature without requiring sealing or atmospheric control of the reaction systems.

As we reported elsewhere [16], incorporation of anions by co-milling is regarded as a solid state ligand exchange. We have also studied associated mechanisms for the favorable chemical interaction between some drugs and inorganic excipients [17–21]. Those mechanochemical processes include a two-electron transfer route like an acid–base reaction, and a one-electron mechanism under the concept of radical recombination. Usually, they occur simultaneously [21,22]. Such a forced ligand exchange is significantly enhanced when the ligand field symmetry is imbalanced [23,24].

Co-milling an inorganic mixture, comprising acidic oxides like SiO_2 or TiO_2 with basic hydroxides like $Mg(OH)_2$ or $Ca(OH)_2$, gives rise to the precursors of the complex oxides [25–29]. These series of solid state processes could be rather straightforwardly explained by neutralization at the interface of dissimilar solids, liberating a water molecule and leaving a hetero bridging bond [27–29].

In the present study, we examine the solid-state processes at the interfacial region between nano-particulate n-TiO_2 and poly(tetrafluoroethylene) (PTFE) under mechanical stressing. Fluorine was chosen for two reasons, i.e. (i) due to the close proximity of the ionic radii of F^- (e.g. the effective value of the Shannon diameter, 133 pm [30]) to that of O^{2-} (140 pm), and (ii) its potential to functionalize titania toward photosensitivity [31,32], although any applicational studies are out of the scope of the present report. PTFE was chosen

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as an OC of fluorine source because of its availability of stable fine particulates. Emphasis is laid on the mechanisms of the solid state processes at the boundary between PTFE and *n*-TiO_2.

2. Experimental methods

2.1. Sample preparation

As starting materials, anatase nanoparticles (Toho Titanium, TA50, average particle size 20 nm) and finely divided PTFE (Sigma-Aldrich, <1 μm) were used as-received. Mechanical stressing was performed by using a planetary mill (Fritsch, Pulverisette 7) with a 45 mL vial and 15 balls of 10 mm in diameter made from yttrium stabilized zirconia (YSZ). A mixture comprising 3 g TA50 and 0.3 g or 0.6 g PTFE was subjected to milling at 720 rpm for up to 3 h. The milling operation was carried out in a tightly sealed vial without evacuating or controlling the background gas. Annealing was carried out in air up to 300 °C for 1 h.

2.2. Characterization

The diffuse reflectance spectra (DRS) of milled powders were measured in most cases in the wavelength range between 300 nm and 800 nm using a UV–vis–NIR spectrometer (Perkin Elmer, Lambda 900) equipped with a Praying Mantis accessory (Harrick). In some cases, the range was extended to the near infrared region, i.e. to 3000 nm. Diffuse reflectance spectra were also observed with a high performance FTIR spectrometer (Brucker, Equinox 55) to further examine the chemical changes of the ingredients of the co-milling.

Thermal analysis (TG-DTA) was performed by Netzsch STA409, using a heating rate of 10 K/min in air. Elemental analysis was performed by energy dispersive X-ray spectroscopy (EDXS), using an EDAX Genesis 4000 attached to a scanning electron microscope (JEOL, JSM-6400). High-resolution transmission microscopy (HRTEM) was made at 200 kV using a field-emission instrument with small spherical aberration's constant $Cs=0.5$ mm (JEOL, JEM-2100F – UHR). EDXS was calibrated by comparison with well crystallized TiO_2 microparticles (Alfa Aesar, 99.99%). Changes in the crystallographical properties were monitored by conventional X-ray diffractometry (Philips PW1820).

Anion incorporation was further examined by X-ray photoelectron spectroscopy (XPS). XPS data were collected with an Axis Ultra instrument (Kratos Analytical, Manchester, UK) under ultrahigh vacuum condition ($<10^{-8}$ Torr) and using a monochromatic Al $K\alpha$ X-ray source (1486.6 eV) in the Surface Analysis Facility of the Interdisciplinary Centre for Electron Microscopy at EPFL. The emitted photoelectrons were sampled from a 700×350 μm^2 area with a 90° photoelectron take-off angle. The adventitious carbon 1*s* peak was calibrated at 285 eV and used as an internal standard to compensate for any charging effects. Both curve fitting of the spectra and quantification were performed with the CasaXPS software, using relative sensitivity factors given by Kratos.

3. Results and discussion

3.1. Changes in the electronic spectra by co-milling

After milling a mixture comprising the white powders of titania and PTFE, its color turned rapidly into dark gray and then black with increasing milling time. Associated unique diffuse reflectance spectra are shown in Fig. 1. We recognize that the shift of the absorption edge occurs at the early stage of milling, while the prolonged milling brings about a significant increase in the absorption intensity at lower energies in the visible and the near infrared (NIR) region. As the content of PTFE was increased from 10% to 20% of TiO_2, the absorption effect in the visible region was reduced. This is one of the typical mechanochemical phenomena, explained by the cushioning effect, i.e. the mechanical stress is reduced due to the increasing fraction of the soft ingredient, PTFE.

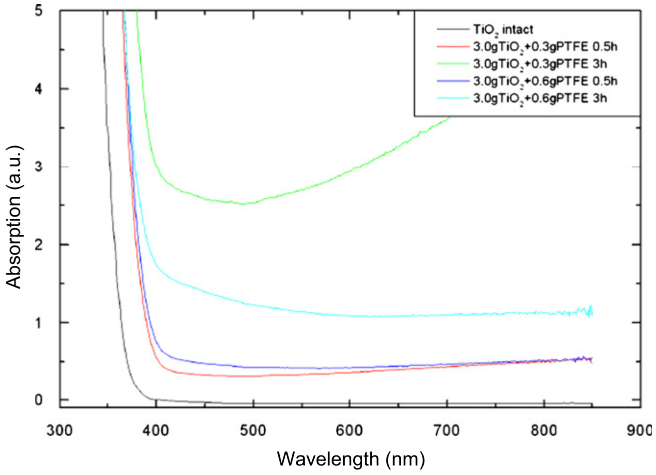

Fig. 1. UV–vis diffuse reflectance spectra of co-milled samples.

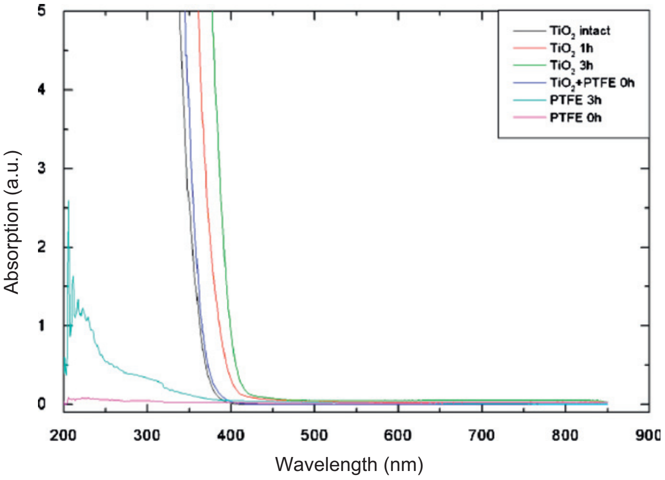

Fig. 2. UV–vis diffuse reflectance spectra of separately milled samples.

When titania or PTFE is milled separately, no spectral changes were observed, except for a slight shift of the absorption edge, in the case of titania, and a slight absorption in the UV range for PTFE, as shown in Fig. 2, although both samples appeared white to bare-eye inspection. Therefore, the absorption in the visible–NIR region, shown in Fig. 1, must be a consequence of the chemical interaction between titania and PTFE induced by the co-milling.

3.2. Introduction of oxygen vacancies

In the diffuse reflectance spectrum extended to the NIR region, a broad absorbance band peaked at around 8800 cm^{-1} (approx. 1140 nm, or 1.09 eV) was observed, as shown in Fig. 3. In view of the broadness of the observed electronic absorption band, there may be several ways of deconvolution, other than the one shown in Fig. 3. It is nonetheless recognized that there are components attributed to oxygen vacancies associated with F-type color centers [33], designated as peaks 1 and 2 at around 8000 cm^{-1}