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Nanosized titania modified with tungsten and silver: Microstructural characterisation of a multifunctional material

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ABSTRACT

With the ever-growing interest in nanotechnologies, the area of metal oxides is playing an increasingly dominant role. Amongst them, titanium dioxide (TiO_2) nanoparticles are attracting increasing interest, owing to their unique physicochemical properties, and widespread applications – *i.e.* photocatalysis, energy materials, antibacterial agents, gas-sensors.

We characterised the microstructure of titania nanopowders – synthesised *via* an aqueous sol–gel method and modified with silver and/or tungsten – using XRD data, through the whole powder pattern modelling (WPPM) procedure. An overall linear dependence of the lattice volume expansion was observed – the volume increased with the lowering of the crystalline domain size. Concerning the dislocation density, no specific trend depending on the modifying cation was reported. However, for the samples fired at 600 °C, the undoped titania sample had a much larger number of screw dislocations in the rutile phase, while the Ag-modified sample had a much greater number of edge dislocations in the anatase phase.

1. Introduction

The development of nanotechnologies is currently one of the most interesting topics in the field of sciences. Due to their unique physicochemical, surface, magnetic and catalytic properties, nanoparticles (NPs) provide solutions to problems that cannot be dealt with using conventional technologies. Applications are manifold, and metal oxides continue to play a dominant role [1]. Amongst metal oxides, titanium dioxide (TiO_2) deserves a special mention: it arose as the most popular semiconductor material for photocatalytic applications, after the discovery of the "Honda–Fujishima effect" [2]. Nowadays, nano-dimensioned titania is attracting increasing interest owing to its unique physicochemical properties and widespread applications, that include, asides from photocatalysis, solar energy conversion/water splitting, sensors, photochromic devices, antibacterial surfaces and, more recently, electrode material in lithium ion batteries [3–11]. Its performances – for a given application – depend on the crystalline structure, morphology, and size of the material [12].

Being a wide band gap (E_g) semiconductor (E_g of anatase is 3.2 eV, that of rutile is 3.0 eV), TiO_2 requires UV-light to be activated as a photocatalyst. A recently suggested solution for the energy-harvesting of visible-light is the deposition of noble metal NPs onto the surface of a semiconductor, so as to form a metal-semiconductor composite photocatalyst [13]. This works because noble metals, owing to their surface plasmon resonance (SPR) [14–16], are able to strongly absorb visible-light. Moreover, the photogenerated electrons and holes can be efficiently separated by the metal-semiconductor interface, thus enhancing the photocatalytic property [17].

In the present work, a series of TiO_2, 1 mol.% W-doped, 1 mol.% Ag-doped and 1 mol.% W/Ag-co-doped (the ratio between W and Ag was 1:1) TiO_2 nanopowders were synthesised *via* an aqueous sol–gel route [18]. Such materials showed themselves to be excellent photocatalysts (under both UV and visible-light irradiation), antibacterial agents, and also to possess tuneable photochromic and SPR properties [18–20]. Structural and quantitative phase analysis of these samples is reported previously [19]. Here, the aim was to obtain a quantitative description of the nanopowders' microstructure, using diffraction data analysed by whole powder pattern modelling (WPPM), considered to be a state-of-the-art methodology [21–26].

2. Experimental

2.1. Sample preparation

As we reported previously [18,19], aqueous titanium(IV)hydroxide sols were made from the acid-catalysed peptisation of hydrolysed titanium(IV)isopropoxide (Ti-*i*-pr,

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$Ti(OCH(CH_3)_2)_4$). The dried gels were thermally treated at 450 and 600 °C in a static air flow furnace – heating rate from room temperature (RT) to the desired temperature at 5 °C min^{-1}, followed by 2 h soaking time, with natural cooling. Undoped titania samples were referred to as Ti450, and Ti600, where the number represents the maximum temperature attained. Modified gels were indicated by adding the W- or Ag-chemical symbols; with W/Ag-standing for co-doped.

2.2. Sample characterisation

XRPD data for the microstructural refinements were collected with a $\theta/2\theta$ Panalytical X'Pert Pro diffractometer (NL), with graphite monochromated Cu Kα radiation, equipped with a fast RTMS detector (20–115° 2θ range, with a virtual step scan of 0.02° 2θ, and virtual 1500 s per step). Divergence and anti-scattering slits of 1/2° and 1/4°, respectively, were mounted in the incident beam pathway. The pathway of the diffracted beam included a Ni filter, and a soller slit (0.01 rad). The WPPM method [21,22,26], through the PM2K software [27] (which allows for refinement of model parameters *via* a non-linear least squares routine), was employed for a microstructural analysis of the powders. The WPPM method is a reciprocal space based technique of diffraction pattern analysis. Essentially, WPPM models the diffraction pattern by combining the different effects that microstructural features – crystalline domain size and strain – have on the diffraction pattern line profiles. Hence, with such method, a pattern is produced directly from physical models describing the microstructure of the examined material, then the model parameters are fitted to the measured data.

The instrumental contribution, described by a pseudo-Voigt function, was obtained by fitting a large set of peak profiles from the NIST SRM 660b standard (LaB_6), according to the Caglioti et al. relationship [28]. Anatase (space group (SG) $I4_1/amd$), rutile (SG $P4_2/mnm$) and, when present, brookite (SG *Pbca*), were included in the WPPM modelling. Afterwards, these parameters were refined: background – modelled using a 4th-order Chebyshev polynomial function – peak intensities, specimen displacement, and lattice parameters. Crystalline domains were assumed to be spherical, and distributed according to a lognormal size distribution; dislocations were presumed to be the main defect in the powders, and hence the only source of anisotropy in the line profile broadening. Both edge and screw dislocations (with density of ρ_e, and ρ_s, respectively), were assumed to be present in the $\langle 1\,0\,\bar{1}\rangle\{1\,0\,1\}$ slip system [29], with Burgers vector equal to $(a_0^2 + c_0^2)^{1/2}$, where a_0 and c_0 are the lattice parameters.

TEM (Hitachi H9000, JP) and HR-TEM – JEOL 2200FS (JP) microscope equipped with a field emission gun, operated at 200 kV – analyses were also performed. Samples were prepared by dispersing the nanoparticles in isopropanol, and evaporating a drop on carbon-coated copper grids.

3. Results and discussion

3.1. Microstructural analysis

The WPPM results are depicted in Figs. 1–3, and in Tables 1 and 2. Samples fired at 450 °C are composed of anatase, rutile, brookite and amorphous phase, in different amounts; at 600 °C, the TiO_2 polymorphs present are anatase and rutile, together with amorphous phase (Table 3 and [19]).

The unit cell parameters of anatase and rutile are virtually identical for the whole set of samples, at both firing temperatures (Table 1). The exception to this was anatase (and to a much lesser extent, brookite) in Ag-Ti450 – their unit cell volumes are slightly expanded. It has been reported by Armelao et al. [30] that at low

Table 1
Agreement factors and unit cell parameters of anatase, rutile and brookite, calculated *via* the WPPM modelling.

Sample	Agreement factors			Unit cell parameters								
				Anatase			Rutile			Brookite		
	R_{wp} (%)	R_{exp} (%)	χ^2	$a = b$ (nm)	c (nm)	Volume (nm^3)	$a = b$ (nm)	c (nm)	Volume (nm^3)	a (nm)	b (nm)	c (nm)	Volume (nm^3)
Ti450	7.90	5.99	1.32	0.3785(1)	0.9503(5)	0.136(1)	0.4594(1)	0.2959(1)	0.062(1)	0.5190(9)	0.9144(7)	0.5445(3)	0.258(1)
W-Ti450	6.58	5.43	1.21	0.3788(1)	0.9502(12)	0.136(1)	0.4598(1)	0.2959(1)	0.063(1)	0.5219(2)	0.9085(4)	0.5430(4)	0.257(1)
W/Ag-Ti450	6.86	5.58	1.23	0.3793(2)	0.9496(7)	0.137(1)	0.4599(1)	0.2959(1)	0.063(1)	0.5205(10)	0.9477(14)	0.5317(11)	0.262(2)
Ag-Ti450	13.06	11.67	1.12	0.3843(10)	0.9534(18)	0.141(1)	0.4598(1)	0.2960(1)	0.063(1)	0.5342(9)	0.9117(13)	0.5440(5)	0.265(1)
Ti600	9.55	7.78	1.23	0.3775(1)	0.9485(7)	0.135(1)	0.4585(1)	0.2954(1)	0.062(1)				–
W-Ti600	7.94	5.82	1.36	0.3779(1)	0.9494(1)	0.136(1)	0.4588(1)	0.2954(1)	0.062(1)				–
W/Ag-Ti600	9.54	8.16	1.17	0.3779(1)	0.9481(8)	0.135(1)	0.4587(1)	0.2954(1)	0.062(1)				–
Ag-Ti600	8.22	6.19	1.33	0.3777(1)	0.9494(3)	0.135(1)	0.4586(1)	0.2955(1)	0.062(1)				–