Journal of Colloid and Interface Science 460 (2015) 29–35

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

Anatase/rutile bi-phasic titanium dioxide nanoparticles for photocatalytic applications enhanced by nitrogen doping and platinum nano-islands

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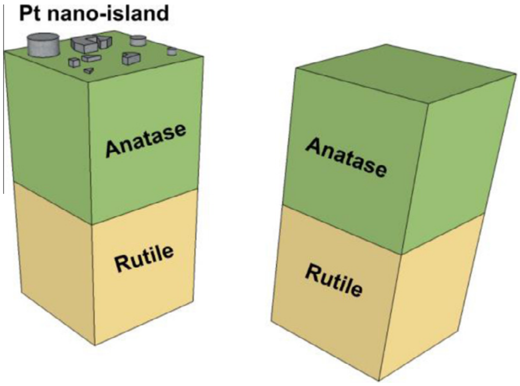
GRAPHICAL ABSTRACT

Bi phasic nanoparticles of TiO_2 containing anatase rutile and doped/enhanced variants thereof.



ARTICLE INFO

Article history:
Received 30 June 2015
Revised 11 August 2015
Accepted 13 August 2015
Available online 19 August 2015

Keywords:
Titania
Photocatalysis
Bi-phasic
Nanoparticle
Water purification

ABSTRACT

Titanium dioxide (TiO_2) bi-phasic powders with individual particles containing an anatase and rutile hetero-junction have been prepared using a sequential layer sol–gel deposition technique to soluble substrates. Sequential thin films of rutile and subsequently anatase TiO_2 were deposited onto sodium chloride substrates yielding extremely fragile composite layered discs that fractured into "Janus-like" like powders on substrate dissolution. Nitrogen doped and platinum sputtered analogues were also prepared, and analysed for photocatalytic potential using the photodegradation of Rhodamine B, a model organic pollutant under UV and visible light irradiation. The materials were characterised using X-ray diffraction, X-ray photoelectron spectroscopy, energy dispersive X-ray spectroscopy, Raman spectroscopy and scanning electron microscopy. This paper sheds light on the relationship between anatase and rutile materials when in direct contact and demonstrates a robust method for the synthesis of bi-phasic nanoparticles, ostensibly of any two materials, for photocatalytic reactions or otherwise.

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http://dx.doi.org/10.1016/j.jcis.2015.08.027

1. Introduction

Photocatalytic reactions remain at the pinnacle of man's attempts to harness the energy of the sun. We can use such reactions to create clean safe drinking water [1–4], reduce the rate of hospital acquired infections [5–9] and potentially meet our energy needs by harvesting solar energy directly into hydrogen gas in the case of solar water splitting [10–13]. TiO_2 is by far the most studied photocatalyst with much interest aimed at shifting the electronic properties to create visible light photocatalysts from the UV light photocatalysts that are common in pure TiO_2 [14,15]. It is cheap, stable and a highly effective photocatalyst in the UV part of the spectrum, with applications ranging from paint and toothpaste to photo-voltaic cells [16–18].

In their seminal 1972 work, Fujishima and Honda demonstrated TiO_2 had the potential to split water on UV photo-irradiation [19] and since then, research into titania and other semiconducting materials for water-splitting has increased exponentially [20]. For the last four decades, development of earth-abundant TiO_2 has centered on anatase [21–24], rutile [25–27] and indeed mixed phase powders and films [28–32], however elucidating precise mechanisms of photocatalytic processes in titania systems have proven elusive and somewhat controversial [28,32–34]. The lifetime of the excited species however is a major factor in the activity of the photocatalysts [10,21,25] so the stabilisation of excited species within ether a rutile or anatase phase does have a beneficial effect on the photoactivity. The small difference in band gap, (anatase, 3.2 eV versus 3.0 eV for rutile) and their relative positions, suggest that manipulation of rutile in an anatase/rutile heterojunctioned system would be more facile to achieve visible light activation [28,33]. However, rutile suffers from fast exciton recombination effects so the excited state is shorter lived and therefore is a less effective photocatalyst compared to anatase [25]. A detailed mechanistic study by Scanlon et al. (centered on such bi-phasic nanoparticles) resulted in a paradigm shift in the understanding of the semiconductor photo-physics that occurs when both anatase and rutile are in intimate contact [28]. XPS studies on particles that contain equal and differing amounts of anatase and rutile have shown how the band alignments occur such that anatase is able to accept the electrons from rutile both at the top and bottom of the band gap such that holes migrate to the rutile and electrons migrate to the anatase. This was subsequently supported by photocatalytic tests [33]. In anatase–rutile systems a fundamental stabilisation effect exists whereby the anatase stabilises the rutile photoexcited states by removing the electron while the rutile stabilises the anatase by removing the holes. This synergy between the phases results in enhanced photocatalytic activity [28].

Creating intimate contact between 2 or more semiconducting materials comes with a plethora of difficulties. The interface between 2 different materials of 2 different crystal structures often sees the formation of defects which tend to encourage exciton recombination; a problem in core shell structures in core/shell semiconductor quantum dots [35–38]. "Crystal templating" can also occur, when depositing one layer on top of another, with the second phase adopting the morphology of the first, with annealing temperatures required for different phases adversely affecting the phases in the resultant composite material [33,39–41]. Exciton recombination can also readily occur over the small distances experienced in sub-10 nm sized "Janus-like" nanoparticles, so ideal materials, whether they be films or particles, should have a grain size greater than 100 nm.

In this paper, we demonstrate the synthesis of "Janus-like" nanoparticles by sequentially depositing rutile and then anatase titania *via* sol–gel dip coating with intermediate annealing steps at 700 °C and 500 °C to form different crystalline layers on a sodium chloride substrate. Post-deposition, the substrate was dissolved away using deionised water, leading to the formation of rutile/anatase Janus-like particles. Some samples were sputtered with platinum, leading to expected enhanced performance [42,43] in the photo-induced degradation (under UV and visible light) of Rhodamine B dye. Rhodamine is a model aromatic pollutant, whose proposed mechanistic photocatalytic degradation proceeds *via* a deethylation followed by isomerisation into aromatic dicarboxyl species followed by ring opening to linear carboxylate species. Detailed mechanistic descriptions can be found elsewhere [44,45]. Nitrogen doping was also introduced to some samples thus increasing the visible absorption profile [46] of the anatase titania through the addition of tetramethlethylenediamine (TMEDA) into the titanium(IV) butoxide sol [47].

2. Experimental section

2.1. Materials

Rhodamine B (determined by HPLC, ⩾95%), sodium chloride (ReagentPlus®, ⩽95%), N,N,N′,N′-tetramethlethylenediamine (ReagentPlus®, 99%), titanium(IV) butoxide (reagent grade, 97%) and titanium(IV) oxide, anatase powder, −325 mesh, ⩾99% trace metals basis were purchased from Sigma Aldrich Ltd. Acetylacetone (AnalaR), acetonitrile (AnalaR), 1-butanol (98.5%), 2-propanol (tech. grade) and sodium fluoride (99%) were purchased from VWR Ltd. All other solvents used were of the highest possible grade and purchased from Sigma–Aldrich Ltd. UHQ Deionised water with a resistivity of not less than 18.2 $M\Omega\,cm^{-1}$ (Millipore) was used for aqueous solutions and substrate dissolution. All other solvents used were of the highest possible grade and purchased from Sigma–Aldrich Ltd. UHQ Deionised water with a resistivity of not less than 18.2 $M\Omega\,cm^{-1}$ (Millipore) was used for aqueous solutions and substrate dissolution.

2.2. Methods

Rutile/anatase bi-phasic Janus-like nanoparticles were prepared by dip-coating a soluble substrate in a titanium(IV) butoxide sol–gel, with subsequent intermediate annealing steps at 700 and 500 °C to form the rutile and anatase. If required, the top anatase layer was sputtered using a platinum target. The substrate was then dissolved away with deionised water, forming the nanoparticles. The particles were then evaluated for photocatalytic activity through the degradation of a model organic pollutant, Rhodamine B. This versatile, stepwise synthesis allows for the synthesis of complex layered nanoparticles for advanced functionality, Fig. 1.

Substrate preparation: Soluble substrates were prepared by subjecting finely ground sodium chloride (8 g, solubility 360.9 g/L of water at 303 K, melting point 801 °C) to 10 tons of pressure in a 32 mm dye press (Retch PP-55) for 10 min, creating homogeneous smooth surfaced pellets.

Titanium sol–gel synthesis: Multi-phasic nanoparticles were synthesised using a sol–gel method, based on the protocol by Powell et al. [47] Briefly, titanium(IV) butoxide (50 mmol, 17.0 mL) was added to a mixture of acetylacetone (25 mmol, 2.57 mL) and 1-butanol (50 mmol, 4.58 mL) under vigorous stirring, giving a transparent yellow sol. After 1 h, a mixture of 2-propanol (150 mmol, 11.5 mL) and deionised water (3.64 mL) was added before further stirring (*ca.* 1 h). Acetonitrile (40 mmol, 2.09 mL) was then added and the whole system sealed and allowed to age overnight (*ca.* 10 h) before dip-coating. Sols were stable up to 6 months if stored in an air-tight container.