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Photocatalytic hydrogen generation from water–methanol mixtures using "black" anatase obtained by annealing of titanate nanotubes

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ABSTRACT

Digestion for an extended period of a commercial nanoparticulated TiO_2 sample under strong basic conditions (10 M NaOH) leads to the formation of titanate nanotubes with long aspect ratio. The most remarkable observation was the appearance of light-brown colour in the titanate sample that is reflected in the presence for this titanate nanotube sample of a continuous absorption in the visible region decreasing in intensity towards the red. Titanate nanotubes were annealed under hydrogen atmosphere at 350 and 500 °C. The last temperature leads to the reconstitution of anatase phase and an increase in the intensity of the black colour. The photocatalytic activity of the set of titanium samples was tested for hydrogen generation from water–methanol mixtures under monochromatic visible light (532 nm) or UV light (355 nm) or under simulated sunlight. It was determined that the most active sample in all conditions was the one that after NaOH digestion was submitted to hydrogen annealing at 500 °C. This sample exhibits even higher activity than that observed for "black" titania prepared as previously reported by direct treatment of nanoparticulated TiO_2 with H_2 without NaOH digestion.

1. Introduction

In the context of photocatalytic hydrogen generation from water–methanol mixtures there is a continuous interest in the development of more efficient photocatalysts [1–8] TiO_2-based materials have been the most widely used photocatalysts for this reaction [1–3,7,8]. It had been found that certain parameters including the crystal phase [9–11], the presence of dopant elements [12–17], the morphology [18,19] and structure [19] of the material exert a strong influence of the resulting photocatalytic activity. Related to our work are several reports in where titanium dioxide had been submitted to annealing under hydrogen atmosphere to obtain "black" TiO_2 nanoparticles [20]. It was found that *black* titania nanoparticles (loaded with 0.6 wt% Pt) exhibit enhanced photocatalytic activity for hydrogen generation from water [20]. It has been proposed that the *black* TiO_2 sample exhibits an enhanced photocatalytic activity due to the increased light absorption in the visible region. Characterisation of *black* titania suggests that thermal treatment with hydrogen produces the appearance of a black solid due to the partial amorphization of the outermost layers of the TiO_2 nanoparticle [20]. Formation of "black" TiO_2 nanotubes displaying visible-light ($\lambda > 450$ nm) photocatalytic activity for the oxidation of acetaldehyde has also been reported [21]. In this precedent, it was found that the black colour of titania nanotubes arises from chromium contamination from the stain steel reactor in which the thermal annealing was performed [21]. Titania nanotubes annealed at various temperatures and exhibiting visible light absorption have also been used as photocatalyst for the degradation of dyes [22].

Continuing with this research aimed at developing more efficient titania photocatalysts by submitting TiO_2 to hydrogen annealing, in the present manuscript we report that titania nanoparticles formed by thermal treatment of titania nanotubes under hydrogen exhibits an enhanced photocatalytic activity for hydrogen generation from water–methanol mixture that is even higher than the activity of an analogous sample of "black" titania obtained from the direct treatment of TiO_2 nanoparticles by hydrogen.

2. Materials and methods

2.1. Sample preparation

Five titanium samples (M0–M4) were used in the present study (see Scheme 1) the TiO_2 precursor (M0) used for nanotube production was a commercial TiO_2 powder (Aldrich, Anatase) consisting

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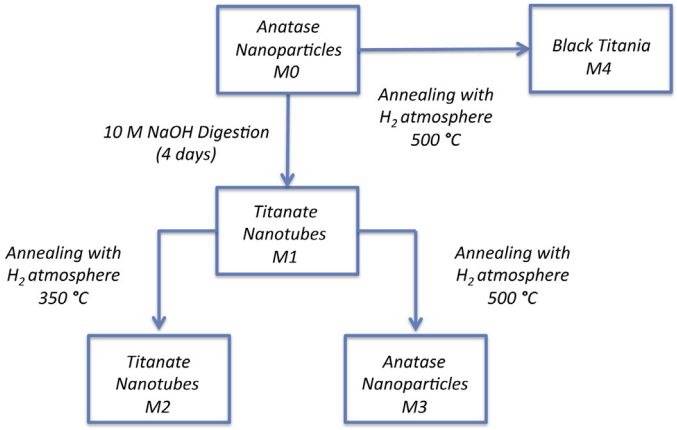

Scheme 1. Preparation procedure of the samples under study.

of pure anatase phase. 3.6 g of TiO_2 powder (precursor M0) was treated with 90 mL of aqueous 10 M NaOH solution in a Teflon-lined autoclave (total volume 200 mL) at 125 °C for 4 days. After treatment the solid was collected by filtration and washed by suspending the solid with 2 L HCl solution (pH 1.5) and finally washed with water until neutral pH. Sample M1 was obtained after drying at 120 °C for 2 days. The final annealing process give rise to two samples denoted as M2 and M3 that were obtained placing 150 mg of M1 in a tubular quartz reactor using a H_2 flow of 100 mL/min during 5 h at 350 °C (sample M2) or 500 °C (sample M3). An additional sample denoted as M4 was obtained by heating the commercial sample M0 in a quartz reactor at 500 °C under a H_2 flow (100 mL/min) for 1 h time as it was reported in the literature by Naldoni et al. [23].

Note that no platinum nanoparticles were deposited on any of the photocatalysts.

2.2. Photocatalytic tests for hydrogen production

A suspension of the catalyst (25 mL, 1 g L^{-1}) was sonicated for 10 min and placed in a closed reactor with an irradiation window of 12.56 cm^2 provided with temperature and pressure controllers. The reactor was placed in a thermostatic bath with a set point temperature of 25 °C. The suspension was purged with an argon flow of 2 psi for 15 min prior to irradiation. The photoreactions were performed by using the third (355 nm) or the second (532 nm) harmonic of a Nd:YAG laser (Lumonics, 50 mJ $pulse^{-1}$, 1 Hz) and a solar simulator (Thermo Oriel 1000 W) with an irradiation spot of 100 cm^2. The light of the solar simulator was filtered through an Air Mass 1.5 filter and contains approximately 5% of UV irradiation at 10 cm distance. This set of irradiations with monochromatic laser or polychromatic (simulated sunlight) provides information about the photoresponse of the photocatalyst in each spectral region. The amount of hydrogen collected in the head space of the reactor was analysed by injecting 100 μL in a gas chromatograph using a MOLSieve column, argon as carrier gas and a TC detector.

3. Results and discussion

The titania samples under study were prepared starting from titanate nanotube (M1) that was in turn obtained from TiO_2 (M0, 20 nm) digestion under strong basic condition following reported

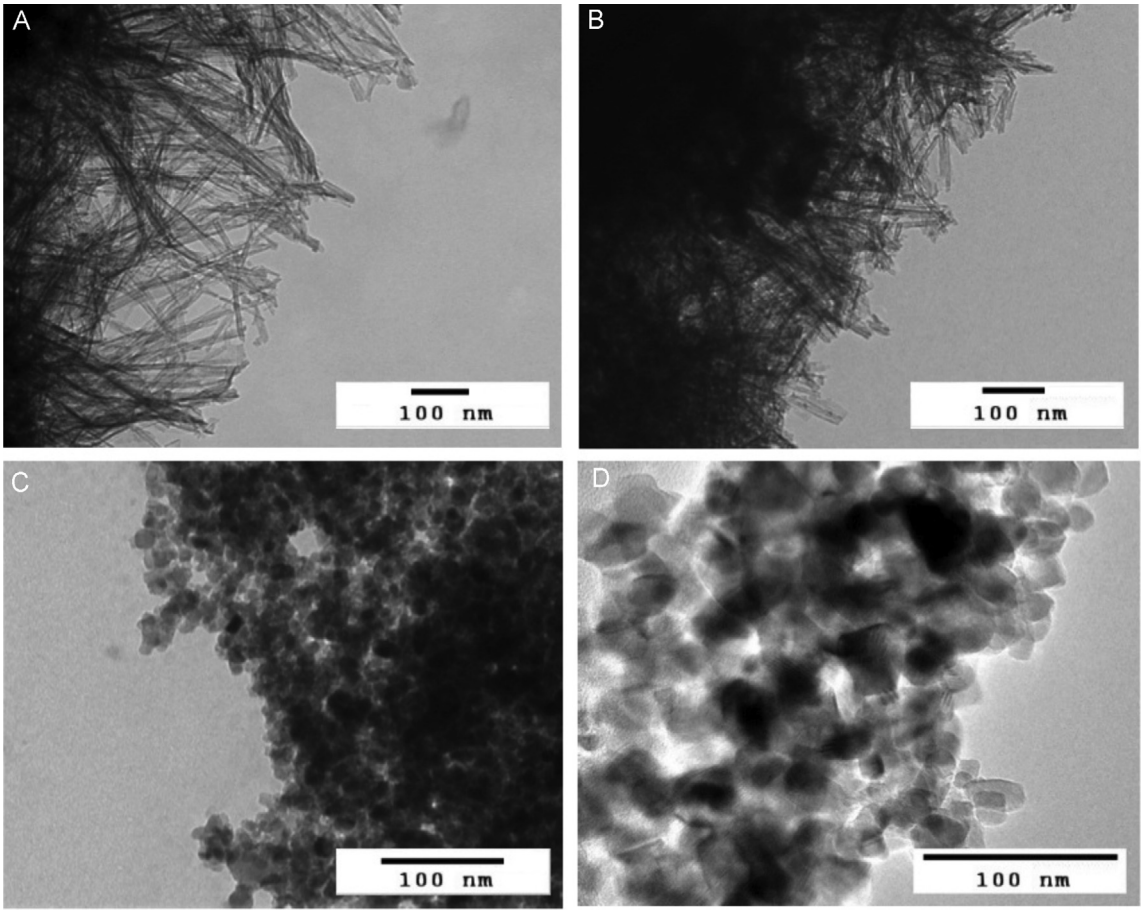

Fig. 1. TEM images recorded for M1 (A), M2 (B), M4 (C) and STEM micrograph of M3 (D).