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Highly photoactive Brookite and Anatase with enhanced photocatalytic activity for the degradation of indigo carmine application

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ABSTRACT

TiO_2 Brookite, and Anatase powders were prepared by a facile and low temperature solution based method. XRD diffractometry was performed to confirm their phase composition and crystallinity. Morphology was further confirmed by TEM. N_2 adsorption was used to determine surface area and pore size distribution. The difference in capacitive properties of both materials and the determination of the flat band position was obtained by Mott-Schottky analysis. Diffuse reflectance and Tauc plots allowed to obtain the band gap value. The degradation of Indigo Carmine dye with both catalysts in a photo-electrochemical microreactor was assessed by UV–vis, and Raman spectroscopy. Both materials were more active than the benchmark commercial Degussa P25 sample in the order P25 < Anatase < Brookite and explained in terms of energy band positions.

1. Introduction

Titanium dioxide (TiO_2) is a sophisticated material of interest for multiple ranges of applications due to its intrinsic semiconducting properties, high resistance to corrosion, low toxicity and low cost. It has been used in a wide spectrum of applications like cosmetics, coatings, sensors, dye-sensitized solar cells (DSSC), photocatalysis and batteries [1]. The commonly natural polymorphs of TiO_2 found are rutile ($P4_2/mnm$), Anatase ($I4_1/amd$) and Brookite (Pbca) [2]. These different crystal structures directly affect the electronic and surface properties of each of the polymorphs. The principal investigated polymorphs of TiO_2 are Rutile and Anatase while less explored are the properties of Brookite, and this is mainly due to the difficulty to obtain Brookite in pure form as reflected in the number of studies on this material that are not as abundant as other crystalline phases [3]. This condition has produced many reports centered in the preparation procedure to propose a formation mechanism [4–11].

At laboratory conditions, Brookite has been synthesized by various approaches, such as hydrothermal [12,13], aqueous precipitation/sol-gel [14–17], and template-assisted [18] methods. A widely used chemical technique for the preparation of Brookite powders is the hydrothermal method but it faces an inherent lack of crystalline phase selectivity [4]. Often mixtures of phases are found during syntheses processes if parameters are not carefully maintained and in the vast majority of data, the literature reports traces of the other two phases. Indeed, the factors that determine the specific formation of Brookite phase are hard to predict (precursor, pH, reagent ratios, temperature or pressure) and thus, the information obtained from one particular methodology is not easily transferable to other approaches. Therefore, it is clear that one of the most difficult challenges is to achieve pure crystalline Brookite.

Another greatly desirable characteristic in TiO_2 is to attain a high surface area which is demanded from most of the current nanotechnological applications. For instance, in DSSC and batteries the porosity and the surface area are linked directly to the electrochemical kinetics and electron diffusion pathways that greatly determine the performance of the final devices [19]. The gain of control in the morphology and surface area of the nanostructures allows the tunability of the electronic and structural properties of these materials and such a reason has attracted many efforts [12,19–23].

As previously mentioned, a major issue to study systematically the photocatalytic properties of the single crystalline phase are related to the phase purity. The understanding of the energetics

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of TiO_2 materials is of great importance, and therefore the determination of the band gap and flat band values. However, many experimental approaches found in the literature occur in great disagreement either in optical or electronic values for Brookite since their results are obtained from Brookite samples not entirely crystalline. On the other hand, several computational studies based in density functional theory (DFT) have been done for Anatase and Rutile, while for Brookite are not as often. The new approaches for this crystalline phase bring interesting information that should be considered by work-groups to confirm with their experimental values [24].

The photocatalytic activity of Brookite has been, however, undertaken in several applications. DSSC cells have been prepared using pure Brookite and compared with Anatase demonstrating that the former is a promising material and that the performance of the cells greatly depends also on the morphology of the materials [25]. In hydrogen evolution, thin films of mixed-phase Anatase and Brookite were prepared and assessed under visible light irradiation [26] and nanorods were used in aqueous methanol solutions [21]. The modification of Brookite powders with Pt nanoparticles have been also used in the photocatalytic dehydrogenation of 2-propanol [27]. The photodegradation of organic molecules has been reported for chlorophenol [22] and acetaldehyde [28], rhodamine B [29–31], but, all these reports showed lower performances when compared with Anatase phase. However, when hollow-templated Brookite structures were assessed with the same rhodamine B, the degradation activity was enhanced and explained in terms of the increased exposed area [32]. This same explanation was given when the degradation of dichloroacetic acid was assessed using Brookite nanorods and were less active than Anatase, but more active than P25 when used in the degradation of phenol [33]. On the other hand, Brookite nanoflowers were evaluated in the degradation of methyl orange and exhibited higher activity than Anatase and Anatase/Brookite mixtures in spite of having a lower specific surface area [12,23]. Nevertheless, the influence of the crystalline planes determined markedly the photoactivity of Brookite nanorods as observed with the improved degradation of toluene after performing a chemical etching [13].

Although some studies have been done to explain the origin of an improved photoactivity of Brookite catalysts, the characterization approaches: physicochemical and electro-chemical, are seldom observed in the same report [3]. In this work, low temperature solution-based syntheses were used to produce Brookite and Anatase powders possessing similar surface area, which were used to produce photoelectrodes by spin-coating technique. The influence of the deposited mass was studied in the photoelectrochemical responses and used to understand the energetics for each material. Finally, a home-made photo-electrochemical microreactor was used to perform the degradation of potassium carmine indigo trisulfonate (InC) under UV–vis irradiation.

2. Experimental

2.1. Preparation of TiO_2 Anatase and Brookite materials

The synthesis process of TiO_2 Anatase consisted of thermolysis of titanium oxysulfate (Sigma Aldrich) in an aqueous solution, followed with a post-heat treatment [20]. Briefly, titanium oxysulfate was firstly dissolved in ultrapure water with a concentration of 0.9 M by slightly heating to 90 °C. The precipitation of TiO_2 is then obtained by heating the solution at 90 °C for 4 h. The powder is recovered by filtration, and washed with ultrapure water. TiO_2 Anatase was further obtained by post-heat treatment at 400 °C for 2 h under air atmosphere. Secondly, to prepare TiO_2 Brookite, the synthesis was performed with anionic species, i.e., lithium oxalate (Sigma Aldrich), followed by a post-heat treatment process [19]. Briefly, titanium and lithium salts were dissolved simultaneously in the ultrapure water by slightly heating to 90 °C. The molar ratio between titanium and the oxalate group was fixed at 1. Titanium oxalate hydrate, $Ti_2O_3(H_2O)_2(C_2O_4)\cdot H_2O$, was firstly obtained by the precipitation process at 90 °C for 4 h. The precipitated powder was recovered by filtration, and washed with a large amount of ultrapure water, and dried at 80 °C overnight. Thereafter, TiO_2 Brookite was obtained by thermal decomposition of $Ti_2O_3(H_2O)_2(C_2O_4)\cdot H_2O$ at 400 °C for 2 h under air atmosphere.

2.2. Electrode preparation

The photo-electrodes were prepared by spin-coating technique with a home-made device. The suspensions were prepared with a concentration of 15 mg/mL of each of TiO_2 material in ethanol. An addition rate of 60 μL/min with a rotating speed of 1800 rpm were used to drop-cast over a conducting glass substrate (SOLEMS, FTO 20 Ω). After spin-coating, a thermal annealing was performed at 400 °C (10 °C/min, 1 h) under air. Electrical contact to the FTO was done with silver conducting paint (RadioSpares, 186-3593) to a copper wire and isolated with epoxy resin (3 M, Scotch-weld DP-190).

2.3. Physicochemical characterization

XRD measurements of TiO_2 powders were carried out on an EMPYREAN PANALYTICAL. X-ray diffractometer using Cu-Kα radiation (λ = 0.15406 nm). The XRD spectra were obtained using high resolution with the step-scanning mode, a narrow receiving slit (1/16°), and a counting time of 240 s per 0.05°. Scans were recorded in the range of 20°–90°. The identification of the phases was made with reference to the Joint Committee on Powder Diffraction Standards International Center for Diffraction Data (JCPDS-ICDD) database.

The morphology of particles was examined by TEM on a JEOL JEM-2001 equipped with a LaB_6 filament. The samples were characterized under an accelerating voltage of 200 kV and a resolution of ca. 0.19 nm.

Nitrogen adsorption isotherms were recorded at 77 K on a Micromeritics ASAP 2020 device. The specific surface area and pore size distribution were calculated using the Brunauer–Emmett–Teller (BET) and Barrett–Joyner–Halenda (BJH) methods, respectively.

Diffuse reflectance was performed with a spectrophotometer (Cary 5000, VARIAN) from 200 to 800 nm with an interval of 1 nm. A $BaSO_4$ spectrum was used, in the spectral range, as blank.

2.4. Photo-electrochemical characterization

Electrochemical measurements were performed with a galvanostat/potentiostat (Biologic, SP300) in a cell provided with a quartz window facing the working electrode through which it was illuminated. A N_2-saturated 0.5 M H_2SO_4 was used as supporting electrolyte. A glassy carbon and RHE were used as counter and reference electrode, respectively. Cyclic voltammetry was performed to stabilize current density after 20 cycles (ν = 100 mV/s). Linear sweep voltammetry (LSV) were performed (ν = 5 mV/s) to obtain photo-current values, j_{ph}. Photo-current transients (at a ν = 5 mV/s) were obtained by light chopping (Lambda SC shutter controller) with on-off periods of 5 s. Action spectra were recorded by polarizing at 1.0 V vs RHE and recorded under UV–vis illumination with