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Preparation of titanium dioxide nanostructures facilitated by poly-L-lysine peptide

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Abstract

In this work, we have synthesized titanium dioxide by sol–gel process using titanium isopropoxide as precursor; the shapes obtained were nanorods ranging in size from 20 to 40 nm in presence of poly-L-lysine (PLL) peptide. The resulting materials were calcinated in order to obtain a crystalline phase; afterwards the powders were characterized by means of scanning electron microscopy (SEM), energy-dispersive spectroscopy (EDS), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The results show that the synthesis of titanium dioxide nanostructures can be achieved in presence of poly-L-lysine.

Keywords: Nanostructured materials; Sol–gel process

1. Introduction

The alkoxide method that is based on the hydrolysis of a metal alkoxide in alcohol solution, has been proposed to produce spherical monodispersed fine particles of metal oxides such as Al_2O_3 [1], SiO_2 [2], Ta_2O_5 [3], TiO_2 [4–6], and ZrO_2 [7]. Among these metal oxide particles, titanium dioxide (TiO_2) is an industrially and technologically important material, that is widely applied as a pigment, catalyst, and photo-conductor [8] and also is of interest in medical and biological fields [9–11]. Nanometer size TiO_2 particles have interesting properties such as high mechanical strength, low sintering temperature, and improved catalytic efficiency, among others [12]. Therefore, many efforts have been directed towards the synthesis of TiO_2 at nanometer scale. The addition of monovalent and multivalent cations like the poly-L-lysine peptide, or the introduction of solutions with peptides within physiological means, lead to the spontaneous assembly of these oligopeptides to form microscopic and macroscopic structures that can be built into different geometric forms [13]. One of the self-assembly systems proposed as a study model, is that formed by the poly-L-lysine peptide where the positive charges interact with the negative charges of glutamate forming folded molecular structures [14]. Although, a sol–gel route in the presence of poly-L-lysine has been used for the preparation of silica nanoparticles [15–17], in this work a similar route is for the first time applied to obtain TiO_2 nanorods.

2. Experimental procedure

In a typical experiment 100 μl of titanium isopropoxide (97%) were put in a 0.6 ml microtube then 200 μl of a solution of poly-L-lysine with concentration of 5 mg/ml of water were added drop by drop; the sample was incubated at 4 °C in order to avoid the fast degradation of the peptide, after that the powders were calcinated at 700 °C for 3 h. Finally, the product was characterized before and after the calcination by a scanning electron microscopy (SEM, JSM 5800) equipped with energy-dispersive spectroscopy (EDS) in an EDAX equipment and Transmition Electron Microscopy in a Philips CM-200 at 200 kV. The crystalline phase of the calcinated powders was identified by X-ray diffraction (XRD) in a Philips X-ray diffractometer X'PRET.

3. Results and discussion

The formation of TiO_2 nanostructures in presence of poly-L-lysine peptide after their calcination is shown in Fig. 1.

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(a)

(b)

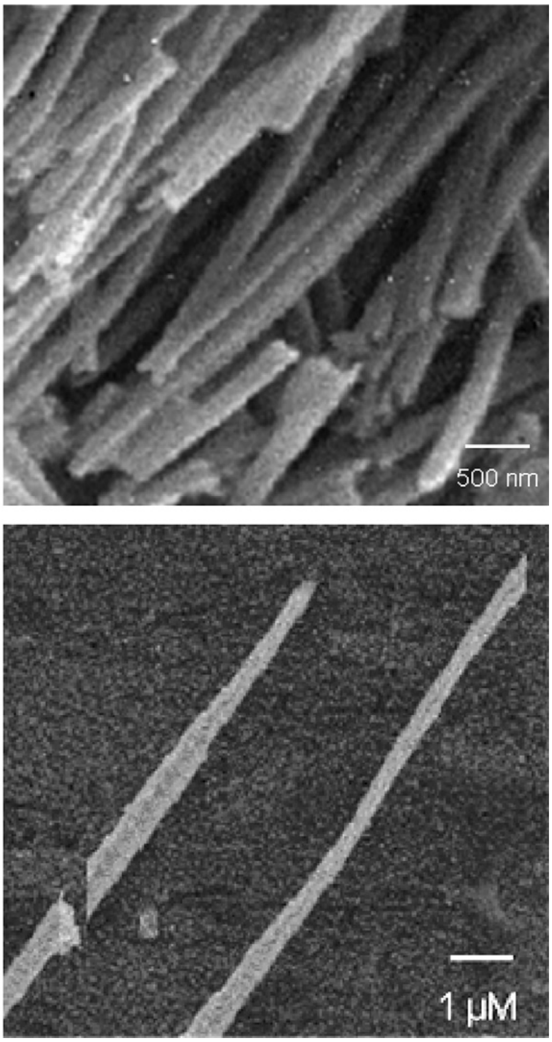

Fig. 1. (a) SEM image of TiO_2 obtained in the presence of PLL. (b) SEM image of a TiO_2 nanostructure obtained in the presence of PLL after calcination at 700 °C.

These nanostructures are mostly nanorods with tubular shape with diameters from 20 to 100 nm. These shape and size were achieved only in the presence of PLL. In Fig. 2 is shown a SEM microphotography of TiO_2 synthesized under the same conditions as that showed in Fig. 1 but without the presence of PLL; the structure has an irregular shape confirming that PLL has a strong influence in the structure of the sample. In Fig. 3, we can see an EDS spectrum which shows the results of the elements that are present in the nanorods which are composed only of titanium and oxygen.

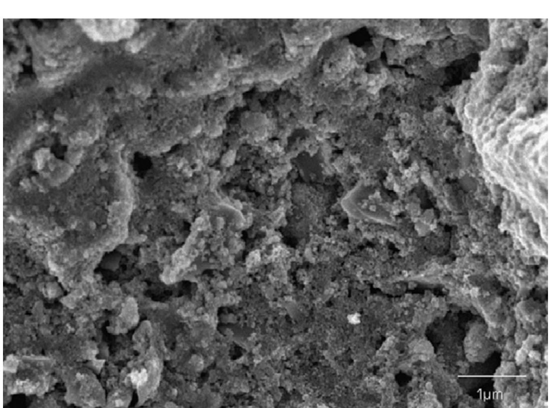

Fig. 2. SEM image of TiO_2 obtained without the presence of PLL after calcinations at 700 °C.

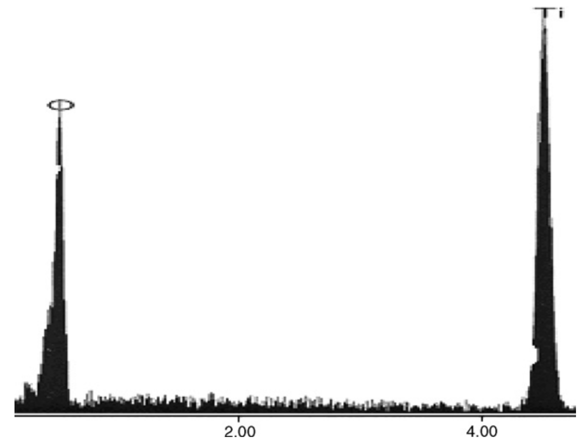

Fig. 3. EDS spectrum of TiO_2 nanorod obtained in the presence of PLL and after calcinations at 700 °C.

The X-ray diffraction pattern of the TiO_2 powders obtained in the presence of poly-L-lysine after calcinations at 700 °C is shown in Fig. 4, the main peaks are displayed at 25.2°, 36.9°, and 53.8° which correspond to planes (1 0 1), (1 0 3) and (1 0 5) of the anatase. Also, there are peaks that evidence the presence of the rutile phase.

In Fig. 5a TEM image of TiO_2 nanostructure obtained in the presence of PLL is shown; this nanostructure has a diameter about 20 nm in tubular form and in the bottom part has a junction leading to a shape like a Y. Its XRD pattern shown in Fig. 5b corresponds to the anatase crystalline phase of the TiO_2. In Fig. 6 another TEM image of TiO_2 nanorods is shown where with two nanorods of diameter between 10 and 25 nm. The electronegative O–R group of the alkoxide renders the metal very susceptible to nucleophilic attack leaving a partial negative charge. The PLL positive charge provides a system capable of forming ionic and

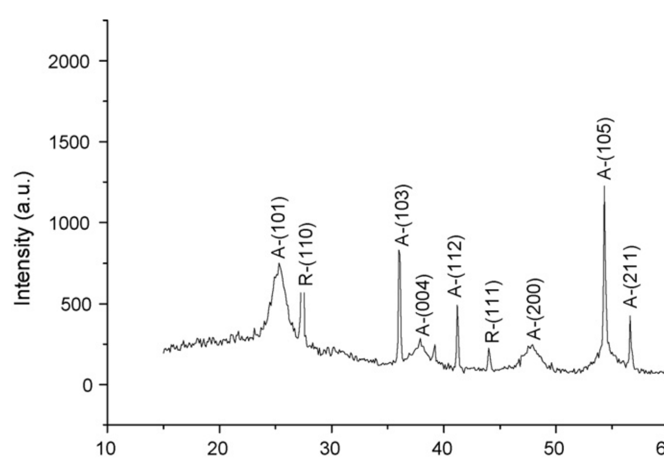

Fig. 4. X-ray diffraction pattern of the TiO_2 powders after calcinations at 700 °C.

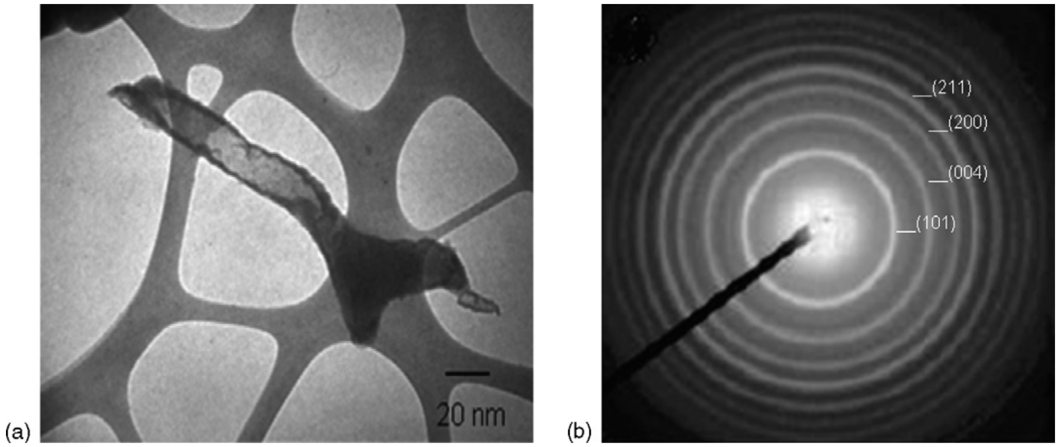

Fig. 5. (a) TEM image TiO_2 nanostructure formed in presence of PLL. (b) X-ray diffraction pattern.

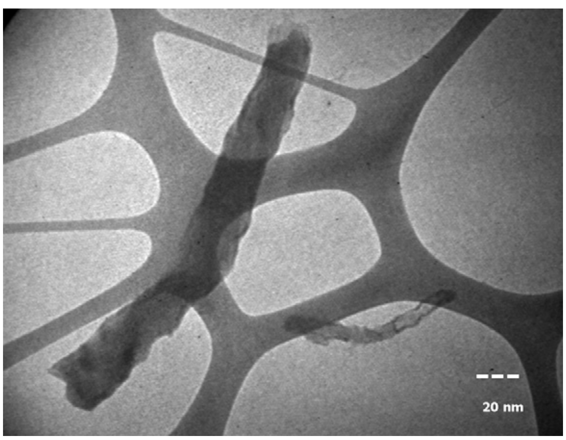

Fig. 6. TEM image of TiO_2 nanorods formed in presence of PLL.

hydrogen bond. Although, the mechanism is still not clear at all, it is believed that the positive charge of the PLL interacts with the negative charge of the organic precursor during the reaction controlling the growth of the particles. In another study made with poly-L-lysine peptide where particles of silica were synthesized with diameters of about 30–600 nm, the diameter depended of concentration of poly-L-lysine peptide[16]. In this system the parameters optimization as well as the detail mechanism is under further investigation.

4. Conclusions

In this work, nanorods of titanium dioxide were obtained by a sol–gel process; the nanometer size was reached in presence of poly-L-lysine peptide that acted as structure directing agent. This is a promising route for the fabrication of TiO_2 structures at nanometer scale and could be extended to similar systems, this kind of materials can be useful for diverse areas as medicine, biotechnology, microelectronics, optics, among others.

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