Materials Letters 123 (2014) 149–152

Contents lists available at ScienceDirect

Materials Letters

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

Preparation, characterization and photoelectrochemical properties of hydrophilic Sn doped TiO_2 nanostructures

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ARTICLE INFO

Article history:
Received 5 January 2014
Accepted 24 February 2014
Available online 12 March 2014

Keywords:
TiO_2
Sol–gel preparation
Hydrophilic
Photocurrent

ABSTRACT

Hydrophilic Sn doped TiO_2 nanostructured thin films have been fabricated using a sol–gel method, and followed by calcination at 450 °C. The samples are characterized by means of XRD, Raman, SEM and contact angle measurements. The XRD and Raman studies revealed that, the higher Sn doping content (3 at%) leads to the formation of mixed phases of TiO_2. SEM micrographs revealed that all samples are porous in nature. The contact angle of TiO_2 nanostructured films varied between 19° and 37° depending upon the Sn content. All the samples are photoelectrochemically active and 2% Sn doping significantly enhances the photoelectrochemical ability of TiO_2 film. The highest photocurrent density of 20 μA cm^{-2} is measured for 2 at% Sn doped TiO_2 in 0.2 M Na_2SO_4 electrolyte, on light irradiation. Time dependent photoresponse tests have been carried out by measuring the photocurrent under chopped light irradiation.

1. Introduction

Titanium dioxide (TiO_2) has been extensively investigated, due to its long-term stability against photo and chemical corrosion, favorable band edge positions, strong optical absorption, nontoxicity, and inexpensive cost [1,2]. However, TiO_2 is a well-known n-type semiconductor with a large band gap (i.e. 3.2 eV for anatase structure and 3.0 eV for rutile structure), it absorbs in the ultraviolet (UV) regime of solar radiation (less than 5%) and thus significantly limits its widespread applications [1,3]. In order to address this fundamental issue, various strategies have been explored to improve the photoresponse of TiO_2 nanostructures, such as tuning its crystallite size and structure [3], doping with metal or nonmetal elements to induce red-shift of bandgap absorption [4,5], sensitizing with other narrow bandgap semiconductor materials like PbS [6], post-growth hydrogen annealing, and fabricating branched structures [7]. Doping with tin (Sn) is an attractive approach especially for TiO_2, as the very similar ionic radii of Ti^{4+} (0.68Å) and Sn^{4+} (0.69Å) would allow easy substitution of Ti^{4+} by Sn^{4+} in the TiO_2 lattice [1,8]. Several reports are available on the preparation of Sn doped TiO_2 nanostructured films and the effect of Sn doping on crystal structure, optical band gap and photocatalytic properties of TiO_2 [8–12]. However, the influence of Sn content on the photoelectrochemical properties of sol–gel derived TiO_2 nanostructures has been studied rarely. In this paper, we report a sol–gel approach for the growth of Sn containing TiO_2 nanostructured thin films and their enhanced photoelectrochemical properties.

2. Experimental section

All the chemicals are of analytical grade and used for the synthesis as such. In a typical synthesis, the gel was obtained by dissolving 1 wt% of polyvinyl alchoal (PVA) in 50 ml distilled water and stirred at 80 °C for 8 h. Titanium tetraisopropoxide (Aldrich) and citric acid (Merck) were added to the resulting PVA gel, while stirring at 80 °C in a molar ratio of 1:3. A clear homogeneous gel was obtained. Sn doping of TiO_2 is obtained by introducing 1, 2 and 3 at% tin tetrachloride pentahydrate [$SnCl_4 \cdot 5H_2O$, Sigma Aldrich] into the above solution. The gel is ultrasonicated at 80 °C and aged for 24 h so that the PVA chains form complex with metal ions. To get the films, a pure and Sn doped TiO_2 polymer gel was spin coated twice onto cleaned glass and ITO substrates. An intermediate drying between coatings is done at 180 °C for 30 min. The prepared films are initially heat treated at 250 °C for 1 h, to promote pyrolysis of the polymer resin which results in an amorphous film, and later crystallized by annealing at 450 °C for 2 h. The prepared films are characterized and analyzed by different characterization techniques. The microstructural information is obtained by JEOL X-ray diffractometer (JDX-8030) studies using

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http://dx.doi.org/10.1016/j.matlet.2014.02.112
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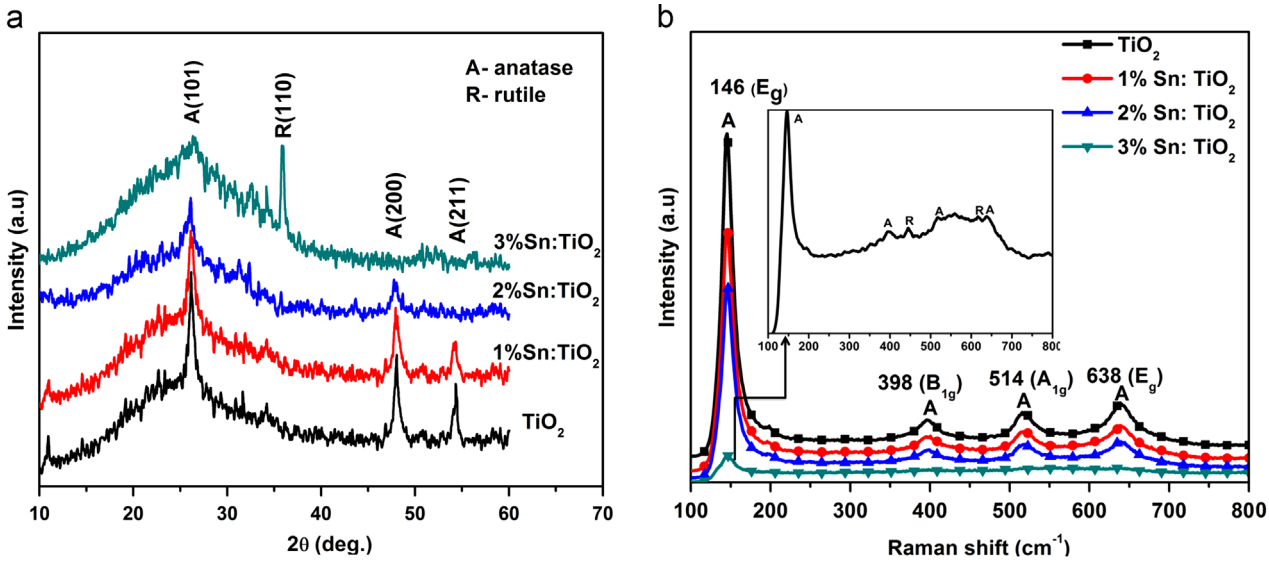

Fig. 1. XRD and Raman patterns of undoped and Sn doped TiO_2 nanostructures.

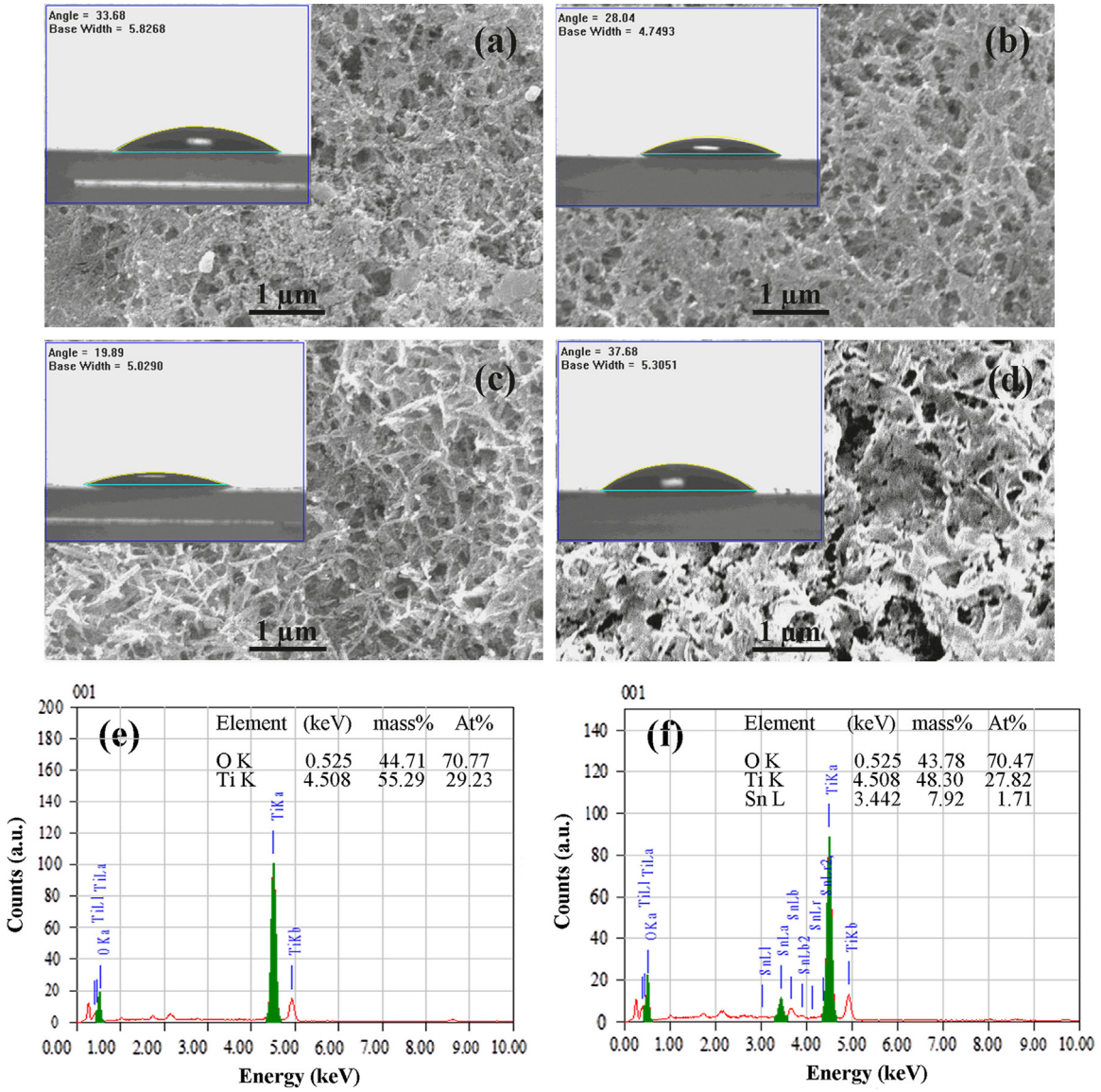

Fig. 2. SEM images of (a) TiO_2, (b) 1% Sn doped TiO_2, (c) 2% Sn doped TiO_2 (d) 3% Sn doped TiO_2 (the insets show images of droplets that formed on the surface of different samples during contact angle measurement), (e) EDX spectrum of TiO_2, and (f) EDX spectrum of 2% Sn doped TiO_2.