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Structural and optical properties of Pd^{2+}-doped mesoporous TiO_2 thin films prepared by sol-gel templating technique

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Pd^{2+}-doped TiO_2 thin films with mesoporous structure were produced on quartz substrate by sol-gel dip coating. The structural, morphological and optical properties of the film were characterized by X-ray diffraction (XRD), Brunauer–Emmett–Teller (BET), transmission electron microscopy (TEM), atomic force microscopy (AFM) and UV/vis transmittance spectroscopy. By increasing the Pd^{2+} concentration from 0 to 6 mol%, the crystallites appeared solely as the anatase phase and their average sizes decreased from 10.5 to 7.1 nm. Addition of Pd^{2+} also resulted in increasing of the specific surface area and decreasing of the pore size of the layer. The transmittance of the films decreased in the visible light region and the absorption edges shifted to the longer wavelengths by increasing of the Pd^{2+} doped concentration. Optical band-gaps of the undoped and 6 mol% Pd^{2+}-doped films were 3.52 and 3.31 eV, respectively. The refractive index of the films decreased from 1.83 to 1.71 and their porosity increased from 56.3 to 63.7% by increasing of the Pd^{2+} doping concentration from 0 to 6 mol%.

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1. Introduction

TiO_2 thin films with mesoporous structure have extensive applications in photocatalysis [1, 2], dye-sensitized solar cells [3, 4], sensors [5], rechargeable lithium batteries [6, 7] and many other applications due to their easy synthesis, great chemical stability, low cost, extraordinary optical and electrical properties and versatile other capabilities [8, 9]. Extensive application of TiO_2 in solar cells is bound to two limitations:

- Wide band-gap of TiO_2 being excitable with ultraviolet radiations having wavelengths below 387 nm. These waves only make a small part of solar spectrum (about 4 %). The return of using solar radiation will then be very low [10, 11].
- Large recombination rate of photo-excited electron-hole pairs causing low percentage usable charges [12].

An appropriate simple solution of these limitations is dopant usage. Quantum sized TiO_2 doping with various transitional metal ions improves interfacial electron transfer rate, recombination rate, charge carrier generation and photo reactivity [13-15].

Various deposition techniques such as electron beam evaporation [16], metal organic chemical vapor deposition (MOCVD) [17], pulsed laser deposition [18], reactive sputtering technique [19], spray pyrolysis [20], hydrothermal process [21] and sol-gel methods [22] have been used for production of TiO_2 thin films.

Besides the above methods, sol-gel technique can be considered as the most influential technique for preparation of the mesoporous thin layers. It can provide good homogeneity, uniform composition and large specific areas via mild processing conditions [23, 24]. A combination of the evaporation-induced self-assembly (EISA) using structure-directing polymer (template) with complexation of molecular inorganic species in precursor can be used to prepare the mesoporous films through sol-gel process [25].

Although the influence of doped transitional metal ions like Fe, Cd, Cr, Nb, Co, Ni and Sn on the thin film TiO_2 is almost known, there is not sufficient information yet made available on the effect of Pd^{2+} on properties of mesoporous TiO_2 thin layers [26-30]. Because of the ionic radius differences imposed on the Ti^{4+}, it is expected that Pd^{2+} doping causes remarkable change on characteristics of the TiO_2 films. This paper indicates the recently obtained findings about the influence of the Pd^{2+}-doping process on structural, morphological and optical properties of the mesoporous TiO_2 thin layers produced by the sol-gel templating process.

2. Experimental

2.1. Materials and chemicals

Titanium tetraisopropoxide [Ti $(O{\cdot}i\text{-}C_3H_7)_4$] 98% (Merck) was used as precursor, hydrochloric acid (HCl) 32% (Merck) was utilized as catalyst, non-ionic triblock copolymer surfactant Pluronic P123 [poly-(ethylene oxide)