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Effect of sintering temperature on photocatalytic activity of cadmium monoxide plus cadmium titanate thin solid films deposited by the sol–gel technique

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ABSTRACT

Cadmium monoxide plus Cadmium Titanate [CdO + $CdTiO_3$] thin solid films were prepared on soda-lime glass substrates by means of the sol-gel technique. Two Titanium [Ti]/ Cadmium [Cd] ratios, 0.54, and 0.67, in the precursor solutions were studied. After the dipping process, the samples were sintered in an open atmosphere during one hour at selected temperatures (T_s) in the range of 350–600 °C. The variation of T_s was in steps of 50 °C. These the thin solid films were analyzed using X-ray diffraction, UV–Vis optical absorption, and atomic force microscopy. The photocatalytic activity (PA) was measured by means of the photobleaching of an aqueous solution of methylene blue (MB) after irradiation with an UV-lamp. The MB concentration was determined by using optical absorption spectra, measured before and after the photobleaching process, and the Beer-Lambert principle. The best PA was obtained for films sintered at 500 °C for both [Ti]/[Cd] ratios studied, as for this T_s value the PA was very similar.

1. Introduction

In chemistry, photocatalysis is the acceleration of a photoreaction in the presence of a catalyst. In catalysed photolysis, light is absorbed by an adsorbed substrate. In photogenerated catalysis, the photocatalytic activity (PCA) depends on the ability of the catalyst to create electron–hole pairs (e^--h^+), which generate free radicals (e.g. hydroxyl radicals [•OH]) able to undergo secondary reactions. The heterogeneous photocatalysis (HPC) is a very interesting current subject due to its application in the decontamination of air, and water through the decomposition of toxic, volatile organic compounds (VOC's) present in these vital fluids [1]. HPC is a process based on the direct or indirect absorption of radiant energy—ultraviolet or visible (UV–Vis)— by a solid material (generally, by a wide gap semiconductor); direct excitation is the more commonly used process. Fig. 1 displays a schematization of the photochemical processes that occur inside a crystalline semiconductor grain. Photons coming from the light source, with a greater energy than the forbidden energy band gap (E_g) are absorbed, and an electron passes to the conduction band leaving a positive hole in the valence band. The electron-hole pair (e^--h^+) travels toward the surface giving place to the oxidation-reduction processes (A and B processes in Fig. 1) which promote the molecular decomposition of the absorbed VOC's. The e^--h^+ pairs that do not react with the VOC's on the surface, recombine and energy dissipation occurs. This recombination can happen either on the surface or in the volume of the grain (C and D processes, respectively, in Fig. 1) [2].

The efficiency of the photocatalytic reaction depends on diverse factors. One of the most critical aspects is the e^--h^+ recombination probability which competes with the separation of the photogenerated charges. The low efficiency, especially when visible light is used, is one of the most severe limitations of the HPC. To increase the efficiency of the photocatalytic process several strategies have been tried, such as: 1) Modification of the semiconductor material in order to extend its response to longer wavelengths. Doping with transition metals have been widely studied [3]. 2) The rising of the e^--h^+ recombination time by means of the coupling of semiconductors of different energy levels. Under optical excitation the photogenerated electrons are accumulated on the valence band of the other semiconductor. In Fig. 2(a) scheme of the zinc oxide [ZnO], and subsequently surface-passivated with chalcogenide material compounds namely cadmium sulphide [CdS] ([ZnO-CdS]) system is exhibited [4]. The use of photocatalysts supported by means of applied electrical potentials, in such a way that they separate the anodic reactions, which reduces drastically the e^--h^+ recombination [5]. Cadmium titanate [$CdTiO_3$] belongs to the semiconductors family based in titanium oxide. It is well known that it crystallizes into the Ilmenite rhombohedral structure below 1000 °C, and it crystallizes into

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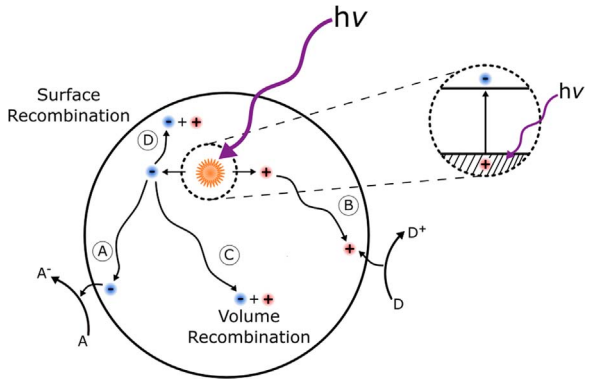

Fig. 1. Processes present in semiconductor-medium interfaces under illumination.

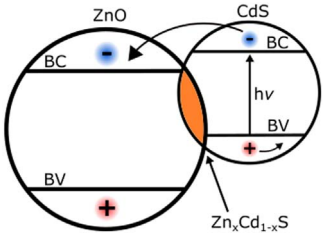

Fig. 2. ZnO-CdS semiconductors coupled system.

the perovskite orthorhombic phase having ferroelectrical properties, at around 1050 °C [6,7].

This oxide has deserved more attention due to its promising applications as sensor material to detect gaseous NO_2 [8], and as material for optical fibers fabrication [9], among others. Nevertheless, its photocatalytic property has not been explored until now. Different methods have been used to obtain Ti-based oxides, in the film format and as powders, among these are: (a) chemical methods as sol-gel [6,7,10], solid state reaction [6], and thermal decomposition (pyrolysis) [11–18]. Sol-gel is a simple deposition technique that presents a low cost set-up, easy to handle, and can be scaled for deposition on large areas. In this work we are presenting some results obtained from the characterization sol-gel deposited Cadmium monoxide plus Cadmium Titanate [CdO + $CdTiO_3$] thin solid films. Sol-gel presents several advantages over the other methods such as homogeneity, stoichiometry control, purity, simple procedure, composition control, multicomponent oxides thin solid films deposition, covering of large plane and complex areas. Because of the difference in the E_g values of the components in the semiconductor coupled system, CdO + $CdTiO_3$ is a good candidate to be tried as photocatalyst. In this work CdO + $CdTiO_3$ thin solid films were prepared by the sol-gel technique. Two precursor solutions were used with [Ti]/[Cd] ratios of 0.54 and 0.67. The layers were sintered in an open atmosphere at different temperatures (T_s) chosen in the range of 350–600 °C, using steps of 50 °C as the T_s-difference. The photocatalytic activity (is defined as "acceleration by the presence of as catalyst". A catalyst does not change in itself or being consumed in the chemical reaction. This definition includes photosensitization, a process by which a photochemical alteration occurs in one molecular entity as a result of initial absorption of radiation by another molecular entity called the photosensitized) was studied through the photobleaching of methylene blue in aqueous solution.

2. Experimental details

2.1. The preparation of the solutions

The Titanium dioxide [TiO_2] precursor solution was prepared starting from the following reagents: For 1.0 mol of Titanium(IV) isopropoxide [$Ti[OCH(CH_3)_2]_4$] (TIP) (98% from Alfa Aesar, Ward Hill, MA, USA), 36.5 mol of Ethanol [C_2H_6O] (98%, from J. T. Baker, Naucalpan, Edo. Mex., México), 0.5 mol of Nitric acid [HNO_3] (98%, from J. T. Baker, Naucalpan, Edo. Mex., México), and 5.0 mol of deionized water [H_2O] were used. Ethanol was divided into two equal parts:

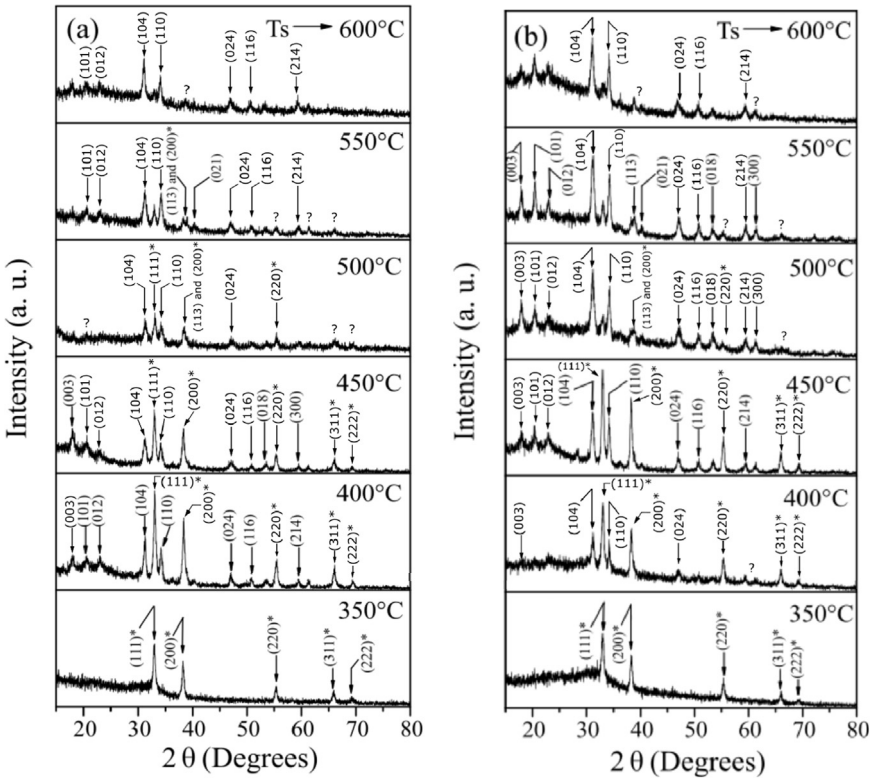

Fig. 3. X-ray diffraction patterns of thin solid films sintered in the 350–600 °C (T_s) range in 50 °C steps, for the [Ti]/[Cd] ratios (a) 0.54, and (b) 0.67.