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The environment effect on the electrical conductivity and photoconductivity of anatase TiO_2 nanoplates with silver nanoparticles photodeposited on {101} crystal facets

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ABSTRACT

The electrical conductivity and the transient photoconductivity of Ag/TiO_2 nanoplates were studied at 300 K, both in vacuum and in air. A solvothermal method was used for the preparation of anatase TiO_2 nanoplates and the embedding of Ag nanoparticles was achieved via the photoreduction of $AgNO_3$ under UVA irradiation. The particle size was controlled by varying the time of illumination and the obtained Ag nanoparticles sizes were in a range of 5–20 nm. The Ag/TiO_2 nanoplates were characterized by X-ray diffraction (XRD) and transition electron microscopy (TEM). The electrical conductivity and the photoconductivity responses were investigated. The influence of environment was also discussed. For some periods of UVA illumination time, photoconductivity reaches higher values in comparison with the pure TiO_2 anatase nanoplates. In air, the influence of the adsorbed on the surface oxygen is obvious, resulting in high recombination rates.

1. Introduction

Nanocrystalline TiO_2 has been intensively investigated because of its favorable environmental and energy applications [1–6]. It has low toxicity, physical and chemical stability, high photocatalytic efficiency and availability at a low price [7–11]. It finds wide application in photocatalysis [12–14], solar cells [13,15–17] gas sensors [18–20], water splitting to generate H_2 and O_2 [21,22], self cleaning surfaces etc. The high efficiency of TiO_2 as a photocatalyst is limited by its wide bandgap (3.2 eV) as well as by its large charge carrier recombination rate [23,24]. Doping is one of the techniques adopted to extend the absorption edge of TiO_2 to the visible region, in order to take advantage of the main part of the solar spectrum. Transition metal-doping can shift the optical absorption edge of TiO_2 from the ultraviolet to the visible range, but it also increases the recombination rate of e-h pairs and causes thermal instability and low quantum efficiency of the photoinduced charge carriers [25].

A considerable amount of research work has been carried out to develop new TiO_2-based photocatalyst that can improve its photocatalytic activity. The appropriate morphological modification can enhance photoactivity [26] and therefore the formation of anatase titania nanocrystals with {001} facets has attracted much attention in the last few years [13,27–30]. Its properties are largely determined by external surfaces exposed, making it a promising industrial semiconductor material. The oxidation and reduction sites on the surface of anatase TiO_2 are spatially separated. The {001} facets provide effective oxidation sites, while {101} facets work as reduction sites. The difference in the surface energy levels of the conduction and valence band for the different crystal facets drives electrons and holes to different crystal facets [30–33]. TiO_2 is a typical semiconductor that absorbs UV light to form pairs of negative electron and positive hole which participate in redox processes at the surface or recombine with each other [34–36]. Several studies have shown that the photogenerated electrons migrate toward {101} facets while photoinduced holes toward {001} facets [37,38]. The relative percentage of the exposed {001} and {101} facets is crucial for the effective separation of the photogenerated pairs and therefore for the improvement of the photocatalytic activity [39,40].

The fabrication of noble metal/TiO_2 composites have been suggested as an important way for the enhancement of the photocatalytic activity [41–43]. The noble metals Ag and Au exhibit capacitive properties which, in turn, facilitate improved charge separation in semiconductor-metal composite systems. There is considerably interest

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in using silver because of its easy synthesis, high efficiency, low cost compared to other noble metals, antimicrobial properties and high oxygen adsorption reactivity [44]. It is capable to capture electrons from the conduction band of TiO_2 under UV irradiation and reduce electron-hole recombination [45]. Because of the difference in Fermi levels of TiO_2 and Ag, Ag can act as a reservoir of photogenerated electrons [46]. It is shown, in recent studies, that the photocatalytic activity was enhanced when Ag nanoparticles were photodeposited on the {101} crystal facets of anatase TiO_2 nanoplates [47–49].

The study of the photoconductivity contributes greatly to the interpretation of the competition between photogeneration, recombination and trapping of carriers of semiconducting materials [50–52]. Recombination is a major limiting factor in attaining high photoconductivity values and the role of Ag deposited by a photochemical reduction on anatase TiO_2 nanoplates is a challenge for investigation. To the best of our knowledge, although widespread applications of TiO_2 are credited to its high level of photoconductivity [53], there has been no report on the photoconductivity behavior of nanosized Ag deposited by a photochemical reduction on the {101} crystal facets of anatase TiO_2 nanoplates.

The aim of the present work is to study the structural, electrical and transient photoconductive properties in vacuum and in air of anatase TiO_2 nanoplates with Ag nanoparticles photodeposited on {101} facets. A photochemical reduction of Ag^+ to Ag nanoparticles was applied under UVA irradiation for different periods of time. The molar ratio of Ag to the TiO_2 anatase nanoplates was 1:10.

2. Experimental details

2.1. Preparation of TiO_2 nanoplates with Ag nanoparticles photodeposited on the surface

A solvothermal method was followed for the preparation of anatase TiO_2 nanoplates with dominant {001} facets using titanium isopropoxide [$Ti(C_3H_7O)_4$, 3 mmol] as a precursor and hydrofluoric acid aqueous solution [HF 40%, 0.6 ml (0.03 mol)] as a capping agent [48]. A photodeposition procedure was then carried out for the surface modification of the TiO_2 nanoplates with Ag nanoparticles embedded on the {101} facets. The nanoplates were immersed in $AgNO_3$ solution (5 mM) and the mixture was then illuminated with UVA light at room temperature for 1, 5, 10 and 20 min respectively. The molar ratio of Ag to the TiO_2 anatase nanoplates was 1:10 [48].

2.2. Characterization

XRD analysis was curried out with a Siemens D500 Diffractometer using CuK_α radiation source in order to investigate the crystalline phases of pure and Ag/TiO_2 anatase nanoplates. The measurements were taken using the following combination of slits: 1.0°/1.0° 1.0° as aperture diaphragms, 0.15° as detector diaphragm and 0.15° as diffracted beam monochromator diaphragm. The measured 2θ range was scanned in steps of 0.03°/5 s. Morphological observations were carried out with a transmission electron microscope (Philips CM20) operated at 200 kV and equipped with a Gatan GIF200 image filter. The TEM specimens of the Ag/TiO_2 anatase structures were prepared by direct deposition on a carbon coated Cu TEM grid. The chemical composition of the Ag/TiO_2 powders was determined by ICP- AES analysis using a Perkin Elmer OPTIMA 3000 spectrometer. The surface chemical composition of the prepared $AgTiO_2$ powders was examined by X-ray Photoelectron Spectroscopy (XPS). Ultra-high vacuum VG ESCALAB 210 electron spectrometer with a multichannel detector was employed. Mg K_ radiation was used for the excitation and the binding energy spectra were referenced to the C1s 285.0 eV. High resolution scans over narrow energy ranges were recorded around Ti2*p*, Ag3*d*, O1*s* and C1*s* peaks.

2.3. Electrical conductivity and photoconductivity measurements

For photoconductivity and dark conductivity measurements, the prepared powders were consolidated in the form of pellets. The disks with a diameter of 10 mm were 0.95, 1.1, 1.1 and 0.7 mm thick for 1, 5, 10 and 20 min of UVA illumination respectively. Two coplanar silver electrodes with a distance of 0.8 mm between them were vacuum deposited onto the samples. A vacuum cryostat was used and a constant bias voltage of 5 V was applied while the temperature was adjusted using an Oxford ITC502S temperature controller. The light source was a 100 W (white light) Xenon lamp. A heat filter was used for the white light heat filtering. The light intensity on the samples, measured by an Ophir PD300-BB Radiometer head, was 240 W/m^2. The samples were subjected to a cycle of two illumination periods, 20 min each, interrupted by two equal periods in the dark. The photocurrent response during illumination and darkness was measured by a Keithley 6517A electrometer and recorded every 10 s. Before measurement, the samples were annealed at 440 K for 90 min and left to cool down in order to eliminate the persisting effects of previous light exposure. This annealing temperature is low enough to cause changes to aggregates. DSC analysis reported in previous studies [36] has shown that changes in aggregation appear when the samples are calcinated at the high temperature of ~600 °C for 2 h. Subsequently, the samples remained in the dark for 24 h at room temperature before performing the photoconductivity measurements.

3. Results and discussion

3.1. Structure and morphology

Based on the XRD patterns of pure and Ag/TiO_2 nanoplates during the different UVA illumination periods, it was found that the anatase phase was maintained throughout photoreduction process of silver ions on the {101} facets of the nanoplates [48]. The samples with short irradiation time did not show diffraction peaks corresponding to metallic silver. This finding indicates that the silver nanospheres are small in size and also very well dispersed on the {101} facets of nanoplates. Only for the sample irradiated under UVA light for 20 min, XRD spectra (Fig. 1) showed additional peaks of metallic Ag nanoparticles [JCPDS card No. 004-0783ICCDD], indicating their larger size and the success of Ag photodeposition on TiO_2 surface [48]. Diffraction peaks of silver oxides Ag_2O and AgO were absent in all samples, indicating that silver is exclusively in metallic form in the samples. Finally, all samples exhibited some broad Bragg peaks, attributed to the anisotropic growth of nanoplates along the c-axis, thus suggesting that the Ag photodeposition process does not cause any change in the structure.

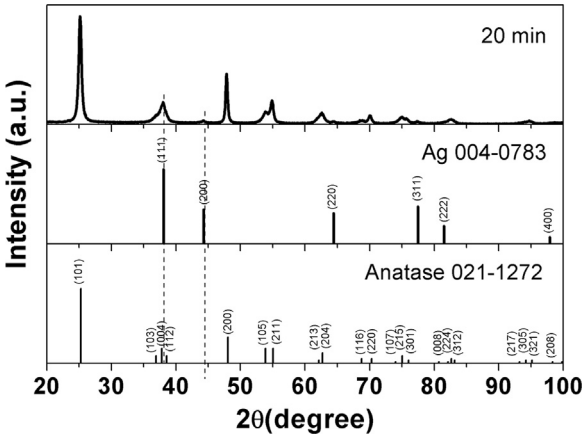

Fig. 1. XRD patterns of anatase TiO_2 nanoplates with Ag nanoparticles photodeposited for 20 min.