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Ag/Fe:TiO_2 nano-catalysts prepared by Fe ion implantation and Ag nanoparticle deposition by electron beam irradiation

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ABSTRACT

TiO_2 nano-catalysts made by the sol–gel method were modified by ion implantation and electron beam irradiation to obtain a more efficient photocatalytic function. The results of photodegradation of methyl orange in aqueous solution demonstrate firstly that the films have a photocatalytic activity which responds to visible light. Secondly, it demonstrates that under ultraviolet excitation the sample with a fluence of 6×10^{15} ions/cm^2 and electron beam irradiated with concentration of $AgNO_3$ aqueous solution at 1×10^{-3} M gives a more efficient photodegradation ability than pure TiO_2 film and other Fe-doped films display almost the same photodegradation ability as TiO_2 film. Thirdly it demonstrates that under sunlight, all modified films exhibit more photodegradation activity than TiO_2 film.

1. Introduction

In recent years, anatase titanium dioxide (TiO_2) as one of the most promising candidates for a photocatalyst has been extensively studied and significant progress achieved [1–3]. However, it has a wide band gap of 3.2 eV and a photocatalytic activity only under ultraviolet (UV). Furthermore, fast recombination of the photoelectron–hole pairs which occurs in nanoseconds limits its catalytic efficiency [4]. Various modification methods have been used to enhance the photocatalytic ability of TiO_2 in the degradation of organic or inorganic compounds [5]. A wide range of transition metal ions (Fe, Zn, V, Cr, Mn, Cu, Co, Mo, etc.) were selected to incorporate with TiO_2 particles mainly in order to narrow the band gap or to introduce intra-band gap states so as to have a visible-light response [6–8]. Noble metal (Pt, Au, Ag, Pd, etc.) nanoparticles were loaded on the surface of TiO_2 particles to prolong the lifetime of the photoelectron–hole pairs [9–11]. For a different mechanism of enhancing photocatalytic activity, the idea of combining transition metal ion implantation and noble metal nanoparticle loading was considered. However, to our best knowledge, such reports have been rare up to now.

Zheng et al. [12] investigated Fe ion implanted TiO_2 films and discovered that they had a visible light photocatalytic activity but their UV photocatalytic activity decreased. Yamashita et al. [8] reported that Fe ion implanted TiO_2 films had a photocatalytic activity under visible light and the same photocatalytic activity as a pure TiO_2 film under UV. We have also fabricated Fe-doped TiO_2 films by ion implantation and investigated their photodegradation ability of methyl orange (MO) in aqueous solution and obtained similar result as Zheng et al. [12] under visible and UV light. Here, we have attempted to fabricate Ag/Fe:TiO_2 films not only to achieve a visible light response to photocatalytic activity, but also to enhance their photocatalytic activity under UV and sunlight.

2. Experimental

2.1. Preparation of Ag/Fe:TiO_2 photocatalytic films

TiO_2 films were prepared on glass slides by the sol–gel method [13]. The thickness of the film is about 500 nm according to SEM cross-section images. The TiO_2 thin film was then placed inside an ion implanter and the system was evacuated to 1×10^{-4} Pa. The accelerating voltage was set as 40 kV. Fe ions were implanted into TiO_2 films by a Metal Vapor Vacuum Arc (MEVVA) ion source with different fluence of 6×10^{15}, 1×10^{16}, 3×10^{16} and

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6×10^{16} ions/cm^2. The machine we used was described in detail in [14]. In order to deposit noble metal nanoparticles, the Fe:TiO_2 films were dipped in $AgNO_3$ aqueous solution with a concentration of 10^{-3} M. All TiO_2 films were placed 5 mm beneath the surface. They were then irradiated immediately by an electron beam from a Linac with an energy of 5 MeV and an average current of 200 μA for 10 min at room temperature in ambient atmosphere. The dose rate was 100 Gy/s. After irradiation, the films were washed thoroughly by de-ionized water and dried at 60 °C for 60 min. They were named as Ag/Fe6E15, Ag/Fe1E16, Ag/Fe3E16 and Ag/Fe6E16, respectively. One TiO_2 film was irradiated by electron beam at the same time and it was named Ag/TiO_2.

2.2. Characterization of Ag/Fe:TiO_2 photocatalytic films

X-ray photoelectron spectroscopy (XPS) analysis was carried out with a VG ESCALAB MK2 XPS spectroscope. The source was non-monochromatic Al Kα (1486.6 eV) X-rays, the working voltage was 13 kV and the anode current was 18 mA. The analyzer mode was in fixing pass energy mode and the pressure of the analysis chamber was 10^{-7}–10^{-8} Pa. X-ray diffraction (XRD) analysis was conducted on a X'PertPRO MPD instrument at normal incidence where the source was Cu Kα X-rays with a wave length of 1.5418 Å and the step length was 0.05°. Scanning electron microscopy (SEM) analysis was carried out with a Hitachi SM4800SEM field, with a resolution of 2.0 nm.

2.3. Photocatalytic efficiency evaluation

To minimize errors resulting from different measurement time, film uniformity and light intensity etc., samples were cut from the same glass slide covered by TiO_2 films with an area of 8.0×25.0 mm^2 and were placed in 1 cm four-sided, transparent quartz colorimetric containers to measure the optical density (OD) values in order to evaluate the photodegradation ability. A 1000 W high-pressure mercury lamp (Institute of Electric Light Source, Beijing) was used as the UV excitation source with a 365 nm band pass filter to select 365 nm excitation. An aqueous solution of MO (3.3 ml) was placed in the colorimetric containers. The solution was irradiated with the catalytic films under continuous stirring using a magnetic stirrer. The UV intensity was measured by an irradiance meter (UV-A, BNU) with a 365 nm sensor. For all experiments an average intensity of around 2.8 mW/cm^2 was used. To measure the degradation of MO under visible light, a 150 W high-pressure sodium lamp with an emission peak above 420 nm was used and 80,000 LUX at the sample position obtained (measured by a photometer ST-85, BNU). The amount of photodegradation of MO under these conditions was determined by the OD at 465 nm by a UV–Visible spectrometer (UV-160, Shimadzu). Photocatalytic degradation of MO under sunlight was carried out in Beijing.

3. Results and discussion

3.1. Characteristics of the films

The SEM micrograph of the sample Ag/Fe6E16 is shown in Fig. 1. Other films are similar to this one. It clearly shows that Ag nanoparticles of less than 50 nm are uniformly. distributed on the flat TiO_2 film surface.

XRD patterns of the original TiO_2 film and the sample Ag/Fe6E16 are given in Fig. 2. All the peaks in the patterns belong to anatase TiO_2, indicating that modification by ion implantation and electron beam irradiation did not change the crystalline phase. By using Sherry's formula, we evaluated the size of the TiO_2 crystals and found it increased slightly from 18 nm to 21 nm. As is known, ion implantation may induce film amorphization, but subsequent electron beam irradiation may cause annealing effect and hence increased crystal size. Because of the sparse distribution of the Ag nanoparticles on the TiO_2 surface as observed by SEM, we cannot detect the presence of Ag in XRD patterns. Since there is

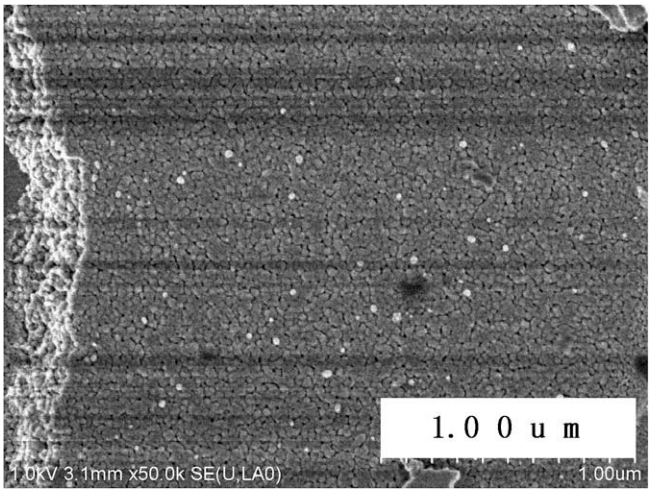

Fig. 1. SEM micrograph of Ag/Fe6E16.

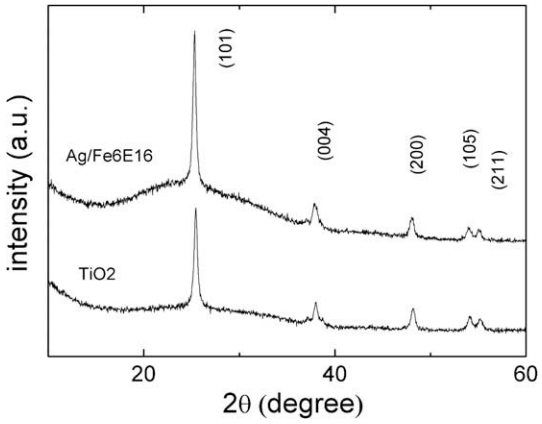

Fig. 2. XRD patterns of the original TiO_2 film and Ag/Fe6E16.

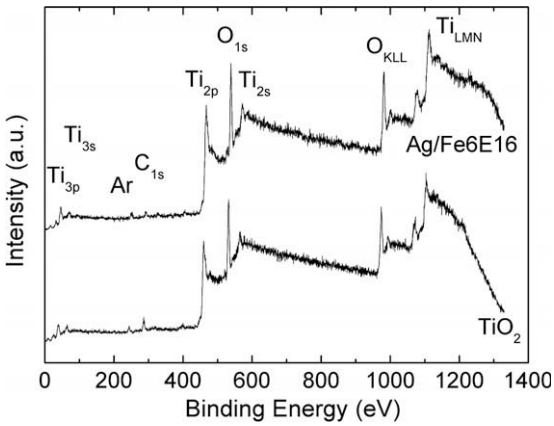

Fig. 3. XPS spectra of original TiO_2 film and Ag/Fe6E16.