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ARTICLE

Photocatalytic Activity and Photodegradation Rate Constant of Au-TiO_2 Nanofilms by Magnetron Sputtering

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Abstract: Au-TiO_2 nanofilms were prepared on indium-tin oxide glass by magnetron sputtering. The growth of well-aligned Au/TiO_2 nanofilms arrays by magnetron sputtering was presented for the first time. The Au/TiO_2 nanofilms were grown on the surface of indium tin oxide (ITO) substrates. The photocatalytic activity of the prepared Au-TiO_2 nanofilms in an aqueous solution of methylene blue (MB) was evaluated under the irradiation of visible-light. The experimental results show that the use of Au in TiO_2 nanofilms improves photocatalytic activity of the MB organic compound significantly in the aqueous solution under the irradiation of visible light, and the photodegradation rate constants of the prepared Au/TiO_2 nanofilms for the photodegradation of MB are larger than that of pure TiO_2 nanofilms.

Key words: magnetron sputtering; Au-TiO_2 nanofilms; visible light; photocatalytic activity; photodegradation rate constant

TiO_2-based materials have attracted great attention because of high activity, nontoxicity, high photo-stability, chemical inertness, low cost and eco-friendly properties of TiO_2[1-3]. The photocatalytic behavior of TiO_2-based materials is controlled by the formation of photo-generated charge carriers (hole and electron), which is induced by ultraviolet (UV) light corresponding to the band gap. To improve the photocatalytic efficiency of TiO_2-based materials and enhance visible-light photoactivity of TiO_2-based materials, various methods, including the use of noble metal[4-7] have been developed to limit the recombination of electrons and holes The use of the magnetron sputtering technique limits potential contamination which is likely introduced in the processes involving the use of aqueous solution and can accurately control the metal loading and the thickness of the coating and the size of the film particles, accelerate the deposition rate, repeat the sputtering process, and realize industrialization easily[8-10].

TiO_2 consists of three different types of anatase, rutile and brookite[11]. The heat treatment at 500 ºC in air for 2 h led to the formation of anatase TiO_2 in the Au/TiO_2 nanofilms[12]. In the crystal structure of anatase, every Ti^{4+} is located in the center of the octahedron, composed of 6 O^{2-}[13]. In the crystal structure, each of the octahedron of the unit cell is connected to the eight adjacent octahedrons, where the four octahedrons share the edge of the oxygen atom pair, and the rest of the four octahedron share the oxygen atoms at the top of the vertex [14]. The band gap of TiO_2 depends on the crystal structure. The band gap of anatase TiO_2 is 3.2 eV [15]. TiO_2, literature in the light under the excitation of electrons mainly from O's 2p rail to Ti's 3d rail[16], and also literature with the absorbed photon excitation of an electron to the conduction band after a generation the positive charge on the hole in the valence band. The excited electrons may be captured by Ti^{3+} and O^-, TiO_2's defects in the lattice structure, or composited with valence band holes[17]. The recombination of photogenerated electrons and holes is one of the reasons to limit the application of TiO_2 photocatalysis[18-20]. Au deposition is without changing the crystal structure. Photo electrons by the modification, from the Au into the conduction band of TiO_2 light, achieved effective separation of photogenerated electron and hole in the visible light conditions[21]. Due to the smaller size of the nanoparticles with surface plasmon resonance effect, under visible light irradiation, Au nanoparticles in the composite electrode can absorb visible

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light and electron hole. The photogenerated electrons produced by the Au can be transferred to the TiO_2 through the Au/TiO_2 interface. The oxidized holes on the surface of Au nanoparticles can react with the water molecules adsorbed on the surface to form the oxidation free radicals[22].

1 Experiment

Au nanofilms on ITO substrates (1 cm×1 cm) were prepared at room temperature (25 °C) by magnetron sputtering in a multifunctional magnetron sputtering instrument (JGP560B) under the condition of high vacuum, using an Au target (purity 99.9%). Experimental parameters of JGP560B are as follows: sputtering power 1.2 kW; average transmittance of the visible light 95%; target current 1 A; target voltage 350 V; air pressure 0.8 V; substrate bias: -100 V; duty cycle 60%; frequency 60 kHz. Prior to deposition, the ITO substrates were ultrasonically cleaned with acetone, ethyl alcohol, and de-ionized (DI) water for 20 min, and dried at room temperature before being placed into the sputtering chamber. Argon gas was flowed into the sputtering chamber after the pressure of the sputtering chamber reached 8×10^{-4} Pa. Pre-sputtering of 3 min was performed to remove surface residuals. The flow rate of argon gas was 30 mL/min and the chamber pressure was 6 Pa during the deposition. The distance between the ITO substrate and the target was 60 mm, and the thicknesses of Au nanofilms were controlled by the sputtering time.

After the deposition of Au nanofilms, a TiO_2 target was used to deposit TiO_2 films with 189 nm thickness on the Au films, using a similar approach and similar conditions. A series of Au/TiO_2 nanofilms with different Au thicknesses were prepared. The prepared Au/TiO_2 bilayer nanofilms were heat-treated at 500 °C for 2 h at a ramping rate of 2 $°C\cdot min^{-1}$ in a furnace in air.

Optical absorptions of the Au/TiO_2 nanofilms in the wavelength range of 300~800 nm were measured using a UV-vis spectrophotometer (Perkin-Elmer, Lambda 750). The banding energy was determined by X-ray photoelectron spectroscopy (XPS) (Escalab 250).

The photocatalytic activity of the prepared Au/TiO_2 nanofilms was evaluated by measuring the degradation behavior of the MB organic compound in an aqueous solution under the irradiation of visible light. The MB aqueous solution (5 $mg\cdot L^{-1}$) of 50 mL was placed in a shallow, round glass vessel with a diameter of 4.5 cm and stirred in the dark at room temperature for 30 min. Three rectangular glass slides of 10 mm×10 mm with the Au/TiO_2 nanofilms were placed in the vessel, which was adequate under the experimental conditions without disturbing the visible light entering the glass vessel. The glass vessel was placed in an ice bath to maintain a constant temperature during the characterization of the photocatalytic activity. A 300 W tungsten lamp (Philips Halogen) with a cutoff filter (λ>420 nm) at a distance of 20 cm above the solution was used to irradiate the aqueous MB solutions. The adsorption of MB on the surface of the Au/TiO_2 nanofilms led to the decrease of the MB concentration in the aqueous solution and the change of the absorbance of the MB aqueous solutions under the irradiation of visible light. To eliminate the effect of background, the photo-induced reactions were performed after mixing the Au/TiO_2 nanofilms with the MB solution in the dark for half an hour to reach a steady state. All the samples for the experiment of photocatalytic activity were calcined at 500 °C.

The photo-induced MB degradation was thus determined from the absorbance of the MB peak at a wavelength of 664 nm, using an UV/vis spectrophotometer (Perkin-Elmer, Lambda 750), from which the MB concentration, c, was estimated as:

$$c=A_0/A \tag{1}$$

where A_0 is the absorbance of MB at the beginning of the irradiation of visible light, and A is the absorbance of MB at time t.

2 Results and Discussion

2.1 XPS analysis

The chemical state of Au in the Au/TiO_2 nanofilms was characterized by XPS. Fig.1a is XPS spectrum of the Au/TiO_2 nanofilm with the Au thickness of ca. 15 nm, which suggests the presence of Au, Ti, and O in the prepared nanofilms by the magnetron sputtering. Fig.1b shows the Au 4f fine XPS spectra of the Au/TiO_2 nanofilms. The binding energies for Au $4f_{7/2}$ and Au $4f_{5/2}$ are found to be ca. 83.11 and 86.81 eV, respectively. This result indicates that Au is present at zero-valence state (Au^0) in the prepared Au/TiO_2 nanofilms and there is no gold oxide [23,24]. The intensity of Au increases with increasing the thickness of Au film, as expected.

It is known that the photocatalytic activity of TiO_2-based materials is dependent on the band gap of the materials, which can be altered by Au. Fig.1c shows the Ti 2p spectra of the Au/TiO_2 nanofilms. The two peaks at ca. 458.5 and 464.2 eV corresponding to the binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels, respectively which are associated with Ti^{4+} in TiO_2 and reveal the presence of the Ti(IV) state. For the pure TiO_2 nanofilms, the peaks in the Ti 2p spectrum associated with the binding energies of Ti $2p_{3/2}$ and Ti $2p_{1/2}$ levels are at 457.8 and 463.5 eV [25], respectively slightly less than the corresponding binding energies of the Au/TiO_2 nanofilms, suggesting the presence of Ti(IV) state. This result indicates a lower electron density of the TiO_2 surface with the presence of Au. The intensity of Ti increases with increasing the thickness of Au film. There is a strong interaction between Au of metallic phase and TiO_2 in the Au/TiO_2 nanofilms.

Fig.1d shows the O 1s spectra of the Au/TiO_2 nanofilms. No new peaks are observed except the peaks at ca. 529.6 and

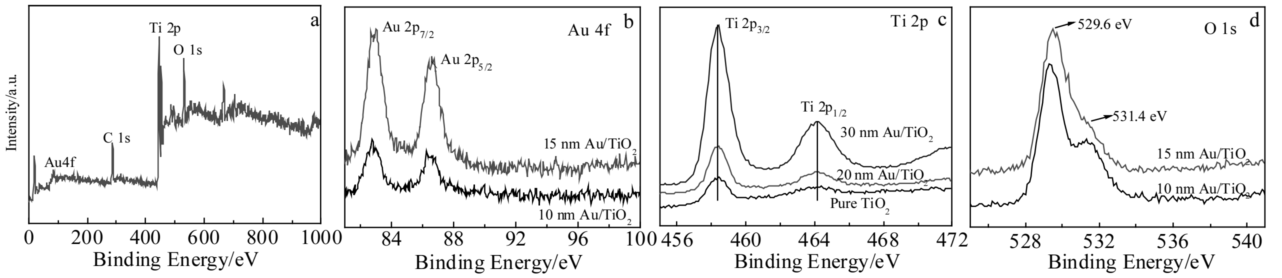

Fig.1 XPS spectra of the Au/TiO_2 nanofilms: (a) the Au thickness of ~15 nm in full region, (b) Au 4f, (c) Ti 2p, and (d) O 1s

531.4 eV, similar to the Ag/TiO_2 nanofilms prepared by magnetron sputtering [26]. The peak at ca. 529.6 eV is ascribed to the Ti-O bonds in the TiO_2 lattice, and the peak at ca. 531.4 eV is related to the oxygen in the surface hydroxyl groups (H-O bonds) [27,28]. The peak with a small intensity is at about 1.8 eV above the major O^{2-} which can be attributed to the surface hydroxyl OH. This result supports the observation that no gold oxide was formed in the Au/TiO_2 nanofilms as revealed in Fig.1a.

2.2 Optical properties of Au/TiO_2 nanofilms

The UV-vis absorption of the TiO_2-based nanofilms was analyzed with a UV-Vis spectrophotometer (HITACHI: U-3900). Fig.2 shows the diffuse reflectance spectra of TiO_2 nanofilm and Ag/TiO_2 nanofilms, in which all the materials were calcined at 500 °C. The pure TiO_2 nanofilm shows the typical absorption of anatase with an intense transition in the UV region, which is due to the excitation of electrons from the valence band to the conduction band. It is evident that all the Au/TiO_2 nanofilms enhance absorption in both the UV and visible light regions in comparison with the pure TiO_2 nanofilms. The enhanced visible absorption peaks 400~600 nm can be attributed to the transfer of photo-generated electrons from Au islands to TiO_2 nanofilm due to the LSPR effect [29-31]. The SPR of Au islands extends the light absorption of the Au/TO_2 nanofilms to larger wavelengths, which increases the light scattering and activates photo-generated charge carriers through the transfer of plasmonic energy from Au islands to the TiO_2 nanofilms.

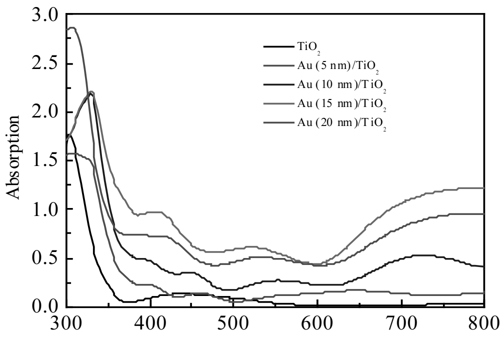

Fig.2 Diffuse reflectance spectra of pure TiO_2 films and Au/TiO_2 nanofilms

All the Au/TiO_2 nanofilms display red-shift absorption in comparison with the TiO_2 nanofilms, suggesting the reduction of the band gap due to the presence of localized energy levels and the increase of the conversion efficiency of solar energy.

It is interesting to note that the absorptions in both ultraviolet light and visible light regions increase with increase of the amount of Au in the Au/TiO_2 nanofilms. The Au/TiO_2 nanofilms prepared with an Au film of 15 nm exhibit strong light adsorption in both UV and visible light regions and will likely have better photocatalytic performance in both UV and visible light regions. The Au/TiO_2 nanofilms prepared with an Au film of 20 nm have the strongest light adsorption around the ultraviolet light of ~310 nm and less light adsorption in visible light region than the Au/TiO_2 nanofilms prepared with an Au film of 15 nm. Such behavior is due to the formation of continuous Au films, as shown in Fig.3d, which become the combination centers of electrons and holes and reduce the surface area of the TiO_2 nanofilm exposed to light.

2.3 Photocatalytic activity of Au/ TiO_2 nanofilms

The photocatalytic activity of the Au/TiO_2 nanofilms was investigated by measuring the degradation behavior of the MB organic compound in an aqueous solution under the irradiation of visible light. Fig.3 shows the temporal evolution of the normalized concentration of the MB organic compound in the aqueous solutions with Au/TiO_2 nanofilms under the irradiation of visible light. For comparison, the results for pure TiO_2 nanofilms are also included in Fig.3. Note that all the materials were calcined at 500 °C. The use of Au in TiO_2 nanofilms improves the photo-degradation of the MB organic compound in the aqueous solution under the irradiation of visible light.

In general, the photocatalytic activity of the Au/TiO_2 nanofilms is dependent on the formation of photoinduced electron-hole pairs from TiO_2 and the transfer of the photogenerated electrons in the conduction band of TiO_2 to Au islands/films. The motion of the photogenerated electrons is directed by thermal motion and electric field around Au islands/films. The Au islands/films act as the reduction sites, at which the electrons are trapped to react with oxygen

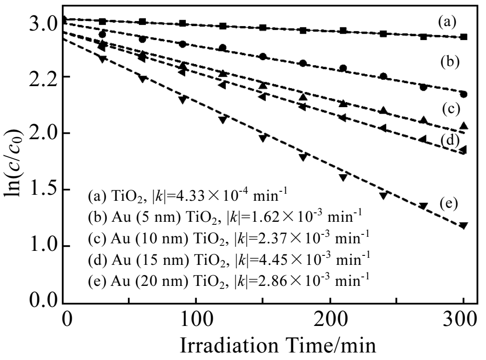

Fig.3 Temporal evolution of the concentration of the MB organic compound in aqueous solution with various Au/TiO_2 nanofilms under the irradiation of visible light (all the materials were calcined at 500 °C)

and form various oxidative species (e.g., ·OH and HO·) [32], which enhance the degradation of MB. Also, the holes left in the valence band of TiO_2 can react with H_2O or hydroxyl (-OH) to produce the reactive oxidative species (such as:·OH), which also react with MB, further leading to the photodegradation of MB.

Under the irradiation of visible light, the electrons in Au films/islands interact with light (electromagnetic wave), leading to selective photon absorption and radiation, as well as enhanced electromagnetic fields around the films/islands, i.e. localized surface plasmons (LSP). The electromagnetic field makes it easy to transfer electrons and accelerates the reaction between electrons and the electron acceptors, which assist photocatalytic process and improve the photo catalytic activity of the Au/TiO_2 nanofilms through LSPR effect. Thus, one can conclude that Au films/islands in the Au/TiO_2 nanofilms enhance the photodegradation of MB through the light-assisted transfer of electrons and the LSPR effect.

2.4 Photodegradation rate constant of Au/TiO_2 nanofilms

It is known that the differential equation describing first-order kinetics is

$$-\frac{\mathrm{d}c}{\mathrm{d}t}=kc \tag{2}$$

where c is the concentration and k is the photodegradation rate constant and $kc \ll 1$. The solution of Eq.(2) gives the temporal evolution of the concentration for the first-order reaction as

$$\ln(c_0/c)=kt \tag{3}$$

It is evident from Fig.3 that the photo-induced degradation of the MB organic compound in an aqueous solution follows the first-order reaction. From the regression of experimental data, the rate constant, k, can be determined. Fig.4 shows the photodegradation rate constants for the photo-induced degradation of MB in the aqueous solutions with different Au/TiO_2 nanofilms. For the same conditions, the pure TiO_2 nanofilms have the lowest removal efficiency of MB, indicating the limited photocatalytic activity of the TiO_2 nanofilms due to poor response to visible-light and low adsorptivity. The rate constants for the aqueous solutions with the Au/TiO_2 nanofilms are larger than that of self-degradation and that with the pure TiO_2 nanofilms, suggesting that Au improves the photocatalytic activity of TiO_2 nanofilms. The Au-assisted removal of MB can be attributed to the LSPR effect of Au islands which activates photo-generated charge carriers through the transfer of plasmonic energy [29,33]. It is worth pointing out that the Au/TiO_2 nanofilms prepared with an Au film of 20 nm in thickness has a smaller photode-gradation rate constant for the removal of MB than the Au/TiO_2 nanofilms prepared with an Au film of 15 nm. Such behavior is due to that there is less surface area available for the photocatalytic activity and the continuous Au films become recombination centers for photo-generated electron-hole pairs. One needs to control the amount and distribution of Au in the Au/TiO_2 nanofilms in improving the photocatalytic activity of Au/TiO_2 nanofilms.

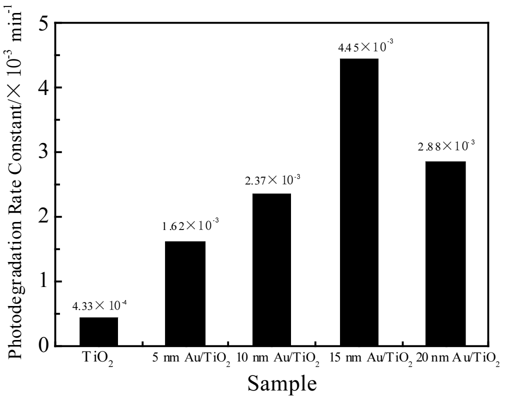

Fig.4 Photodegradation rate constants in the unit of min^{-1} for the photo-induced degradation of MB in the aqueous solutions with different Au/TiO_2 nanofilms

3 Conclusions

1) Au/TiO_2 bilayer nanofilms are deposited on ITO substrates by magnetron sputtering. There are the migration of electrons from TiO_2 nanofilms to metallic Au films/islands and a strong interaction between films/islands and TiO_2 nanofilms at the interface of the nano-heterostructures. The prepared Au/TiO_2 nanofilms exhibit an obviously overlapped light absorption.

2) The use of Au in TiO_2 nanofilms expands the absorption spectrum of TiO_2 and limits the recombination of electrons and holes, thus improving the photo-degradation of the MB organic compound in the aqueous solution under the irradiation of visible light.

3) The photodegradation rate constants for the aqueous solutions with the Au/TiO_2 nanofilms are larger than that of self-degradation and that with the pure TiO_2 nanofilms through the LSPR effect of Au films/islands which activates photo-generated charge carriers via the transfer of plasmonic energy.

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磁控溅射制备的 Au-TiO_2 薄膜的光催化活性和光降解速率常数研究

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摘　要：在ITO玻璃中采用磁控溅射法制备了Au-TiO_2纳米薄膜, Au-TiO_2纳米薄膜生长于ITO基板表面，在可见光条件下, 在亚甲基蓝水溶液中评价Au-TiO_2纳米薄膜的光催化活性。结果表明：贵金属Au的添加显著提高了纯TiO_2纳米薄膜的光催化活性, Au-TiO_2纳米薄膜的光降解速率常数远高于纯TiO_2纳米薄膜的光降解速率常数。

关键词：磁控溅射；Au-TiO_2纳米薄膜；可见光；光催化活性；光降解速率常数

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