

Research Article

Structure and Properties of La_2O_3 - TiO_2 Nanocomposite Films for Biomedical Applications

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The hemocompatibility of La_2O_3 -doped TiO_2 films with different concentration prepared by radio frequency (RF) sputtering was studied. The microstructures and blood compatibility of TiO_2 films were investigated by scan electron microscopy (SEM), X-ray photoelectron spectroscopy (XPS), and UV-visible optical absorption spectroscopy, respectively. With the increasing of the La_2O_3 concentrations, the TiO_2 films become smooth, and the grain size becomes smaller. Meanwhile, the band gap of the samples increases from 2.85 to 3.3 eV with increasing of the La_2O_3 content in TiO_2 films from 0 to 3.64%. La_2O_3 -doped TiO_2 films exhibit n-type semiconductor properties due to the existence of Ti^{2+} and Ti^{3+} . The mechanism of hemocompatibility of TiO_2 film doped with La_2O_3 was analyzed and discussed.

1. Introduction

With the advancement of organ transplantation, biocompatibility, particularly blood compatibility, becomes the most important property required for biomedical materials. It is desired to develop new biomaterials with good physical, mechanical properties and hemocompatibility. Recent studies have shown that TiO_2 films are suitable as surface coatings on biomedical applications due to its good hemocompatibility [1, 2], and researches concerning biomedical aspects are widely increasing [3–5]. The emphases of blood compatible materials research are divided into two aspects, one is the surface properties, and the other is the band and electron structure of the biomedical materials.

It is believed that the first step after blood contacting with the biomaterial is adsorption of plasma protein, which will determine the anticoagulation property of the biomaterial. In our previous paper [6], we studied the surface properties of La_2O_3 -doped TiO_2 films and investigated the interaction between the material surface and plasma proteins. In this paper, we do the farther work and try to achieve deeper understanding of the mechanisms which are involved in blood-biomaterial interaction by investigating the influence

of various La_2O_3 concentrations on the electronic structure and hemocompatibility of TiO_2 nanocomposite films.

2. Materials and Methods

2.1. Preparation of Thin Films. The La_2O_3 -doped TiO_2 films were prepared by the radio frequency (13.56 MHz) magnetron sputtering technique. The n-type Si (100) and quartz were used as the substrates. The targets were mechanically mixed by using TiO_2 powder (in purity 99.9%) and La_2O_3 powder (in purity 99.5%) with the La_2O_3 molar concentration of 0%, 1%, 2%, and 3%, respectively. The substrates were ultrasonically cleaned in acetone and then were mounted on the substrate holder. After being evacuated to a base pressure of 3×10^{-3} Pa, the working chamber was filled with Ar (99.99% purity) and the Ar gas flow was kept constant at 12 SCCM during the deposition process. The samples were prepared in room temperature with a typical work pressure of 4 Pa. The RF power of 200 W was applied in the sputtering process. The samples S1, S2, S3, and S4 are prepared using the targets with a doped La_2O_3 molar content of 0%, 1%, 2%, and 3%, respectively.

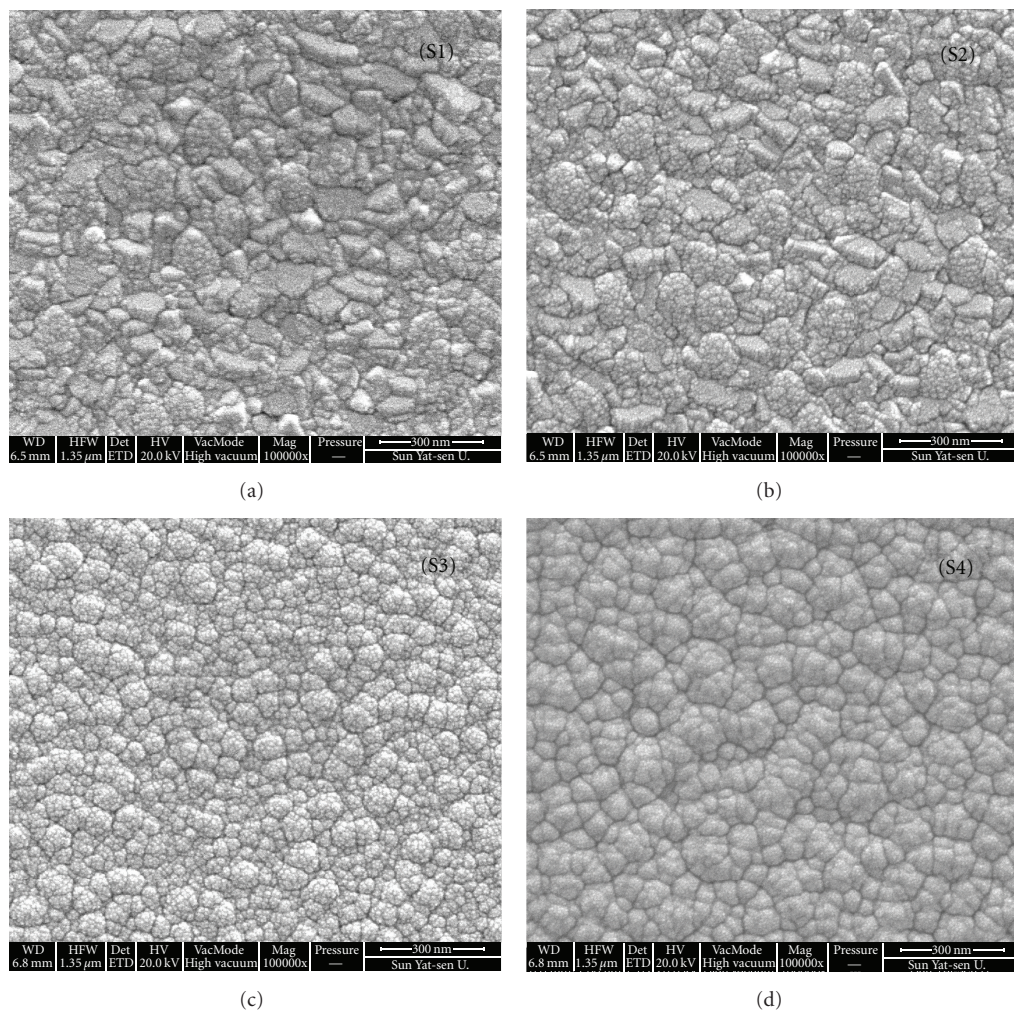


FIGURE 1: Typical SEM images of the surface images of TiO_2 thin films doped with La_2O_3 with various concentrations (a) S1; (b) S2; (c) S3; and (d) S4.

2.2. Characterization of Thin Films. Scanning electron microscopy (SEM, QUANTA 400F) was employed to characterize the surface topography of the TiO_2 nanocomposite films. The compositions were analyzed by X-ray photoelectron spectroscopy (XPS, ESCALAB 250, UK). The XPS spectra were recorded using $\text{Mg K}\alpha$ (1253.6 eV) X-ray source. The binding energy of the $\text{Au } 4f_{7/2}$ core level electron is taken to be 84.0 eV for energy calibration. Spectra were recorded with 20 eV pass energy for the survey scan and with 10 eV pass energy for the $\text{La } 3d$ and $\text{Ti } 2p$ regions. High resolution XPS conditions have been fixed: “fixed analyser transmission” analysis mode, a 7×20 mm entrance slit and 150 W electron beam power. A takeoff angle of 90° from the surface was employed. The spectra were fitted using the Casa XPS v.2.3.13 Software (Casa software Ltd., UK) and by applying a Gaussian/Lorentzian ratio, G/L equal to 70/30. Before measurement, Ar ion etching was performed 8 minutes with an etching rate of 0.025 nm/s in order to eliminate atmosphere contaminants. A double-beam UV-visible spectrometer was used to investigate the optical absorption of the samples. The absorption spectra (in the

wavelength range of 200–700 nm) were obtained by using a bare quartz substrate to eliminate the substrate contribution.

3. Results and Discussion

3.1. Structure Properties. The SEM photographs of TiO_2 nanocomposite films are shown in Figure 1. The surface morphology of the films becomes smooth with increasing of the La_2O_3 content in TiO_2 films, and the grains are uniform. Figure 2 shows the grains size of TiO_2 films decreases from 133 nm to 56 nm. These micrographs, in combination with results derived by XRD, showed in our previous paper [6], suggest that La dopant not only greatly promotes the phase transfer from anatase to rutile and enhances the crystal phase of TiO_2 with preferential growth in the direction of (110), but also can refine grain size of TiO_2 .

3.2. XPS Characterization. The $\text{La } 3d$ spectrum of TiO_2 nanocomposite films, showed in our previous paper [6], indicated that the La exists as La_2O_3 in TiO_2 films. All La_2O_3 -doped TiO_2 films show similar results. As a comparison

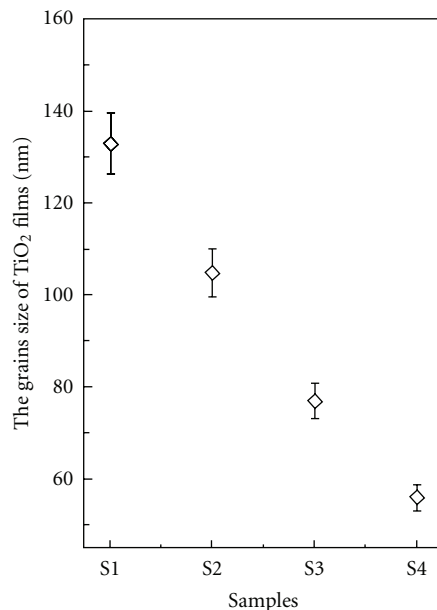


FIGURE 2: The distribution of grains dimensions.

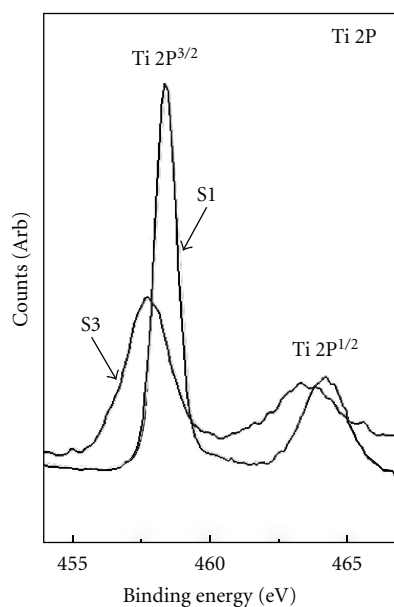


FIGURE 3: XPS spectrum of the Ti 2p region for the surface of S1 and S3.

with undoped sample, the high-resolution XPS analysis of the Ti 2p region obtained on the surface of S1 and S3 was shown in Figure 3. Two pronounced features are observed at binding energies near 458.4 eV and 464.3 eV, corresponding to the Ti 2p_{3/2} and Ti 2p_{1/2} states, respectively. The two peaks of S1 are symmetrical, which indicates that Ti exists as Ti⁴⁺ in TiO₂ films. It is obvious that doping La₂O₃ not only leads to the positions of two peaks of S3 shift towards lower binding energies, but also impels a broad shoulder of the two peaks. The ratio of the area of the two peaks $A(\text{Ti } 2p_{1/2})/A(\text{Ti } 2p_{3/2})$ is equal to 0.7, and the splitting of the

doublet $\Delta E_b = E_b(\text{Ti } 2p_{1/2}) - E_b(\text{Ti } 2p_{3/2})$ is 5.9 eV, which indicates that the doublet was mainly assigned to Ti⁴⁺ and the minor contributions of Ti²⁺ and Ti³⁺ should be taken into account as follows: (1) Ti²⁺ was from Ti₂O₃ species, with the binding energies locating at $E_b(\text{Ti } 2p_{3/2}) = 457.50$ eV and $E_b(\text{Ti } 2p_{1/2}) = 463.30$ eV; (2) Ti³⁺ was from Ti₂O₃ species, with the binding energies locating at $E_b(\text{Ti } 2p_{3/2}) = 457.50$ eV and $E_b(\text{Ti } 2p_{1/2}) = 463.30$ eV [7].

3.3. Optical Absorption Spectra. The optical properties of the films were investigated by UV-visible spectroscopy

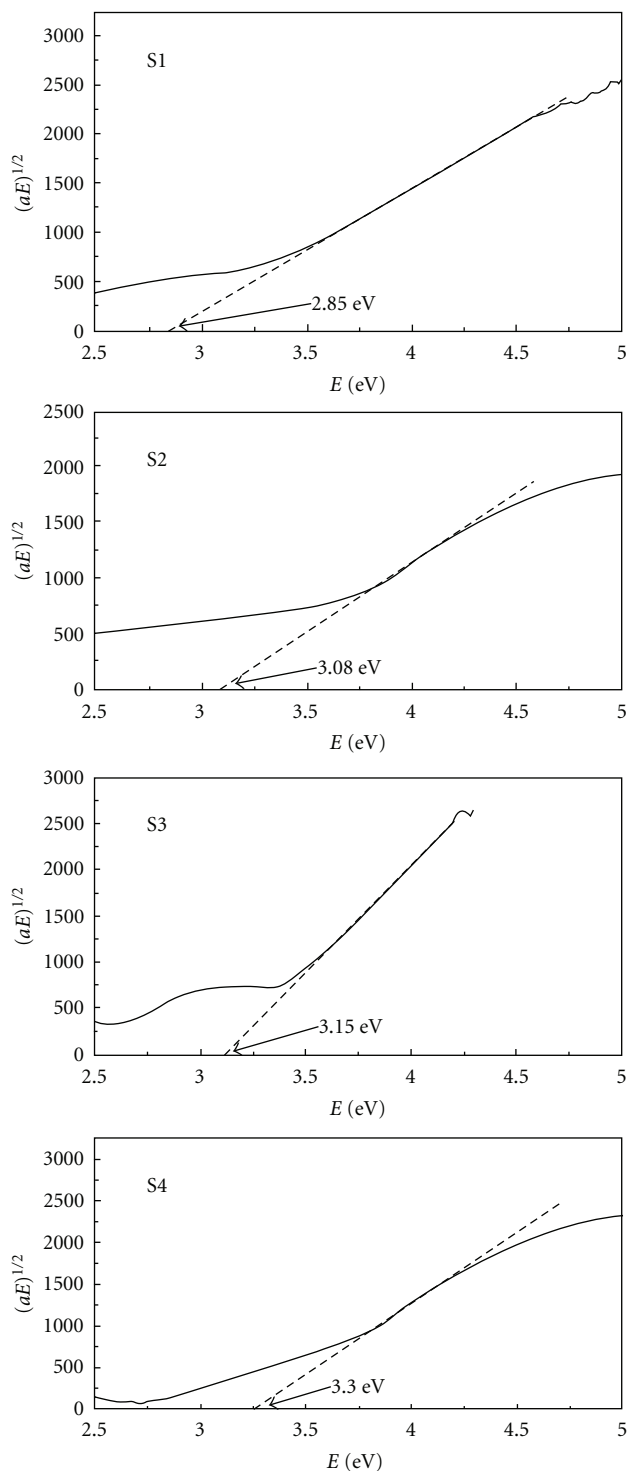


FIGURE 4: Tauc plot of $(\alpha h\nu)^{1/2}$ as a function of photon energy ($h\nu$) for different amount of La_2O_3 -doped TiO_2 thin films.

measurements in the wavelength range of 200–700 nm. Tauc relationship $\alpha E = B(E - E_g)^2$ [8] was used to evaluate the optical gap values (E_g). Figure 4 shows the plot of $(\alpha h\nu)^{1/2}$ as a function of photo energy ($h\nu$) for the films. It is clearly seen that the optical gap varies significantly with the La_2O_3 concentration in TiO_2 films, and E_g of the samples increases from 2.85 to 3.3 eV with increasing of the La_2O_3 content in

TiO_2 films from 0 to 3.64%. It is known that the quantum confinement will affect the electronic properties if the radius of the semiconductor particle is commensurable or smaller than the Bohr radius. As for TiO_2 , the effect of quantum-sized confinement is expected if the particles become smaller than 10 nm (usually 2–3 nm) [9, 10]. According to the measuring results of SEM (showed in Figure 2), the increase

of band gap of TiO_2 could be due to the presence of La_2O_3 . For pure La_2O_3 , the band gap is around 4.3 eV, higher than pure TiO_2 .

The interaction between blood and contacting biomaterials is very complicated and the detailed mechanism of hemocompatibility of TiO_2 films is still not clear. It is demonstrated that the formation of thrombus on biomaterial is correlated with electrons transferring from the inactive state of fibrinogen to the surface of the biomaterial. During the process, fibrinogen decomposes to fibrin monomer and fibrinopeptides. After decomposition, fibrin monomers give rise to polymers and cross-linking and finally form an irreversible thrombus [11]. So fibrinogen plays an important role in hemostasis [12]. Not only does it participate in the coagulation cascade, but also it promotes adhesion of platelets and activates them when adsorbed onto certain solid surfaces [13]. Therefore, after the adsorption of fibrinogen, it is very important to postpone the decomposition of the protein for a biomaterial with good blood compatibility. It is related to the semiconductor property of TiO_2 films.

It is found that the optical band gap La_2O_3 -doped TiO_2 film is about 3.3 eV, and the Ti^{2+} and Ti^{3+} states exist in the TiO_2 film. This makes the film exhibit n-type semiconductor properties. It is proved that fibrinogen has an electronic structure similar to an intrinsic semiconductor with a band gap of 1.8 eV. When fibrinogen adsorbs on the surface of TiO_2 films, the transfer of electrons is determined by the Fermi level of the film and fibrinogen. In order to inhibit the transfer of the electrons from fibrinogen to La_2O_3 -doped TiO_2 film, the Fermi level of La_2O_3 -doped TiO_2 film must be close to the bottom of the conduction band, that is to say, reducing the work function of the film. The existence of Ti^{2+} and Ti^{3+} exhibits this effect. Thus, the perfectly electronic characteristics such as wider band gap and lower work function due to La dopant make La_2O_3 -doped TiO_2 films exhibit better blood compatibility.

4. Conclusion

This study represents the relationship between the electronic structure and hemocompatibility. With the increasing of the La_2O_3 concentrations, the TiO_2 films become smooth, and the grain size becomes smaller. The band gap of the samples increases from 2.85 to 3.3 eV with increasing of the La_2O_3 content in TiO_2 films from 0 to 3.64%. Based on the contact angles and platelet adsorption experiments, La_2O_3 -doped TiO_2 films not only possess excellent surface properties of absorbing human serum albumin (HAS) preferentially, but also exhibit n-type semiconductor properties, which farther inhibit the transfer of the electrons from fibrinogen to TiO_2 films.

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