Micro-nano hierarchical porous titania modified with ZnO nanorods for biomedical applications

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A porous titania structure with micro-isolated holes and grooves is prepared by micro-arc oxidation on titanium and ZnO nanorods are subsequently electrodeposited on the walls of the pores to produce a micro-nano hierarchical structure suitable for biomedical applications. The hydrophilic property of the structure depends on both the porous structure of the titania as well as morphology of the ZnO nanorods. By changing the fabrication parameters, the structure of the hierarchical structure can be adjusted in order to fine tune surface hydrophilic properties. The micro-nano hierarchical structure is suitable hard tissue replacement implants and other medical applications such as photodynamic therapy (PDT).

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used in MAO with the pretreated titanium sheets being the anode and stainless steel sink as the cathode. The samples were suspended in the electrolyte during MAO. The constant voltage mode with a forward voltage of 200 V–500 V, negative voltage of 0 V–100 V, pulse frequency of 50 Hz–1000 Hz, duty cycle of forward 10%–20% and negative 0%–10% was adopted and the oxidation time was 10 min–30 min. After MAO, the specimen was removed and washed with deionized water.

The pore wall surfaces of porous titania were deposited with ZnO nanorods by electrodeposition. The titanium sheets with porous titania surface were first washed with deionized water and dried. The electrodeposition electrolyte containing 1–5 mM Zn²⁺, the same molar amount of hexamethylenetetramine (HMT), and 0.1 M–0.5 M KCl was placed in a constant-temperature water bath at 60 °C–90 °C after purging with air for 2 h–10 h. The samples were placed in the bath as a cathode and the graphite electrode served as the anode. The electrodeposition time was 15 min–90 min and deposition voltage was 1.0 V–2.5 V. After that, the electrodeposited samples were ultrasonically washed with deionized water, and then dried.

An FEI SIRION field-emission scanning electron microscope (FE-SEM) was used to examine the morphology of the porous titania, ZnO nanorods, as well as micro-nano hierarchical structure at an accelerating voltage of 20 kV. The samples were coated with gold prior to SEM. A SHIMADZU XD-3A X-ray diffraction (XRD) instrument was used to determine the phases under the following conditions: Cu Kα radiation, wavelength of 0.15406 nm, acceleration voltage of 40 kV, current of 30 mA, grazing angle of 2°, and scan range of 10°–90°. The measured angle error was less than ±0.01°. The surface contact angles were determined using the liquid drop method on a contact angle goniometer (JC2000B, China). A 10 μL droplet of deionized water was put onto the sample surface to measure the contact angle and each contact angle value was the average of 10 measurements.

3. Results and discussion

The porous titania with micro-isolated holes and grooves produced on titanium by MAO serves as the substrate for the micro-nano hierarchical surface structure. Fig. 1a and b depicts the morphology of the porous titania fabricated by MAO in the constant voltage mode using a voltage of 400 V and frequency of 50 Hz. The holes in the porous titania exhibit a uniform distribution and an isolated circular shape with a uniform diameter of approximately 5 μm. Some small pores can be seen from the wall of the holes. Fig. 1c and d displays the morphology of the porous titania obtained under the same conditions except the MAO frequency which is increased to 800 Hz. The holes also exhibit a uniform distribution and a micro groove structure which can be attributed to the partial fusion of the micropores during the micro-arc discharge.

The formation of porous titania is discussed in the following. Initially, the titanium as the anode has good conductivity and the electrolyte contains a large number of ionic species. After the power is turned on, the anions aggregate onto the surface of the titanium plate under the external electric field and the titanium surface is oxidized to form a porous oxide film. At the same time, the non-conductive oxide film and physically-adsorbed gas on the porous anode surface can cause the partial-discharge effect. The microdischarge phenomenon occurs when the voltage is raised to a certain value. The discharge channel is formed in the interior of the film and then the micro-arc rapidly penetrates the oxide film. At a high MAO temperature, the oxide on the titanium surface and surface particles begin to melt. Partial melting softens the surface and finally, a porous structure is produced on the titanium surface. By increasing the MAO frequency while keeping the processing time and electrical parameters the same, more heat is generated near the electrodes causing a temperature rise in the electrolyte. This high temperature environment is not conducive to the

![Fig. 1. Two porous titania with different porous structures fabricated by MAO on titanium surface: (a) micron isolated holes, low magnification; (b) micron isolated holes, high magnification; (c) micron grooves, low magnification; (d) micron grooves, high magnification.](image-url)
timely condensation of the discharge holes. In fact, with continuous breakdown, the micro-arc holes continue to expand and increase in number. As shown in Fig. 1c and d, the micro-arc discharge holes are changed from a round shape to an elongated groove. In addition, our study also reveals that by adjusting the MAO parameters, the pore size of the porous titania can be regulated. For example, by increasing the voltage or extending the time, both the thickness of the oxide film and pore size increase.

The porous titania is subsequently deposited with ZnO nanorods by electrodeposition to construct the final micro-nano hierarchical structure. Fig. 2 shows the FE-SEM images of structures undergoing ZnO electrodeposition for different time. Before SEM observation, the electrodeposited samples were ultrasonically washed with deionized water. Thus the observed ZnO nanorods may have a good binding with the titania substrate. The fine structure of the hierarchical topology can be readily adjusted by changing the electrodeposition time. After electrodeposition for 15 min, the ZnO crystals exhibit a nanocone shape at a small density. The ZnO nanocones are more concentrated on the internal walls of the pores. However, after 30 min, the ZnO crystals possess a rod structure at a high density. After electrodeposition for 90 min, both the diameter and length of ZnO nanorods show little changes compared with those of 30 minute deposition, but the density is larger and the substrate is covered by the densely distributed ZnO nanorods. Fig. 3 shows XRD patterns of the samples deposited for different time. As the deposition time is increased, the intensity of the diffraction peaks of ZnO nanocrystal increases, indicating that the size and crystallinity of the ZnO nanocrystals increase. Fig. 4 shows the FE-SEM images and that the fine structure of the hierarchical topology can be easily adjusted by changing the electrodeposition time of ZnO nanorods. When the deposition time is 15 min, scattered ZnO crystals are observed from the groove surfaces and after 30 min, the ZnO nanocrystals have a rod-like morphology at a larger density. After 90 min, the entire groove surface on the porous titania substrate is completely covered by ZnO nanorods with a uniform morphology. The ZnO nanorods have a similar distribution along the groove surface of the porous

![Fig. 2. FE-SEM images of different hierarchical topological structures by electrodepositing ZnO nanorods for different time on porous titania surfaces with micro isolated holes: (a) 15 min, low magnification; (b) 15 min, high magnification; (c) 30 min, low magnification; (d) 30 min, high magnification; (e) 90 min, low magnification; (f) 90 min, high magnification.](image-url)
titania and the grooves resemble corals. As shown in Fig. 2e and f, the density of ZnO nanocrystals is larger. Under the same deposition conditions, compared to the porous titania with isolated circular holes, the porous titania with microgrooves can more easily promote deposition of the ZnO nanostructures. The groove is larger than the isolated holes thus increase the surface roughness of the porous titania. The porous titania with microgrooves provide more nucleation sites and better growth conditions for the ZnO nanorods.

Fig. 5 shows the XRD patterns of the sample undergoing deposition for 90 min. According to the hexagonal ZnO crystals characteristic diffraction peaks (JCPDS No. 36-1451), the diffraction peaks at 2θ angles of 31.7°, 36.2°, 47.5°, and 62.8° correspond to, respectively, the crystal planes of (100), (002), (102), and (103). However, the diffraction peak intensity associated with the ZnO crystal plane (002) on porous titania with microgrooves is much larger than that of the porous titania with micro isolated holes, indicating that the ZnO crystals on the former substrate have a larger density and a more preferential growth trend. The results are consistent with Fig. 4e and f.

As hard tissue implant materials, the surface microstructure and hydrophilic properties of titanium and its alloys play important roles in the biological function and behavior of living tissues. The surface microstructure can provide a better attachment site for osteoblasts and promote bone growth. The hydrophilic properties can increase the affinity of biomolecules and improve the biocompatibility of the material.

![XRD patterns of hierarchical topological structures](image)

**Fig. 3.** XRD patterns of the hierarchical topological structures by ZnO nanorods electro-deposited for different time on porous titania substrates: (a) 15 min; (b) 30 min.

![FE-SEM images](image)

**Fig. 4.** FE-SEM images of different hierarchical topological structures by electrodepositing ZnO nanorods for different time on porous titania surfaces with micron grooves: (a) 15 min, low magnification; (b) 15 min, high magnification; (c) 30 min, low magnification; (d) 30 min, high magnification; (e) 90 min, low magnification; (f) 90 min, high magnification.
roles on the biological response of the surrounding cells and body tissues. Here, the surface hydrophilic properties of the micro/nano hierarchical topological structure on the porous titania substrate are assessed by contact angle measurements. Fig. 6 shows the porous titania surface with micro holes and grooves and the contact angle photographs are displayed on the upper right corners. Both types of surfaces exhibit good water spreading ability indicative of superhydrophilicity with a contact angle of close to 0°.

Fig. 7 shows four different hierarchical topological structures produced under different conditions and the upper right corner shows the contact angle photographs. The porous titania has micro isolated holes (Fig. 7a and b) and micro grooves (Fig. 7c and d), respectively. The zinc concentrations in the electrolytes are 2.5 mM (Fig. 7a and c) and 5 mM (Fig. 7b and d). The other electrodeposition parameters are: deposition voltage of 2 V and deposition time of 30 min. There are significantly differences in the hydrophilic properties of the four different structures and porous titania. The surface contact angles on the porous titania with different porous structures increase after modification with ZnO nanorods. The Zn concentrations are 2.5 mM and 5 mM, the contact angles are about 75° and 66°, respectively, whereas those on the porous titania with micro grooves as the substrate are about 35° and 20°, respectively. Our results reveal that the hydrophilic properties of the hierarchical topological structure depend on not only the porous structure of the titania substrate but also on the morphology of the ZnO nanorods.

Fig. 8 shows the fine structures of the two hierarchical structures fabricated on porous titania with micro grooves and zinc ion concentrations of 2.5 mM and 5 mM during electrodeposition. The ZnO nanorods with a uniform morphology have a similar distribution along the groove surface of the porous titania and the topography resembles corals. A close examination reveals that the two samples are different. When the concentration of Zn is 2.5 mM, the ZnO nanorods have a diameter of approximately 200 nm and length about 2 μm, but when the Zn2⁺ concentration is increased to 5 mM, the ZnO nanorods have a large diameter of about 300 nm and similar length of about 2 μm. The results disclose that under these conditions, the change in the Zn concentration in the electrolyte has little effects on the distribution and length of ZnO nanorods but can change the diameters.

As aforementioned, contact angle measurements can reflect the hydrophilic properties and surface energy. MAO produces a rough and porous titania surface enriched with Ti–OH groups which enhance the hydrophilic performance of the titanium implants [16]. At the same time, the wettability is greatly improved. When the porous titania surface is modified by ZnO nanorods, the sample has a roughened surface composed of ZnO nanorods. The composite contact angle on a composite surface with a certain roughness can be expressed as follows [17]:

\[
\cos \theta_r = rf_1 \cos \theta - f_2,
\]

where \( \theta \) is the water contact angle of the flat surface, \( \theta_r \) is water contact angle of the roughened surface, \( r \) is the roughness factor, \( f_1 \) and \( f_2 \), respectively, are the proportion of ZnO nanorods and air in the roughened surface, and \( f_1 + f_2 = 1 \). As shown in Fig. 8, a smaller Zn concentration leads to a smaller nanorod diameter. Thus, the proportion of ZnO nanorods on the roughened surface \( f_1 \) is smaller while that of air \( f_2 \) is larger. As a result, \( \theta_r \) increases, suggesting increased surface hydrophobicity, which is consistent with the experimental results in Fig. 7. Meanwhile, the pore size of the porous titania with micro grooves is larger than that of the one with micro isolated holes. The roughness factor \( r \) of the former is larger. The ZnO nanorods have a similar distribution on the porous titania. Under the same electrodeposition conditions, the water contact angle of the hierarchical topological structure on the porous titania substrate containing micro grooves is smaller than that on the one with a porous titania substrate and micro isolated holes. Therefore, by changing the MAO and electrodeposition parameters, the hierarchical topology can be adjusted and the surface hydrophilic properties can be effectively tuned.

The ultimate issue is the effects on the biological response of cells and body tissues. The bioactive porous titania coating with a micro-nano hierarchical topological has strong adhesion strength and can promote the growth of the bone-like apatite [16,18–20]. The porous titania structure with zinc oxide nanostructures can be utilized to load trace elements and special drugs [21,22] due to the increased exposure. By changing the structure of the porous titania and the
morphology of ZnO nanorods, the surface hydrophilic properties and the subsequent response by the surrounding cells can be controlled \[23,24\]. The micro-nano hierarchical structure has potential applications in artificial tooth roots or artificial joints made of titanium \[1\]. By adjusting the processing parameters, a bioactive porous titania surface layer with a controllable porous structure can be formed on titanium implants by MAO and ZnO nanorods with different morphologies can subsequently be electrodeposited by adjusting the deposition parameters \[25\].

Both the ZnO nanocrystals and porous titania are photosensitive semiconductor materials. Here, the ZnO nanocrystals are uniformly distributed on the porous titania and the heterojunction becomes the bound center for excitons. Therefore, the micro-nano hierarchical topology may play a role in functional photocatalytic composite materials in photosensitizers for photodynamic therapy (PDT) in the treatment of cancer \[26,27\]. In addition, the structure can be used in chemical or electrochemical separation, adsorption, rapid degradation of toxic liquid organic pollutants such as toluene and phenol in ultraviolet or natural light \[28\].

4. Conclusion

A micro-nano hierarchical structure with ZnO nanorods is produced on porous titania and the hydrophilic properties depend on both the porous titania substrate and morphology of the ZnO nanorods. By changing the micro-arc oxidation and electrodeposition parameters, the hierarchical topology can be varied and the resulting surface hydrophilic properties can be tuned. The materials have potential applications in hard tissue replacements, photodynamic therapy, and photocatalytic degradation of toxic liquid organic pollutants.

Fig. 7. Four different hierarchical topological structures produced by changing the porous titania substrates and zinc concentrations in the electrodeposition electrolytes. The upper right corners are the contact angle photographs: (a) porous titania with micro holes, 2.5 mM Zn\(^{2+}\); (b) porous titania with micro holes, 5 mM Zn\(^{2+}\); (c) porous titania with micro grooves, 2.5 mM Zn\(^{2+}\); (d) porous titania with micro grooves, 5 mM Zn\(^{2+}\).

Fig. 8. Structures of two hierarchical topology fabricated on porous titania with micro grooves and different zinc ion concentrations in electrodeposition: (a) 2.5 mM Zn\(^{2+}\); (b) 5 mM Zn\(^{2+}\).
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