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Preparation and Photoelectrochemical properties of TiO_2 nanotube arrays modified with nano-scaled CdSe

Jia-qin Liu[a], Yan Wang, Guang-qing Xu, Hong-mei Zheng, Rong-jun Pan, Yu-cheng Wu[b]

Laboratory of Functional Nanomaterials and Devices, College of Material Science and Engineering, Hefei University of Technology, Tunxi Road 193, Hefei 230009, China

[a]jqliu_hfut@163.com, [b]ycwu@hfut.edu.cn

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Abstract. Highly ordered TiO_2 nanotube arrays (TNTAs) with smooth walls and uniform diameter were prepared by electrochemical anodization. And then solution deposition process was adopted for the modification of the TNTAs with nano-scaled CdSe. The materials obtained were characterized by field emission scanning electron microscopy, UV–visible spectroscopic and photoelectrochemical techniques. The results revealed that the morphologies and growth mechanism for CdSe/TNTAs composites varied with the reaction time in Se^{2-} solutions (c=1.2 mol/L) when nanotubes were firstly imported with Cd^{2+} ions. Optical absorption behavior of the CdSe/TNTAs composites increased with more CdSe nanoparticles. And the photo-response of the obtained nanomaterials was first strengthened and then declined with the sustained increase of the deposited CdSe.

Introduction

Well aligned TiO_2 nanotubes (TNTAs) fabricated by electrochemical anodization of pure titanium foil have attracted tremendous attention because of their huge surface area and ordered structure, leading to the excellent light energy trapping characteristics, superior charge separation and transfer characteristic. Therefore, TNTAs were widely used in various areas, including photocatalysis for hydrogen generation, photovoltaics, gas sensing, drug delivering, lithium anode materials and so on. However, as is well known, TiO_2 is a wide band-gap semiconductor (Eg = 3.2 eV for anatase phase) that can only be excited by ultraviolet radiation which accounts for only a small fraction (≈5%) of the sun's energy compared to the visible light (≈45%). At the same time, the recombination rate of the photo-generated electron–hole pairs for TiO_2 usually shows a high value. Therefore, it is of great importance for the TNTAs to extend its ability to harvest solar energy into the visible part of the spectrum and promote the separation of the photo-generated carriers. This has recently been done by using dyes sensitization, anionic/cationic ions doping, precious metals deposition and modification with narrow band gap semiconductor materials [1-8].

Currently, narrow band gap semiconductor materials, such as CuO/Cu_2O, Fe_2O_3, CdX (X = S, Se, Te), Sb-doped SnO_2, were adopted for the decoration of TNTAs in order to extend the optical absorption edge to the visible region for the nano-array membrane material, as well as to promote the charge separation by isolating the photogenerated electrons and holes in two distinct parts.

CdSe is an n-type and direct transition-type semiconductor material (Eg=1.76eV) with effective capture of the solar energy. When $CdSe/TiO_2$ heterojunctions was formed, the light-generated carriers in CdSe could be injected into the conduction band of TiO_2 and then promote the separation of the charge. Therefore, much effort has been paid to synthesize CdSe sensitized TNTAs[9-13]. TNTAs can be immersed into the liquid system dispersed with CdSe nanoparticles and the amount of CdSe could be adjusted by controlling the time of immersion [9,11]. And the CdSe nanoparticles could also be introduced into the TNTAs via electrochemical deposition method [10,14]，but the deposited CdSe nanoparticles usually attached to the surface of the nanotube arrays, resulting in clogging of the TiO_2 nanotubes and the performance reduction. Therefore, in this paper, CdSe/ TNTAs nanocomposites were achieved with highly ordered TNTAs as substrates and controlled deposition of CdSe via solution deposition process. The growth mechanism of the CdSe nanomaterials within the tubes via solution deposition was proposed and their optical and photoelectrochemical performances were also investigated.

Experiment details

Preparation of TNTAs. In our experiment, TNTAs were prepared by electrochemical anodization. Titanium foils were anodized using the self-designed equipment consisting of a two-electrode configuration with a piece of highly pure platinum as cathode. The anodization process was carried on under constant direct current potential 60 V. Electrolytes were 0.28 wt% NH4F in ethylene glycol and the reaction time 10 hours [15]. After the electrochemical treatment, the samples were rinsed in distilled water and dried in the oven.

Preparation of CdSe/TiO_2 nanocomposites. Chromic nitrate ($Cd(NO_3)_2$) and sodium selenide (Na_2Se) were used as precursors to prepare CdSe. The preparation of Na_2Se was the same as reference [16]. The obtained TNTAs were first immersed in cadmium nitrate solution (1.0 mol/l) for 12h. The samples were then taken out and rinsed with deionized water gently, followed by drying in nitrogen atmosphere. And then the samples were immersed in sodium selenide solution (1.2 mol/L) for various lengths of time for the modification of TNTAs with series of amount of CdSe nanoparticles.

Characterization. Morphologies and microstructures were performed on field emission scanning electron microscopy (FESEM, FEI Sirion-200, operated at 10 kV). A Varian Cary 100 Scan UV–visible spectrophotometer was used to investigate the diffuse reflectance spectra. the diffuse reflectance spectra. Photoelectrochemical measurements of the TiO_2 nanotube array photoelectrodes before and after CdSe decoration were carried out in a 1.0 M Na_2S aqueous solution under AM 1.5 G at 138.4 mW/cm^2 illumination, similarly to that described by Sun et al. [17], using three-electrode system comprising of an Ag/AgCl reference electrode, the nanotube arrays working electrode and Pt foil counter electrode.

Results and discussion

Morphology of the as-prepared TNTAs. The morphology of the TNTAs obtained by anodization is shown in Fig. 1. As shown, the nanotubes were highly ordered with a uniform size of ~120nm, wall thickness of 25nm and cross-section of well aligned nanotubes with an average length of 100μm.

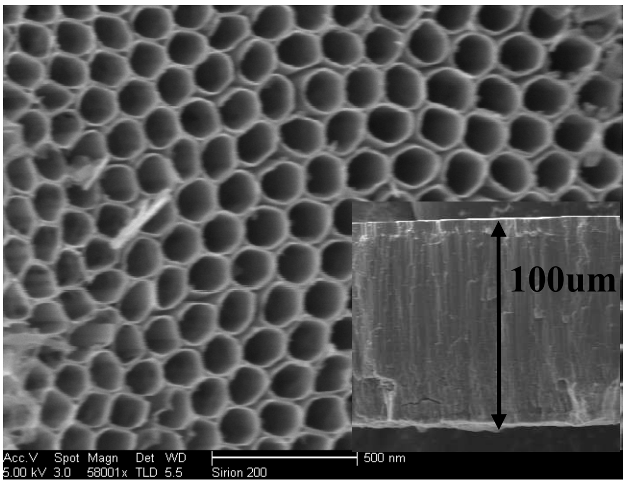

Fig. 1 FESEM images of the obtained TiO_2 nanotube arrays (the inset is the cross-sectional view)

Influence of immersion time on CdSe morphology. Fig. 2 shows the top views of the CdSe decorated nanotube arrays as a function of immersion time after introduction of Cd^{2+} (1.0 mol/l). When the TNTAs were immersed in Se^{2-} solution for 6h, the average inner diameter of the nanotubes decreased to ~50nm, due to the formation of a thin layer of CdSe on the inner wall of nanotubes (Fig. 2-b). When the immersion time increases to 10h, the deposited CdSe shows ~90 nm diameter nanowire morphology with part of the nanotube mouth blocked completely. Most of the formed nanowires do not seem to be contacted with nanotube wall (Fig. 2-c). After 12h immersion, most of the nanotubes mouth was completely filled with CdSe nanowire (Fig. 2-d).

Based on the former investigation of the CdS deposition mechanism in TiO_2 nanotubes[18], it can be concluded that nanotubes inside and outside the Cd^{2+} diffusion shows equilibrium when the nanotube arrays immersed in 1.0 mol/L Cd^{2+} solution for 12h. When the Cd^{2+}/TiO_2 nanotube arrays was then immersed in 1.2 mol/L Se^{2-} solution, Se^{2-} concentration determines the formation of CdSe nanomaterials in nanotubes. When the immersion time is short, the nucleation ion concentration within the nanotubes is lower. The lattice defects on the wall of nanotubes induced heterogeneous nucleation of CdSe which tends to adhere to the nanotube wall, resulting in the formation of a layer of CdSe coaxial tubular structure. When the ion concentration inside and outside of the nanotube reaches the diffusion equilibrium, the nucleation rate within the nanotube will reach a maximum and the formed CdSe nanoparticles will descend onto the bottom of the nanotubes because of the action of gravity. Finally, the CdSe will exist as nanowires inside of nanotubes.

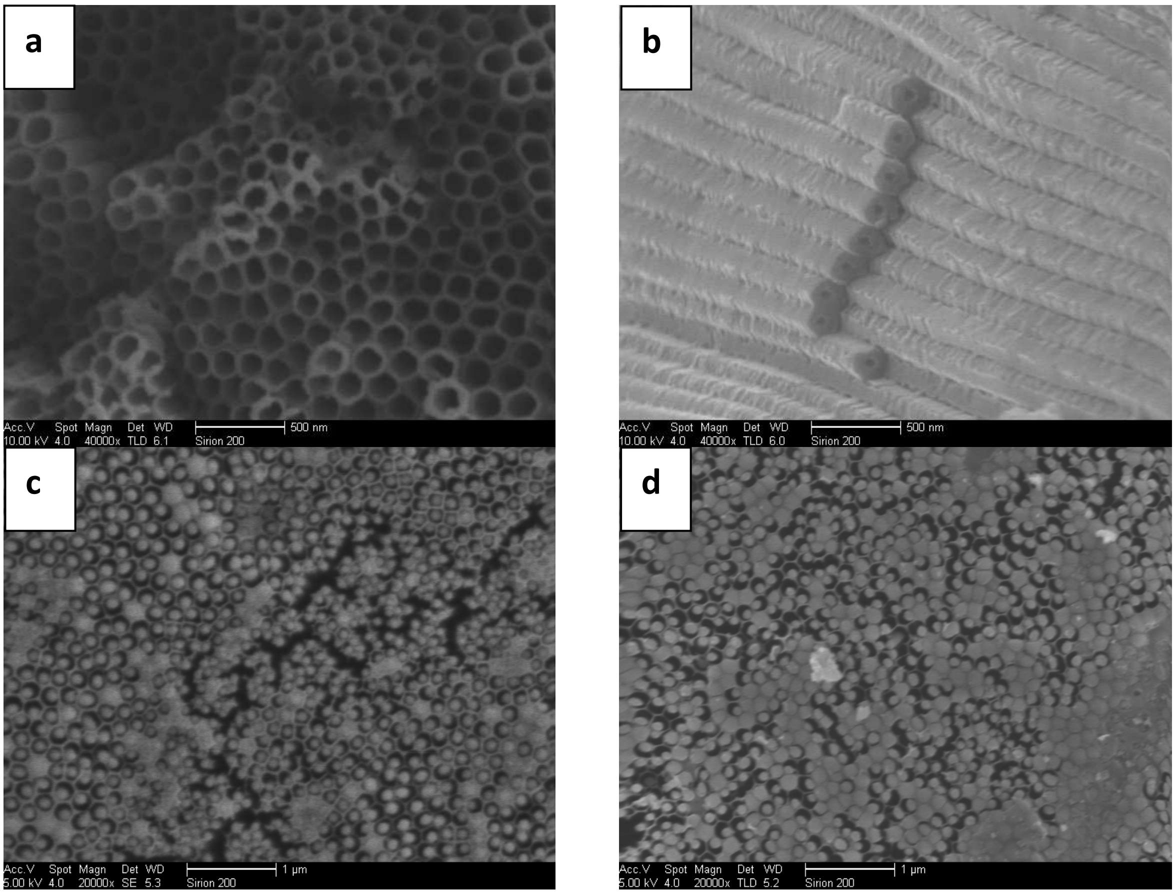

Fig. 2 Effect of immersing time in 1.2 mol/l Se^{2-} on the morphology of deposited CdSe nanomaterial (a. TiO_2 nanotube arrays; b. 6 h; c. 10 h; d. 14 h)

Optical performance of the CdSe/TiO_2 nanocomposites. In this experiment, optical performance of the CdSe modified nanotube arrays was tested. Fig. 3 shows the UV-vis spectra of the as-prepared CdSe/TiO_2 nanocomposites. The bare TNTAs only show strong optical absorption in the ultraviolet region with a very weak absorption in the visible region. After 6h immersion in 1.2 mol/L Se^{2-} solution, samples show a strong light absorption in the ultraviolet region and as well as the visible region with the most significant light absorption within 400~550 nm. As increase of the immersion time, the light absorption strength of the sample is slightly improved with more apparent enhancement in the visible region compared with that in the UV region. When immersion time was extended to 14 h, the CdSe deposition amount was further increased and the light adsorption of CdSe/TiO_2 nanocomposites was further improved both in the ultraviolet region and visible region.

These above results suggest that the modification of TiO_2 nanotube array with CdSe nanoparticles can not only significantly improve the light absorption properties, but also expand their optical absorption limit. With the increase of the amount of CdSe deposition, the light absorption could be strengthed both in the ultraviolet and visible region. And the enhancement is more apparent in the visible region.

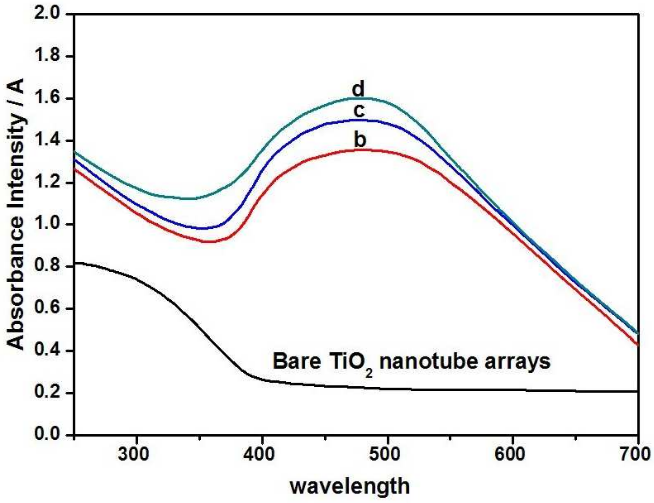

Fig.3 UV-vis spectra of the decorated TNTAs with CdSe. (a. bare TiO_2 nanotubes; b. immersed for 6 h; c.10 h; d.14 h)

Photoelectrochemical properties of the CdSe/TiO_2 nanocomposites. Fig. 4 shows the photocurrent density of the CdSe/TiO_2 nanocomposites with series amount of CdSe. The open circuit voltage of the bare TiO_2 nanotube arrays is about -0.9V and the maximum photocurrent density is approximately 0.3 mA/cm^2. When the TiO_2 nanotube wall is attached with a layer of about 35 nm CdSe, the open circuit voltage reaches -1.37V (vs. Ag/AgCl) and the maximum photocurrent density increases to 7.9 mA/cm^2. After deposition of about 90 nm CdSe nanowires, the open circuit voltage is almost no difference from that with 35 nm CdSe deposition on the nanotube wall, but the maximal photocurrent density declines to 6.9 mA/cm^2. When further extended reaction time in Se^{2-} solution, the variation of open circuit voltage for modified arrays is very small, and the maximum photocurrent density decreases slightly. Fig.5 exhibits the relationships between the maximal photocurrent density and the maximal absorbance intensity of CdSe/TiO_2. It can be concluded that when deposited with 35nm layer of CdSe, the light absorption intensity is about 1.37 V, and the corresponding maximal light current density is 7.9 mA/cm^2. When the deposited CdSe transforms into nanowires, although the light absorption of the CdSe/TiO_2 nanocomposites is enhanced, the maximal photocurrent density dramatically decreases.

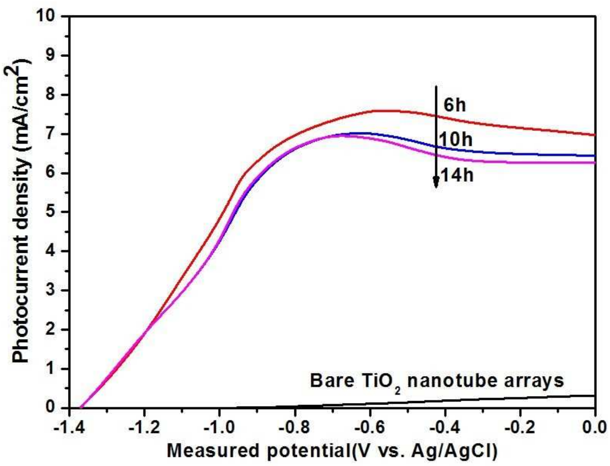

Fig. 4 Photocurrent density vs. potential in 1M Na_2S under AM 1.5G at 100 mW/cm^2 for the bare and decorated TNTAs with Cd^{2+} as the first introduction ion at different immersing time of Se^{2-}

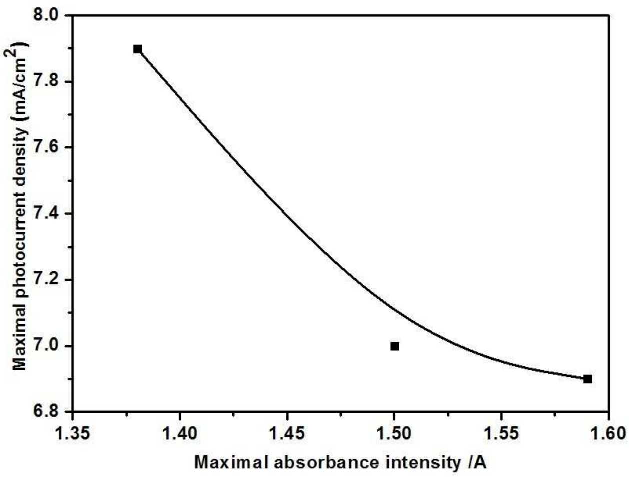

Fig.5 Maximal photocurrent density as a function of maximal absorbance intensity of CdSe/TiO_2 nanocomposites

Summary

In this paper, solution deposition process was adopted for the controllable modification of TNTAs using narrow band gap semiconductor material CdSe. The deposition mechanism varies with the immersion time when the TNTAs with previously imported Cd^{2+} was immersed into 1.2 mol/L Se^{2-} solution. When the immersion time is short, the nucleation ion concentration within nanotubes is low and the lattice defects on the wall of nanotubes induces nucleation of CdSe nanoparticles, which tends to adhere to the nanotube wall and form the nanocoaxial tubular structure. With the extension of the immersion time, the nucleation ion concentration becomes higher. And a large number of CdSe nuclei are easily reunited as sedimentation, leading to the formation of CdSe nanowires grown from the bottom of nanotubes. With the increase of the deposited CdSe nanoparticles in TiO_2 nanotubes, the spectral response range is effective extended and the optical absorption is significantly enhanced.

Acknowledgements

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