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Growth of Cu_2O/TiO_2 heterojunction and its photoelectrochemical properties

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ABSTRACT

In this paper, the Cu_2O/TiO_2 heterostructure is composed of Cu_2O particles and TiO_2 nanoring/nanotube (R/T). The high order TiO_2(R/T) were prepared by two-step anodization. With small diameter Cu_2O particles deposited on the TiO_2(R/T) by a simple thermal decomposition process, the photoelectrochemical properties of the TiO_2(R/T) has been enhanced. As-prepared samples were characterized by scanning electron microscopy, X-ray diffraction and energy dispersive spectrometer. The photoelectrochemical behavior of the samples was studied through electrochemical impedance spectroscopy and photo-to-current conversion efficiency measurement. It was found that the combination of Cu_2O with TiO_2(R/T) could not only improve the carrier separation efficiency, but also extend the optical response range of TiO_2(R/T) to the visible light region. Finally, the mechanism that Cu_2O can enhance the photoelectrochemical properties of TiO_2(R/T) is discussed.

1. Introduction

TiO_2 has great potential to solve energy and environmental problems. However, due to its narrow light absorption band and high carrier recombination rate, the use of TiO_2 has been limited [1]. Researchers usually improve its photoelectrochemical properties by modifying or adding captors. Metal doping or noble metal surface modification was usually used for the performance improvement of TiO_2 [2,3]. Recently, experiments have shown that the charge separation efficiency can be improved by heterojunctions formed between TiO_2 NTs and narrow bandgap semiconductors like CdSe, CdS, Bi_2S_3 and so on [4–6].

The structure of TiO_2 nanotube combined with TiO_2 nanoring has been founded to have better photoelectrochemical properties [7]. It has better light collection cross section and contact area with solution. With the bandwidth of 1.9–2.2 eV and the characteristics of non-toxicity, abundant reserves, low price, Cu_2O has great potential in the development and utilization of sunlight. However, Cu_2O photocarriers are unstable and its carriers are very easy to be recombined, which limits its application [8].

Theoretically, Cu_2O can broaden the absorption spectrum of TiO_2 from the ultraviolet region to the visible region, and the band positions can effectively transfer electrons [9]. However, the size of Cu_2O particles made by traditional method is so large that it blocks the pores of TiO_2 NTs, which restrict TiO_2 NTs to exerting its advantages. Recently, a new method of preparing Cu_2O particles by thermal decomposition can solve it [10].

2. Experimental section

2.1. Preparation of TiO_2(R/T) combined structure

TiO_2(R/T) is obtained from Ti foil by two-step anodic oxidation (see Scheme 1 in Supporting Information). Anodic oxidation was carried out in a glycol system containing 0.25 wt% NH_4F and 1.5 vol% deionized water with a two-electrode system. After the anodizing, the film formed by the primary oxidation was removed and then the second anodic oxidation was carried out. After 2 h, the samples were cleaned by ultrasonic with ethanol and deionized water respectively. Finally, the synthetic TiO_2(R/T) arrays can be achieved by heating to 450 for crystallization.

2.2. Synthesis of Cu_2O-TiO_2 heterojunction

The Cu_2O-decorated TiO_2(R/T) arrays can be obtained by thermal decomposition of $Cu(Ac)_2$(see Scheme 2 in Supporting Information) [10]. First, the previously prepared TiO_2(R/T) was immersed in solution of 1 mmol/L of $Cu(Ac)_2$ for 1 h, and then the samples were rinsed with deionized water at 45 °C and dried at 70 °C. The next step is to decompose the $Cu(Ac)_2$ molecules into Cu_2O with a temperature of 400 °C for 2.5 h.

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2.3. Photoelectrochemical measurements

Photoelectrochemical measurements were performed using the typical three-electrode system of an CHI660E electrochemical workstation (see Scheme 3 in Supporting Information).

2.4. Characterization

The morphology and structure of the Cu_2O-TiO_2(R/T) were observed by SEM (ZEISS, the acceleration voltage was 15 kV). An energy dispersive spectrometer (EDX) fitter to the SEM and the mapping corresponding SEM image areas were applied for elemental analysis. The samples are also characterized by XRD (X-ray diffraction) patterns.

3. Results and discussion

3.1. General characterization

Fig. 1a presents an array of tubular structure under the nanoring. The nanoring thickness is smaller than that of nanotubes (Fig. 1b). Each nanoring has a diameter of about 100 nm and a wall thickness of 10 nm. TiO_2 nanotube diameter was about 40 nm and the length was about 3.2 μm. Since the concentration of $Cu(Ac)_2$ solution is relatively low, and most of them were attached to the inner wall of NTs, it is not easy to find Cu_2O particles in Fig. 1c. EDX and XRD was used to further characterize the samples [11].

Fig. 1d shows the XRD pattern (see Scheme 4 in Supporting Information). Compared with the pure TiO_2(R/T) structure, a small diffraction peak appeared in the Cu_2O-TiO_2(R/T) at the position of 36.54 diffraction Angle (Fig. 1d. Inset image), which indicates that the sample contains Cu_2O.

EDX results shows the result after thermal decomposition of 1 mmol/L $Cu(Ac)_2$ (Fig. 1e). This data further indicates the existence of Cu and it is in agreement with the XRD results. Figure g1, g2 and g3 are mapping of O, Ti and Cu elements respectively, which is consistent with the results in Fig. 1e.

3.2. Optical property

The IPCE of TiO_2(R/T) has two obvious peaks in the wavelength of about 340 nm and 385 nm (Fig. 2a). The peak around 385 nm belongs to the TiO_2 in TiO_2 nanotube, and the peak around 340 nm belongs to the TiO_2 nanoring in TiO_2(R/T) [12]. After the loading of Cu_2O, The IPCE of the sample is enhanced not only in the range of 300–400 nm, but also in the range of visible light above 400 nm. The peak at wavelength of 375 nm (red line) is still caused by TiO_2(R/T) while the enhancement around 300–400 nm is caused by PN junction between Cu_2O and TiO_2(R/T) (see Supporting Information), which can reduce charge recombination. In the visible wavelength part, the enhancement of IPCE mainly comes from the absorption of visible light by Cu_2O.

3.3. Photoelectrochemical properties

Fig. 2b presents the photocurrent density–time characteristics of TiO_2(R/T) and Cu_2O-TiO_2(R/T). When turn on the light, the photocurrent of TiO_2(R/T) shows a tendency of rapid attenuation from a high current to a low current, while that of Cu_2O-TiO_2(R/T) shows an upward trend. With the accumulation of time, both of them tend to be stable, and the photocurrent of TiO_2(R/T) before and after loading Cu_2O is about 9 $\mu A/cm^2$ and 23 $\mu A/cm^2$ respectively, which indicates that Cu_2O can effectively improve the photoelectrochemical properties of TiO_2(R/T) by reducing the electron-hole recombination. When turn off the light, the dark current of

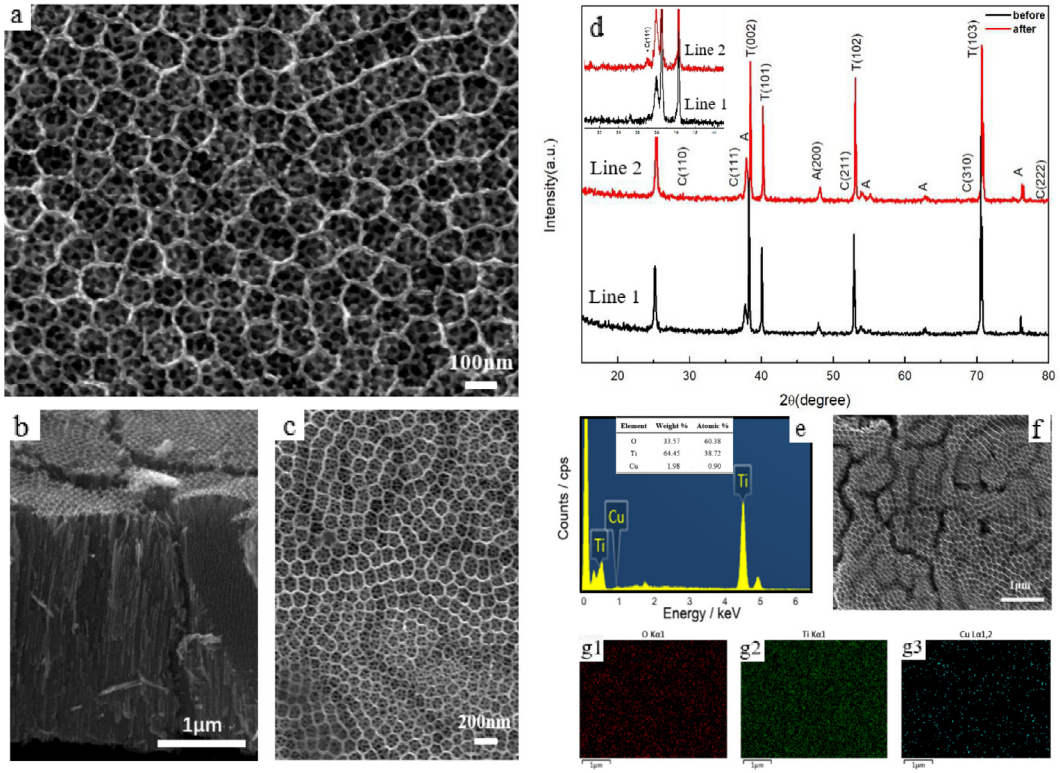

Fig. 1. a SEM for TiO_2(R/T). b Cross section view of a. c SEM for Cu_2O-TiO_2(R/T). d XRD of TiO_2(R/T) (Line 1 A, anatase; T, titanium; C, cuprous oxide) and Cu_2O-TiO_2(R/T) (Line 2). Insert plot refers to a larger view of the area around C(1 1 1). e Corresponding EDX spectrum of f. f Top-view SEM of Cu_2O-TiO_2(R/T). g Corresponding area element mapping of f (g1 O, g2 Ti, and g3 Cu).

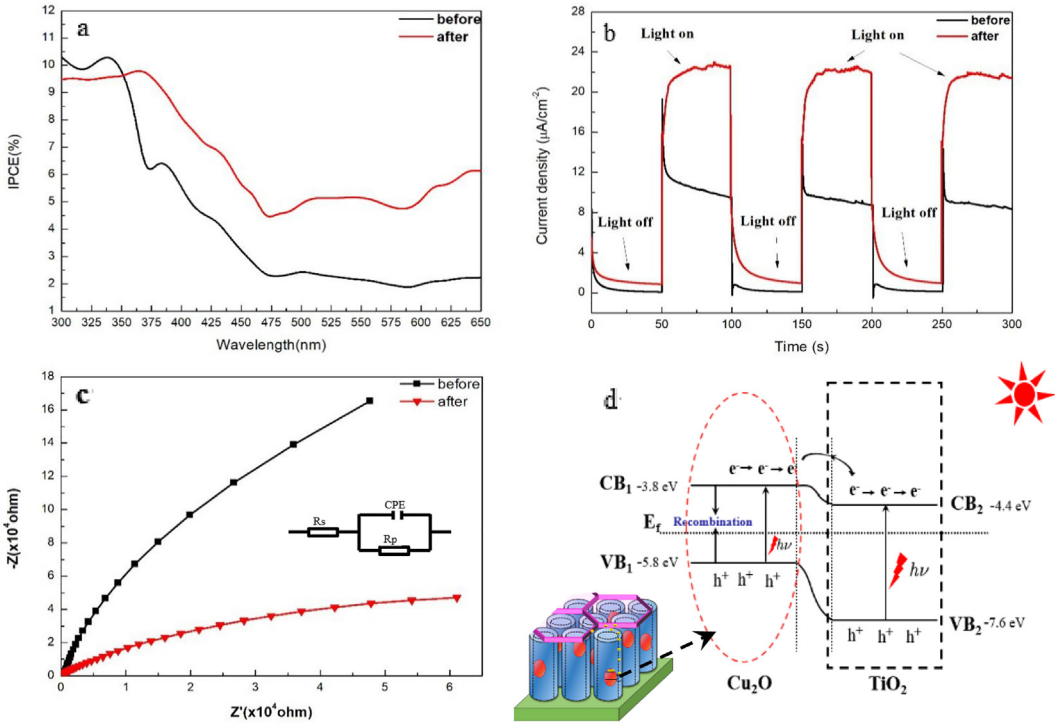

Fig. 2. a The IPCE of TiO_2(R/T) (black) and Cu_2O-TiO_2(R/T) (red) respectively. b The photocurrent of TiO_2(R/T) before and after loading Cu_2O respectively. c EIS spectra of TiO_2(R/T) and Cu_2O-TiO_2(R/T) respectively. d The photoelectric schematic diagram of Cu_2O-TiO_2(R/T).

TiO_2(R/T) decreases rapidly, while that of Cu_2O-TiO_2(R/T) decreases exponentially. This is because, Cu_2O-TiO_2(R/T) heterojunction still acts as an obstacle to the electron-hole recombination. In addition, Cu_2O has a wide band gap which leads to a good response to visible light, so the photocurrent of Cu_2O-TiO_2(R/T) can be greatly improved, which is consistent with the result of IPCE.

Fig. 2c is a typical Nyquist plot of TiO_2(R/T) and Cu_2O-TiO_2(R/T). The arc radius of Cu_2O-TiO_2(R/T) is significantly less than that of TiO_2(R/T) and a smaller half arc means faster moving interface charge to electron donors-receptor or photoproduction electron-hole. The inset in Fig. 2c is the equivalent circuit diagram of Cu_2O-TiO_2(R/T). Rs represents the resistance of solution, Rp represents the resistance of transferring charge from the surface of Cu_2O-TiO_2(R/T) to the surface of solution, and CPE represents the constant phase element. Both photocurrent images and EIS spectra reveal that the loading of Cu_2O can give TiO_2(R/T) a better photoelectrochemical properties (see Supporting Information).

Fig. 2d shows the charge separation mechanism diagram of Cu_2O-TiO_2(R/T) photoanode. The improvement of photochemical properties is attributed not only to visible light, but also to charge separation efficiency. Firstly, Cu_2O has a good response to visible light because it is a narrow band gap semiconductor and no requirement for momentum condition. Secondly, with the formation of PN junction between Cu_2O and TiO_2, a potential barrier is formed between Cu_2O and TiO_2. In addition, both the bottom of conduction band and the top of valence band of Cu_2O is higher than that of TiO_2. Therefore, photoexcited electrons will directly transfer from the conduction band of Cu_2O to the conduction band of TiO_2. Meanwhile, the heterojunction can help these photoexcited electrons to transfer quickly, thus inhibiting carrier recombination [13].

4. Conclusions

In general, we successfully prepared the Cu_2O-TiO_2(R/T) heterostructure by means of two-step anodization and thermal decomposition of $Cu(Ac)_2$. XRD, SEM and EDX showed the distribution of Cu_2O. Photocurrent images showed that the deposition of Cu_2O can increase the photocurrent of TiO_2(R/T) effectively. The EIS spectrum reflected the electron action between photoanode and dielectric. IPCE spectrum indicated that Cu_2O can broaden the optical response range of TiO_2(R/T) to the visible light region. However, it remains to be studied how much Cu_2O should be combined on TiO_2(R/T) and how the length ratio of TiO_2(R/T) affects the overall heterostructure performance.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Author contribution statements

Dengyu Yu and Dengji Yu carried out the experiment. Yunfang Zhang helped supervise the project. Fang Wang and Jun Dai conceived of the original idea. All authors discussed the results and contributed to the final manuscript.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.matlet.2019.127225.

References

[1] S. Kim, J. Yeo, W. Choi, Simultaneous conversion of dye and hexavalent chromium in visible light-illuminated aqueous solution of polyoxometalate as an electron transfer catalyst, Appl. Catal. B-Environ. 84 (2008) 148–155, https://doi.org/10.1016/j.apcatb. 2008.03.012.

[2] L.L. Kelly, D.A. Racke, P. Schulz, H. Li, P. Winget, H. Kim, P. Ndione, A.K. Sigdel, J. Brédas, J. Berry, S. Graham, O.L.A. Monti, Spectroscopy and control of near-surface defects in conductive thin film ZnO, J. Phys.-Condens. Mat. 28 (2016), https://doi.org/10.1088/0953-8984/28/9/094007.

[3] A. Fujishima, X.T. Zhang., D.A. Tryk., TiO_2 photocatalysis and related surface phenomena, Surf. Sci. Rep. 63 (2008) 515–582, https://doi.org/10.1016/j.surfrep.2008.10.001.

[4] A.K. Ayal, Z. Zainal, H.N. Lim, et al., Fabrication of CdSe nanoparticles sensitized TiO_2 nanotube arrays via pulse electrodeposition for photoelectrochemical application, Mater. Res. Bull. 106 (2018) 257–262, https://doi.org/10.1016/j.materresbull.2018.05.040.

[5] J. Xie, W. Hong, M. Meng, M. Tian, C. Kang, Z. Zhou, C. Chen, Y. Tang, G. Luo, Synthesis and photocatalytic activity of cerium-modified CdS-TiO_2 photocatalyst for the formaldehyde degradation at room temperature, Z. Anorg. Allg. Chem. 644 (2018) 1570–1575, https://doi.org/10.1002/zaac.201800315.

[6] Z.C. Guan, X. Wang, P. Jin, Enhanced photoelectrochemical performances of ZnS-Bi_2S_3/TiO_2/WO_3 composite film for photocathodic protection, Corros. Sci. 143 (2018) 31–38, https://doi.org/10.1016/j.corsci.2018.07.037.

[7] F. Wang, Y. Liu, W. Dong, M.R. Shen, Z.H. Kang, Tuning TiO2 photoelectrochemical properties by nanoring/nanotube combined structure, J. Phys. Chem. C 115 (2011) 14635–14640, https://doi.org/10.1021/jp203665j.

[8] P.E. de Jongh, D. Vanmaekelbergh, J.J. Kelly, Cu_2O: electrodeposition and characterization, Chem. Mater. 11 (1999) 3512–3517, https://doi.org/10.1021/cm991054e.

[9] W. Zhu, B.H. Chong, K. Qin, L. Guan, X. Houb, G.Z. Chen, Cuprous oxide/titanium dioxide nanotube-array with coaxial heterogeneous structure synthesized by multiple-cycle chemical adsorption plus reduction method, RSC Adv. 6 (2016) 59160–59168, https://doi.org/10.1039/C6RA06893F.

[10] Y. Liao, P. Deng, X. Wang, D. Zhang, F. Li, Q. Yang, H. Zhang, Z. Zhong, A facile method for preparation of Cu_2O-TiO_2 NTA heterojunction with visible-photocatalytic activity, NRL 13 (2018) 221, https://doi.org/10.1186/s11671-018-2637-8.

[11] Y. Li, Y. Wang, J. Kong, H. Jia, Z. Wang, Synthesis and characterization of carbon modified TiO_2 nanotube and photocatalytic activity on methylene blue under sunlight, Appl. Surf. Sci. 344 (2015) 176–180, https://doi.org/10.1016/j.apsusc.2015.03.085.

[12] J. Xue, Q. Shen, W. Liang, X. Liu, B. Xu, Controlled synthesis of coaxial core–shell TiO_2 /Cu_2O heterostructures by electrochemical method and their photoelectrochemical properties, Mater. Lett. 92 (2013) 239–242, https://doi.org/10.1016/j.matlet.2012.10.127.

[13] L.Y. Xiang, J. Ya, F.J. Hu, L.X. Li, Z.F. Liu, Fabrication of Cu_2O/TiO_2 nanotube arrays with enhanced visible-light photoelectron catalytic activity, Appl. Phys. A 123 (2017) 160, https://doi.org/10.1007/s00339-017-0799-3.