Electrochemical synthesis of Zinc oxide/polymer/phosphotungstic acid composites for a UV detector

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ZnO is an ideal material for UV detection. However, due to the surface effect of ZnO, the photosensitivity of the ZnO based UV detector needs to be improved. In this study, we deposited a hydroxyl group functionalized (3,4-propylenethiophene) polymer (PProDOT-OH) film onto a hydrothermally grown ZnO nanoarray by electrochemical deposition method to prevent the corrosion of ZnO by phosphotungsten acid (PWA), and then PWA was drip-coated on the composite film to prepare the ZnO/PProDOT-OH/PWA composite based UV detector. The structure and morphology of the composite were characterized by SEM, UV-vis, FT-IR, XRD, Raman, EDS, XPS analysis, illustrating the phosphotungstic acid was uniformly coated on ZnO/PProDOT-OH surface and confirming the composite was successfully synthesized. The UV detection performance was studied through preparing a UV detector with the composite material and results indicate that the introduction of PWA could enhance the responsivity of the ZnO/PProDOT-OH composite-based UV detector.

Keywords: UV detector, ZnO, phosphotungsten acid, composite.

INTRODUCTION

As a new type of direct band gap semiconductor material, ZnO has a band gap of 3.37 eV and an exciton binding energy as high as 60 meV^{1, 2}. Compared with GaN materials, ZnO has the advantages of lower growth temperature, smaller lattice mismatch, easier doping and lower price^{3–5}. Because of these advantages, ZnO material has gradually become one of the most popular materials for the preparation of UV detectors. Since Mollow et al. discovered that ZnO materials have photoresponse to UV radiation in the 1940s, researchers have begun to study on ZnO-based UV detectors⁶. Yang Peidong et al. prepared a ZnO nanowire-based UV detector with a chemical meteorological deposition method⁷, the sensitivity of the detector is 4–6 orders of magnitude, and its response time is less than 1s, which showing good UV response characteristics. Bai et al. prepared a ZnO nanowire based UV detector on a PET flexible film⁸, the device has an on-off ratio of about 120,000, a photocurrent of 14.1 mA and a dark current of 110 nA, which exhibiting excellent performance, however, the photocurrent response time of this device exceeds 500 s, and the recovery time is as high as 570 s, and this kind of performance is suitable for some fields where the current requirement is high but the response time of the device is low. Therefore, it is necessary to develop an UV detector that can balance the both response time and responsivity.

Since the first heteropoly phosphomolybdic acid was successfully synthesized by J. Berzerius in 1826, polyoxometalate has a history of more than 150 years and has become an important research field of inorganic chemistry^{9–12}. Many studies have confirmed that heteropoly acids have similar electronic structure characteristics to semiconductors^{13, 14}. When light is irradiated, heteropoly

acid molecules will attain energy, and the electrons in the molecule can transit from the highest full electron molecular orbital HOMO to the lowest empty molecular orbital LUMO to produce an empty orbital^{15–18}. This property makes heteropolyacids receive extensive attention in the field of photoelectrochemistry^{19, 20}. Sun et al. prepared a detector device made of phosphotungstic acid and TiO₂ composite material by a knife coating method²¹. Compared with the pure TiO₂ detector device, the photocurrent of the phosphotungstic acid/TiO₂ composite material detector device was increased by about 2000 times. It can be inferred that heteropoly acids can be introduced into semiconductor-based UV detectors to prepare better heteropoly acid/semiconductor composite UV detectors. The composites with better properties can be obtained by modifying ZnO with heteropoly acid, but heteropoly acid may cause the corrosion of ZnO, so we consider coating ZnO with polymer (PProDOT-OH) film first and then introducing heteropoly acid to avoid the corrosion of ZnO.

In this study, we deposited a hydroxy-functionalized (3,4-propylenethiophene) polymer (PProDOT-OH) film onto a hydrothermally grown ZnO nanoarray by electrochemical deposition method, and then phosphotungsten acid (PWA) was drip-coated on the composite film to prepare the ZnO/PProDOT-OH/PWA based UV detector. Because the high electronic transition ability of ZnO/PProDOT-OH at low energy, and recombination of photogenerated electrons with ZnO can be inhibited by the coupling effect between ZnO and polymer, Moreover heteropoly acid is a good type of electron acceptor and can also be used as a trap for electrons. It can act as a bridge for electron transmission, capture the photogenerated electrons generated by the conduction band (VB) of semiconductor materials, and then transfer them

to improve the photoelectric performance of materials. we hypothesize that the introduction of phosphotungstic acid into ZnO can obtain a UV detector with better photoelectric properties than pure ZnO nanoarrays.

EXPERIMENTAL

Preparation of the ZnO/PProDOT-OH/PWA composite

The monomer of PProDOT-OH was synthesized based on a literature report²². ZnO nanoarrays were prepared according to the hydrothermal method used in the literature²³. Firstly, the seed layer of ZnO nanoarray was prepared by sol-gel method. An aqueous solution for the growth of ZnO was prepared using hexamethylenetetramine (25 mM) and zinc nitrate (25 mM). Then, place a piece of FTO coated with a ZnO seed layer in an autoclave oven at 95 °C for 4 hours. Secondly, to fabricate the ZnO/PProDOT-OH composite, ProDOT-OH monomers were electropolymerized on hydrothermally grown ZnO nanoarrays by cyclic voltammetry in 0.01 M ProDOT-OH monomer and 0.05 M tetrabutylammonium hexafluorophosphate (TBAPF₆) dichloromethane as solvents, and a thin PProDOT-OH polymer film was formed on ZnO nanoarrays, indicating that the monomers were successfully polymerized onto ZnO nanoarrays. Finally, ZnO/PProDOT-OH/PWA is prepared by dripping phosphotungstic acid ethanol solution onto ZnO/PProDOT-OH composite. The phosphotungstic acid (PWA) ethanol solution with a concentration of 30 mM was slowly dripped onto the ZnO/PProDOT-OH composite and then dried naturally to obtain ZnO/PProDOT-OH/PWA ternary composites.

Fabrication of the UV detectors

Two pieces of FTO conductive glass which respectively grown with ZnO nanoarrays and ZnO/PProDOT-OH/PWA were affixed back-to-back and clamped with a clip to fabricate the device. Notably, the silver pulp was used as the contact point. Use an electrochemical instrument (CHI660) to measure the photoresponse (I-T) and I-V characteristics of the device under UV irradiation with

a wavelength of $\lambda = 365$ nm, and the light intensity was 0.4 mW/cm² provided by a ZF-20A dark box four UV analyzer that purchased from Shanghai Yuezhong Instrument and Equipment Co., Ltd.

RESULTS AND DISCUSSION

SCANNING ELECTRON MICROSCOPE (SEM)

Figure 1 shows the scanning electron microscope of ZnO, ZnO/PProDOT-OH and ZnO/PProDOT-OH/PWA. Figure 1(a) and (d) show the top-view and cross-sectional SEM images of the uniformly formation of pure ZnO nanoarray, respectively. From Figures 1(b) and (e), it can be seen that PProDOT-OH grows on the ZnO nanoarrays in a fibrous form, and is densely distributed on the ZnO nanoarrays. Figure 1(c) is the top-view scanning electron microscope of ZnO/PProDOT-OH/PWA composites. It can be found that phosphotungstic acid is uniformly coated on ZnO/PProDOT-OH, and its morphology is obviously different from that of ZnO/PProDOT-OH, indicating that ZnO/PProDOT-OH/PWA was successfully prepared. The difference between the ZnO/PProDOT-OH/PWA and ZnO/PProDOT-OH can also be found from the cross-sectional view of the ZnO/PProDOT-OH/PWA in Figure 1(f).

UV-vis spectra

The UV-vis spectra of ZnO, PWA and ZnO/PProDOT-OH/PWA composites are shown in Figure 2(a). It can be seen that ZnO and ZnO/PProDOT-OH/PWA both exhibit a ZnO band edge absorption at 365 nm, and the PWA and ZnO have strong absorption peaks in the UV light region. The absorption peaks of about 287–365 nm in ZnO/PProDOT-OH/PWA composites are formed by the overlapping of UV absorption peaks of PWA and ZnO, which is consistent with the previous literature report²¹.

Figure 1. Top-view SEM images of (a) ZnO (b) ZnO/PProDOT-OH, (c) ZnO/PProDOT-OH/PWA, cross-sectional SEM images of (d) ZnO, (e) ZnO/PProDOT-OH, (f) ZnO/PProDOT-OH/PWA

Figure 2. (a) UV-vis, (b) FTIR, (c) XRD, (d) Raman spectra of ZnO, PWA, ZnO/PProDOT-OH/PWA composite

FT-IR spectra

Figure 2(b) presents the FT-IR spectra of ZnO, PWA and ZnO/PProDOT-OH/PWA composites. As shown in Figure 2(b), the absorption peaks near 3377, 2920, 1695, 1408, 870 cm^{-1} belong to hydroxyl groups adsorbed on the surface of ZnO²⁴. In which, the absorption peaks at 1614 cm^{-1} and 1323 cm^{-1} attribute to the stretching vibration of C=C and C-C in the thiophene ring, while the absorption peaks at 1139, 1080 and 1020 cm^{-1} are associated with the stretching vibration of C-O-C and C-S-C, respectively²⁵. ZnO/PProDOT-OH/PWA have strong characteristic absorption peaks at 1614, 1323, 1139, 1080, 1020, 845, 700 cm^{-1} . In a word, the characteristic peaks of PProDOT-OH are appeared in the spectra of ZnO/PProDOT-OH/PWA, indicating that PProDOT-OH were successfully deposited on ZnO nanoarrays. In PWA and ZnO/PProDOT-OH/PWA, the characteristic peaks at 3589, 1654, 1070, 882, 904, 811 cm^{-1} belong to P-Oa, W=Od, W-Ob-W and W-Oc-W stretching vibrations in PWA, respectively²⁶. The characteristic peaks of PWA can be observed in both pure PWA and ZnO/PProDOT-OH/PWA composites, which indicated that the PWA has been successfully recombined into ZnO/PProDOT-OH.

XRD analysis

Figure 2(c) shows the XRD pattern of ZnO and ZnO/PProDOT-OH/PWA composite. As is shown in Figure 2(c), the XRD spectra of ZnO and ZnO/PProDOT-OH/PWA composites show several characteristic peaks of ZnO. The diffraction peaks at $2\theta = 34.61^\circ$, 36.82° , 47.8° and 62.9° correspond to ZnO (002), ZnO (101), ZnO (102) and ZnO (103), respectively²⁷. The peak of (002) is stronger than (101), (102) and (103), indicating that

the ZnO nanoarrays prepared in this work tended to grow along the c-axis. However, the diffraction characteristic peak of ZnO (002) in ZnO/PProDOT-OH/PWA composites is weaker than that in pure ZnO, which may be because ZnO is covered by PProDOT-OH polymer. The characteristic diffraction peaks of ZnO and PWA can be found in ZnO/PProDOT-OH/PWA at the same time, indicating that ZnO/PProDOT-OH/PWA have been successfully prepared. The diffraction peaks at $2\theta = 26.8^\circ$, 38.01° , 51.8° , 62.06° , 66° are the diffraction peaks of FTO conductive glass base.

Raman spectra

The Raman spectra of ZnO, PWA and ZnO/PProDOT-OH/PWA is displayed in Figure 2(d). As shown in the Figure, two peaks can be seen in the Raman spectra of ZnO nanoarrays and composites at 439 cm^{-1} and 584 cm^{-1} , which are originated from the E_2 and A_1 (LO) modes of ZnO. However, the A_1 (TO) and E_1 (TO) did not appear in the Raman spectra, which indicates that the ZnO nanoarrays are highly oriented along the C axis²⁸. In Raman spectra, PWA has absorption peaks around 544, 914 and 1010.9 cm^{-1} , and these three absorption peaks can also be observed in ZnO/PProDOT-OH/PWA, indicating that PWA has been successfully integrated into ZnO/PProDOT-OH films.

Elemental mapping and Energy-dispersive spectroscopy

The scanning electron microscope mapping images of ZnO/PProDOT-OH/PWA are shown in Figure 3. It can be seen that there are seven elements of C, O, S, F, Zn, W, and P in composites. The C, O and S in the mapping diagram are derived from the polymer PProDOT-OH, while the O and Zn are from the semiconductor ZnO.

Figure 3. Mapping images of ZnO/PProDOT-OH/PWA composite

Figure 4. EDS images of ZnO/PProDOT-OH/PWA composite

The uniform distribution of F and P elements can also be observed in the diagram, and these elements were originated from the TBAPF₆ which was used as the electrolyte for the polymer deposition. In addition, the relatively uniform of W in the composites confirmed that PWA has been successfully compounded into ZnO/PProDOT-OH. Figure 4 shows the EDS images of ZnO/PProDOT-OH/PWA composites. It is also clear from EDS that ZnO/PProDOT-OH/PWA have been successfully prepared.

X-ray photoelectron spectroscopy

Figure 5 presents the XPS spectra of ZnO/PProDOT-OH/PWA composite. The full spectrum of the composite shows the signal peaks corresponding to C1s (281.78 eV), O1s (528.88 eV), S2p (162.88 eV), Zn2p_{1/2} (1044.88 eV), Zn2p_{3/2} (1019.78 eV), W4f_{7/2} (34.88 eV) and W4f_{5/2} (38.78 eV), respectively, and indicating that the existence of C, O, S, Zn, W and P elements on the ZnO/PProDOT-OH/PWA composite. The S 2p spectra show the double peaks of the orbital spin splitting at 164.41 (S 2p_{3/2}) and 163.01 eV (S 2p_{1/2}) that originated

from PProDOT-OH. O 1s displays the peaks at 530.12 and 532.56 eV for C-O and C-O-C. The binding energies of W4f_{7/2} and W4f_{5/2} are 34.88 eV and 38.78 eV, respectively, that derived from the W atom in PWA. The binding energy peak at 139.58 eV comes from P2p in PWA. The XPS results once again proved that PWA was successfully compounded into ZnO/PProDOT-OH, which was consistent with the test results of UV-Vis, FTIR and Mapping and EDS.

Photoelectric performance of the composite

Figure 6 shows the I-V curves of ZnO and ZnO/PProDOT-OH/PWA composite-based UV detector. Both ZnO and ZnO/PProDOT-OH/PWA composite-based UV detectors have good rectifying characteristics, which show that the introduction of PWA does not affect the structure of the ZnO-based UV detector, and the photocurrent of the device increases obviously. As can be seen in Figure 6(a) and (b), the photocurrent of the detector increased from the original 0.9 mA to 9.1 mA after the introduction of PWA, which leads to the improvement of the photoresponsivity (R), external quantum efficiency (EQE%) and the detection rate (D) of the ZnO/PProDOT-OH/PWA based UV detector. Related to pure ZnO-based UV detectors, the optical responsivity (R) of ZnO/PProDOT-OH/PWA composite increased from the original 2.5 A W⁻¹ to 42 A W⁻¹, the external quantum efficiency (EQE%) increased from 850% to 14240%, and the detectivity (D) increased from the original 2.21*10¹¹ Jones to 2.8*10¹² Jones. The photoresponsivity(R) can be calculated by the following formula:

$$R = (I_{ph} - I_{dark}) / (P \cdot S)$$

Where I_{ph} represents the photocurrent of the UV detector, I_{dark} denotes the dark current of the UV detector, P is the UV light intensity, and S is the light-receiving area.

Figure 5. XPS spectra of ZnO/PProDOT-OH/PWA composite

The comparison between the UV detection properties of the composite prepared in this work and the previously reported materials is shown in Table 1.

Figure 7 shows the Tafel curves of the ZnO and ZnO/PProDOT-OH/PWA. As shown in Figure 7, the photocurrent of the ZnO nanoarrays UV detector that measured under 365 nm UV radiation is significantly improved than without UV illumination. Compared with the ZnO UV detector, the photocurrent of the composite-based UV detector is enhanced after the introduction of PWA, which is caused by the synergism between PWA and ZnO.

Figure 8 shows the I-T curves of the ZnO and ZnO/PProDOT-OH/PWA as illuminated by UV radiation at 365 nm. It can be seen from the figure that the rise time (T_{rise}) and fall time (T_{fall}) of the pure ZnO based UV detector were 395s and 752s, the photocurrent is 0.91mA, and after the introduction of PWA the T_{rise} and T_{fall} were decreased to 154 s and 333 s, respectively.

When the UV light irradiates on the surface of ZnO semiconductors, ZnO can absorb photons and immediately produce the photogenerated electron-hole pairs, which rapidly increases the electron density in the ZnO, resulting in the instantaneous increase of photogenerated current. The slow rise is mainly caused by the defects and oxygen vacancies on the surface of ZnO, which is related to the adsorption and desorption of oxygen molecules on the surface of ZnO. The longer light response time of the pure ZnO UV detector is mainly due to the slow transmission speed of photogenerated carriers that caused by the defects and oxygen vacancies on the of ZnO. As a kind of semiconductor material, PWA has a molecular orbital structure that similar to the WO_3 and TiO_2 semiconductor oxides, and it is a kind of excellent electron acceptor. After introducing the PWA into ZnO, it can adsorb the photogenerated electrons inside ZnO to its molecules, to achieve the purpose of inhibiting photogenerated carrier recombination, and

Figure 6. I-V behaviors of ZnO and ZnO/PProDOT-OH/PWA composite

Figure 7. I-V curves of ZnO and ZnO/PProDOT-OH/PWA composite

Table 1. Characteristics of bed of particles³²

Materials	λ (nm)	$R(A \cdot W^{-1})$	D^* (Jones)	EQE(%)	Ref.
In-doped ZnO NRs	390	2.5	1.44×10^{11}	—	29
Ga doped ZnO	374	1.68	—	55.7	30
ZnO thin-films	365	24.38	4.6×10^{12}	8283	31
ZnO/NPB	360	0.037	3.66×10^9	12.86	32
ZnO NWs	360	0.39	1.9×10^9	>100	33
ZnO	365	2.5	2.2×10^{11}	850	This work
ZnO/PProDOT-OH/PWA	365	42	2.8×10^{12}	14240	This work

Figure 8. Time response curves of ZnO and ZnO/PProDOT-OH/PWA composite

further enhance the photoelectric conversion ability of the composite material.

Figure 9 presents the time-dependent photocurrent response of UV detectors prepared by ZnO and ZnO/PProDOT-OH/PWA composite. As shown in Figure 9, the ZnO/PProDOT-OH/PWA composite-based UV detector shows good UV detection performance. Under 365 nm UV illumination, the photocurrent reaches the maximum values within a certain period of time and maintains this state, which indicates that the composite-based UV de-

tector exhibited good stability. Compared with the pure ZnO-based UV detector, after the introduction of PWA, the ZnO/PProDOT-OH/PWA composite-based UV detectors show fast, stable and repeatable photoconductive switching behavior. The excellent photoelectric response properties of ZnO/PProDOT-OH/PWA composite can be attributed to the fact that oxygen adsorption and desorption play an important role in the photoconductive gain of ZnO nanorods in the photoelectric response process. However, the process of oxygen adsorption and

Figure 9. Time-dependent photocurrent response of ZnO and ZnO/PProDOT-OH/PWA composite

desorption on the surface of ZnO is relatively slow, and there are oxygen vacancies and many defects on ZnO nanoarrays, which will affect the transportation of photo-generated carriers and lead to the slow conduction process of photogenerated carriers³⁴. When PWA is introduced into ZnO, it can act as an electronic bridge because of its good electron absorption properties, thus prolonging the recombination time of photogenerated carriers in ZnO, which has achieved the purpose of improving the photoelectronic properties of the composite.

CONCLUSION

In this paper, PProDOT-OH polymer was electro-deposited on hydrothermally grown ZnO nanoarrays by electrochemical deposition method to prevent the corrosion of ZnO by PWA, and then PWA was introduced into ZnO/PProDOT-OH by dripping method to prepare ZnO/PProDOT-OH/PWA composite, and the UV detection properties of the composite were studied through assembling UV detectors. Under the irradiation of 365nm UV light, the responsivity of the ZnO/PProDOT-OH/PWA composite based UV detector is 42 A W^{-1} , which is 16.8 times higher than that of pure ZnO nanoarrays UV detector (2.5 A W^{-1}), the external quantum efficiency (EQE%) is increased from 850% to 14240%, and the detection rate (D) is increased from the original 2.21×10^{11} Jones to 2.8×10^{12} Jones. Compared with pure ZnO-based UV detectors, the introduction of PWA can significantly improve the photoresponsivity of UV detectors. This study has potential application value in the fields of ZnO-based UV detectors.

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