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ARTICLE TYPE

An one-pot method to preparation of ZnO/Ag/Polypyrrole composite for zinc alkaline secondary battery

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ZnO/Ag/Polypyrrole (ZAP) composite was synthesized by a facile one-pot method, in which silver ammonia complex ion was reduced to metallic silver using pyrrole monomer as reducing agent, meanwhile, pyrrole monomer was oxidized and form polypyrrole. When evaluated as anode material for zinc alkaline secondary, it demonstrated a superior electrochemical performance. This material presented the much more stable cycle performance and better reversibility in galvanostatic discharge-charge test. These virtues are due to the good conductivity of silver and trapping effect of polypyrrole, which retain the zincate ions in the vicinity of electrode rather than dissolving into electrolyte.

As the most used anode material for alkaline primary battery, zinc electrode possess a unique set of advantages such as low equivalent weight, high specific energy density, abundance and low toxicity, and is the most electropositive metal that is relatively stable in aqueous and alkaline media without significant corrosion.[1-5] Because of the electrochemical redox reaction of zinc in alkaline electrolytes is easily reversible, plus the virtues of zinc electrode mentioned above, large amount of researchers want to apply zinc electrode to secondary battery system. Unfortunately, when evaluated as anode material for secondary battery, the non-uniform dissolution and deposition of zinc species during extensive charge–discharge cycling usually result in serious electrode dendritic growth and shape change, which is harmful to battery performance and cycle life.[6-9] In order to mitigate these problems, many different approaches have been attempted. Among the various of approaches, surface modifications have been considered as an effective method to improve electrochemical performance of electrode in various of battery systems.[4,10-15] Lee et al.[16] prepared TiO_2-coated ZnO by sol-gel method, it suppresses the dissolution of Zn by forming a passive surface layer. Yang et al.[17] prepared In_2O_3 doped ZnO with plate-like morphology which shows low resistivity and higher capacity retention. Other than metal oxides, organic materials are effective to retain the discharge product on zinc electrode due to their fine porous structure and re-complexation of zincate ions.[18] Vatsalarani et al.[19] found that a fibrous network of polyaniline coating allowed the movement of hydroxide ions but restricted the diffusion of zincate ions.

In this study, an attempt has been made to prepared ZnO/Ag/polypyrrole composite for combining the advantages of metallic and organic modification. It is well known that the silver is an excellent conductor of electricity, plus the re-complexation of zinc species with polypyrrole that mitigates dendritic growth and shape change, so it can be expected that the as-prepared composite would present the better cycle performance than pristine ZnO.

Fig. 1a shows the FT-IR spectra of ZAP which characterized by five obvious absorption bands appearing at 3430, 1623, 1384, 1082 and 492 cm^{-1}, respectively. The strong absorption at 3430 cm^{-1} is assigned to N−H stretching in polypyrrole or O−H stretching in absorbed water.[20] Another strong absorption at 492 cm^{-1} is assigned to Zn-O bond due to the high content of ZnO in composite. Others absorptions at 1623, 1384 and 1082 cm^{-1} are the characteristic absorption which can be assigned to the vibration of conjungated double bond in pyrrole ring, although there is some degree of shift to higher wavenumber with comparison of pure polypyrrole.[21,22] The shift in wavenumber is due to the interaction between polypyrrole and Ag nanoparticles and influence the skeletal vibrations, this phenomenon can also be observed in other polypyrrole/metal oxide composites. In detail, the presence of C=C double bond stretching of pyrrole ring leads to the appearance of absorption at 1623 cm^{-1}, the absorption at 1384 and 1082 cm^{-1} is associated to C−H in-plane vibration and bending, respectively. These absorption bands demonstrate the existence of polypyrrole in the composite.

Fig. 1b shows the XRD pattern of pristine ZnO and ZAP composite. It is obvious from curve A that the XRD pattern of pristine ZnO matches well with that of standard ZnO with the hexagonal wurtzite structure (JCPDS card 36-1451). As to ZAP composite, the diffraction peaks corresponding to ZnO can also be observed clearly, indicating the hexagonal wurtzite structure of ZnO in ZAP composite have not been changed during the synthesis process. Besides the diffraction peaks for ZnO, the diffraction peaks assigned to metallic silver at a 2θ of 38.0°, 44.3°, 64.5° and 77.3° can be noticed obviously, which proved that the silver-ammonia complex ion has been reduced to metallic silver.

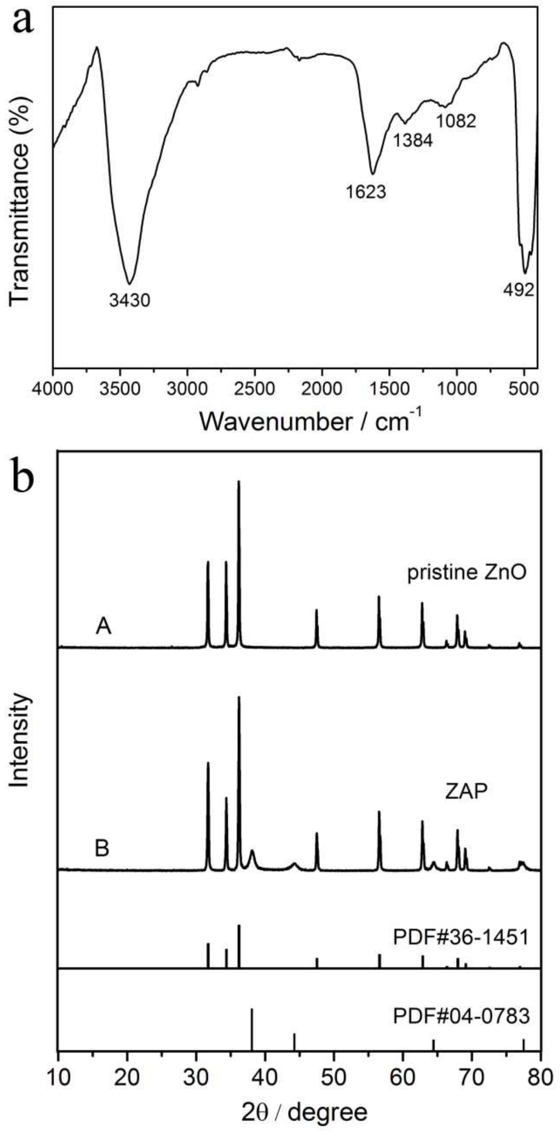
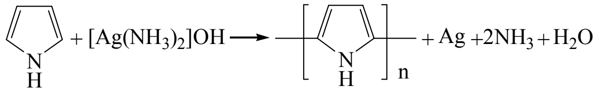


Fig. 1 a. FT-IR spectra of as-prepared ZAP composite; b. XRD patterns of pristine ZnO (curve A) and ZAP composie (curve B), the standard PDF card of wurtzite structure ZnO and metallic silver are presented in the bottom.

Generally, polypyrrole is usually prepared by oxidation reaction of pyrrole in a chemical route. And the most-used oxidizing agent is ferric chloride and ammonium persulfate.[23-26] Fe(III) will be reduced to Fe(II) when it oxidizes pyrrole, the standard reduction potential of Fe(III) to Fe(II) is 0.771 V. So in theory, if an oxidizing agent possesses higher reduction potential than Fe(III), it is capable to oxidize pyrrole. The standard reduction potential of Ag(I) to Ag(0) is 0.7996 V, so it has the ability to polymerize pyrrole monomer, and itself would be reduced to metallic silver simultaneously, the presumed reaction equation is presented as follow:



The morphologies of ZnO and ZAP composite have been shown in Fig. 2. It can be seen in Fig. 2a that the pristine ZnO particle presents a hexagonal prism morphology with smooth surface, the size of ZnO particles is about 200-500 nm. Fig. 2b shows the morphology of ZAP composite, it is obvious that there is some tiny metallic silver particles attached on the surface of ZnO particles with uniform distribution. In order to further understand the structure and component of ZAP composite, the TEM has been performed and the results can be seen in Fig. 2c. The morphology of ZAP observed in TEM is consistent with that in SEM, and the size of metallic silver particles is around the 50 nm, the smaller size of Ag particles is beneficial to the improvement of electrode conductivity and current distribution, leading to a smaller electrode polarization. What is more important is polypyrrole(PPy) coating film upon surface of silver can be observed in TEM image (indicated by arrow in the inset of Fig. 2c), and the interplanar distance of 0.236 nm corresponding to (111) crystal planes for metallic silver can be observed in Fig. 2d, which indicates that the ZnO/Ag/polypyrrole composite is synthesized successfully. In addition, the specific surface areas of pristine ZnO and ZAP composite estimated with the Brunauer–Emmett–Teller (BET) method are 5.98 and 6.49 m^2g^{-1}, respectively. In principle, higher surface area of materials are preferred for better electrochemical performance due to the more active sites.

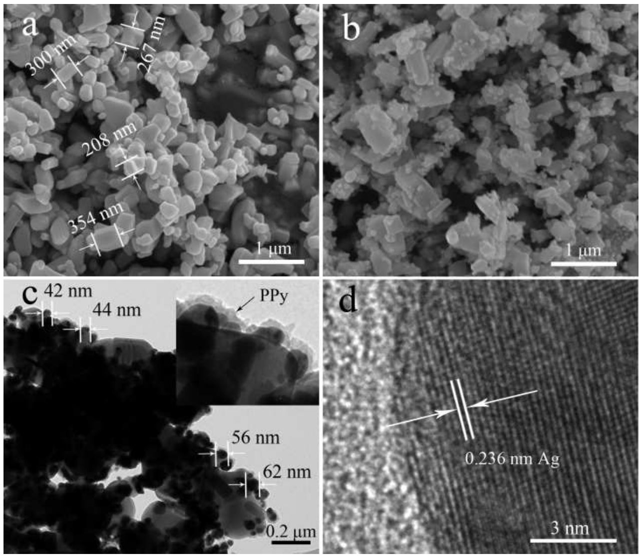


Fig. 2 SEM images of (a) pristine ZnO and (b) ZAP composite; (c) TEM image of ZAP composite, the inset is magnified image of ZAP; (d) HR-TEM image of metallic silver particles over surface of ZnO.

The galvanostatic discharge-charge analysis at 1C rate over the voltage range of 1.2 to 1.9 V is performed in order to investigate the cycle performance curves of ZnO electrode and ZAP electrode. As can be seen in Fig. 3a that both the ZnO and ZAP electrode suffer relative low discharge capacity in initial few cycles because of activated process. As to pristine ZnO (curve A), it reaches the highest discharge capacity rapidly and declines swiftly in subsequent cycles. By comparison, it takes more cycles (about eight cycles) for ZAP electrode to reach its highest discharge capacity compared to pristine ZnO (about three cycles).

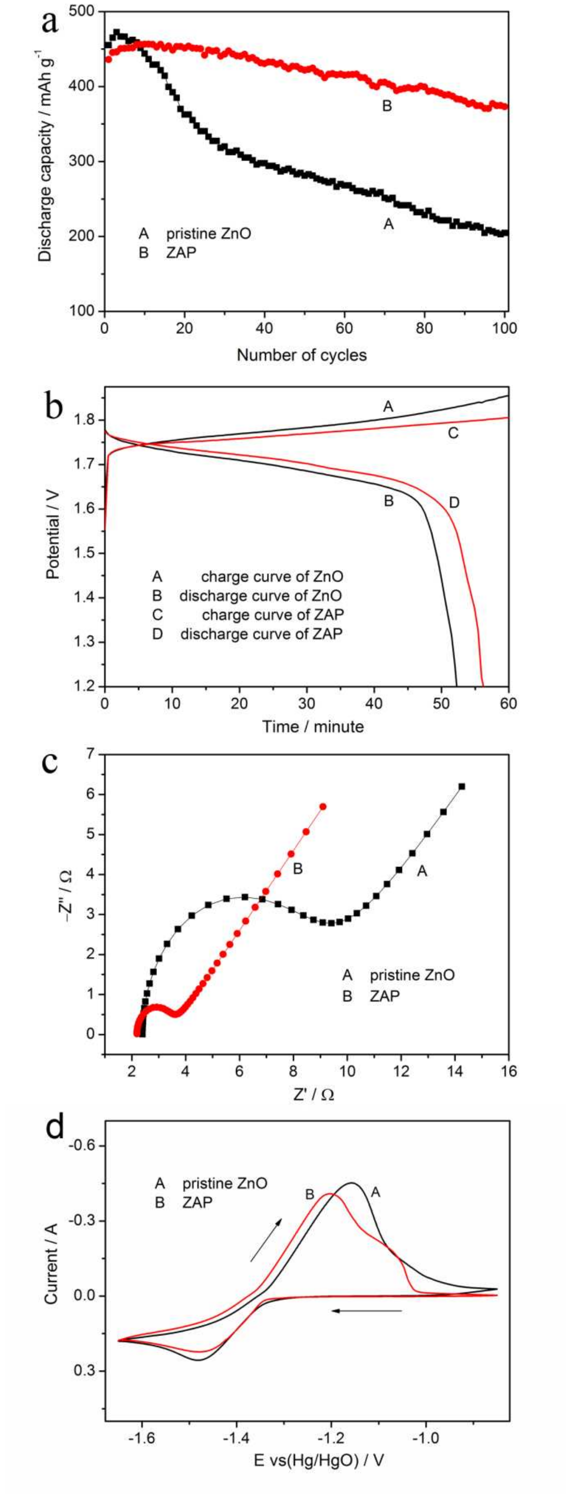


Fig. 3 (a) Cycle performance of pristine ZnO (curve A) and ZAP composite (curve B); (b) The charge (curve A) and discharge (curve B) curves of ZnO, charge (curve C) and discharge (curve D) curves for ZAP composite; (c) The typical Nyquist diagrams for pristine ZnO electrode (curve A) and ZAP electrode (curve B); (d) Cyclic voltammetry of pristine ZnO (curve A) and ZAP composite (curve B) at 10th cycle.

This phenomenon could be ascribed to the reason that silver nanoparticles and polypyrrole modified on the ZnO surface can reduce the contact surface of the ZnO and electrolyte, which prolongs the active process of ZAP electrode. Although the electrochemical performance of pristine ZnO electrode in the initial stage of cycle is better than that of ZAP electrode, the latter presents a much better capacity retention in succeeding cycles. The capacity retention of ZAP electrode is measured to be as high as 82% after the 100 cycles, while there is only 43% for the pristine ZnO electrode. The results obviously indicate that ZAP composite possesses a better cycle stability than pristine ZnO. It can be explained by the metallic silver and polypyrrole over the surface of ZnO particles. The excellent conductivity of metallic silver provides small polarization for ZAP electrode, furthermore, the polypyrrole plays an important role of surface trapping layer, which has the re-complexation effect with zincate ions, keep zincate ions in the vicinity of electrode rather than dissolving into electrolyte for pristine ZnO. The advantages of ZAP electrode can also be reflected in charge/discharge curves. Fig. 3b show that the typical charge/discharge curves at 10th cycle of pristine ZnO (curve A) and ZAP electrode (curve B). It is noticeable that ZAP electrode has the relative lower charge plateau and higher discharge plateau compared with pristine ZnO electrode, which implied that the reversibility of ZAP electrode is better than that of pristine ZnO electrode due to the decrease of the resistance benefited from silver addition.

Electrochemical impedance was employed to investigate the electrode reaction kinetics, the corresponding Nyquist plots of pristine ZnO and ZAP electrode at 10th cycles with 100% state-of-charging are shown in Fig. 3c. We can observe that the Nyquist plots are characterized by a semicircle in the higher frequency region (the arc radius represents the magnitude of charge-transfer resistance) and a straight line in the lower frequency region (Warburg impedance (Z_w) which is characteristics of the semi-infinite diffusion). Randles–Ershler type equivalent circuit is adopted to analyze the Nyquist plots. And the charge-transfer resistance (R_{ct}) can be calculated from the diameter of high-frequency arc, which is 6.1 Ω, 1.2 Ω for pristine ZnO electrode and ZAP electrode, respectively. The lower R_{ct} demonstrates that the conductivity of electrode is improved, and the kinetics process of electrochemical reaction is facilitated. Otherwise, the Warburg impedance for ZAP electrode is 0.08 Ω, which is larger than 0.04 Ω for pristine ZnO, indicating that the decoration on the surface of ZnO particle exerts some influence over the diffusion between the solution and electrode. So taking the two factors into account, the improvement on the initial charge-discharge curves of ZAP is not obvious.

Fig. 3 d shows the cyclic voltammetry of pristine ZnO and ZAP composite at 10th cycle. It can be seen that the interval between anode peak and cathodic peak is 0.325 and 0.275 V for pristine ZnO and ZAP composite. The smaller interval indicates that the reversibility of ZAP is better than that of ZnO. But there is another anode peak around -1.06 V observed for ZAP while no similar anode peak observed for ZnO. This two anode peaks phenomenon is caused by two electrochemical reaction during the discharge process:[27]

$$\mathrm{Zn} + 4\mathrm{OH}^- = \mathrm{Zn(OH)}_4^{2-} + 2\mathrm{e} \qquad (1)$$

$$\mathrm{Zn} + 3\mathrm{OH}^- = \mathrm{Zn(OH)}_3^{-} + 2\mathrm{e} \qquad (2)$$

Equation (1) occurs when the hydroxide ion is abundant, some times later, the supply of hydroxide ion has been suppressed by the existence of decoration, then equation (2) will happen, leading to the appearance of the second anode peak. This phenomenon is consistent with the result of EIS analysis.

Conclusions

By using silver ammonia complex ion and pyrrole monomer as oxidizing agent and reducing agent respectively, we have been able to directly one-pot synthesize ZnO/Ag/Polypyrrole composite that presents superior electrochemical performance than pristine ZnO. An FT-IR spectrum confirms the formation of polypyrrole, and XRD results demonstrates the existence of metallic silver. Furthermore, SEM and TEM images reveal the morphology and structure of ZAP composite, in which we can see that the small metallic silver particles are coated with polypyrrole, and the polypyrrole coated Ag is decorated upon the surface of prismatic ZnO particles. When evaluated as anode material for Zn-Ni secondary battery, ZAP electrode exhibits much higher capacity retention about 82% than 43% for pristine ZnO electrode after 100 cycles. In view of good cycle performance, this material presents a promising application in the zinc-based secondary batteries.

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Notes and references

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