

Details on the experimental steps of the synthesis, electrode assembly and tests

1 Materials preparation

ZnO/PPy composites were prepared by using a polymerization of the monomer in the present of ZnO particles accompanied by continuous sonication and mechanical stir. The pyrrole monomer obtained from Sinopharm Chemical Reagent Co., Ltd. was distilled under reduced pressure. ZnO particles were obtained from Xilong chemical Co., Ltd. Ammonium persulfate (APS), p-toluenesulfonic acid (p-TSA) were both purchased from Sinopharm Chemical Reagent Co., Ltd., NaOH was obtained from Tianjing Chemicala Reagent Research Institute, and they were used as received without further treatment. In a typical synthesis, 0.6 g ZnO was dispersed in 20 mL distilled water under sonication. 1.5 mmol sodium p-toluene sulfonate (prepared from NaOH and p-toluenesulfonic acid) and 1.85 (Sample 1) or 3.7 (Sample 2) mmol pyrrole monomer were added to above ZnO suspended solution under constant sonication and continuously stirred for 5 min. Afterward, 0.9 mmol Ammonium persulfate was promptly mixed into the above solution at room temperature. The resulting solution was kept under sonication and stir for 40 min. During the polymerization, the color of the system changed from white to grey slowly, and sample 2 is blacker than sample 1. The products were filtered and washed thoroughly with distilled water (to remove the unreacted ammonium persulfate and sodium p-toluene sulfonate) and then with methanol (to remove the oligomers). The filtered sample was dried in a vacuum oven at 333 K for further analysis. Pure PPy was also synthesized following the same procedure as described before but without ZnO. The amount of polymer in the total composition is determined by the mass difference before and after calcinations treatment in the oxygen atmosphere at 873 K for 90 min. The content of polymer for sample 1 and sample 2 is 5.1% and 11.4% respectively.

2 Characterization of ZnO/PPy composites

Fourier transform infrared (FT-IR) spectroscopy of as-prepared samples was conducted on a Nicolet Nexus-670 FT-IR spectrometer (as KBr discs, with wave number 400-4000 cm^{-1}). The morphology and structure were observed on scanning electron microscope (SEM) (JSM-6360LV) and transmission electron microscope (TEM) (JEOL-2010). The phase structure was determined by X-ray diffraction (XRD) (Philips X' Pert Pro).

3 Preparation of ZnO/PPy electrodes

For fabrication of ZnO/PPy electrodes, 85wt. % of ZnO/PPy powder was mixed with 10wt. % acetylene black and 5wt. % PTFE (served as conductive agent and binder respectively). And the mixture was grinded with agate mortar until it became muddy mixture with proper viscosity. Then above muddy mixture was incorporated to a copper mesh which served as current collector with rolling depression technology. For comparison, similar zinc electrode with bare ZnO was fabricated. The obtained electrodes were dried at 333K in a vacuum oven for further testing. And the active material loading of electrode is about 30 mg per electrode.

4 Electrochemical performance tests

Two-electrode cell was adopted (include working electrode and counter electrode) in galvanostatic charge-discharge cycle test. A sintered $\text{Ni}(\text{OH})_2$ electrode served as counter electrode, and as-prepared ZnO/PPy electrodes as the working electrode. 6.0 M KOH solution with saturated ZnO was used as the electrolyte, multilayer polypropylene micro-porous membranes as the separator. The capacity of $\text{Ni}(\text{OH})_2$ electrode was three times higher than working electrode in the aim of making sure that the capacities of cells was controlled by working electrode. The two-electrode system were charged at 1C for 1h and discharged at 1C down to 1.2V cut-off. Cycle test was performed with a battery test apparatus NEWWARE BTS-610 (Newware Technology Co., Ltd., China).

For electrochemical impedance spectroscopy (EIS) and Tafel plot analysis, a three-electrode cell was used with an Hg/HgO electrode as the reference electrode, a sintered Ni(OH)₂ electrode as counter electrode, and as-prepared ZnO/PPy electrodes as the working electrode. EIS was conducted over the frequency range from 100 kHz to 0.01 Hz, the amplitude of the ac potential perturbation was 5 mV. And EIS data was fitted using the software of Zview. The Tafel plot analysis was conducted at a constant scan rate of 0.5 mVs⁻¹. Above testing were conducted with RST 5000 (Zhengzhou Shiruisi Technolohg Co., Ltd.) electrochemical workstation.