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LETTER

Facile fabrication of silver/polypyrrole composites by the modified silver mirror reaction

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Introduction

Noble metal nanomaterials (gold, silver, palladium)/Polypyrrole (PPy) composites are attractive materials due to PPy's excellent environmental stability, good redox properties, and the ability to give high electrical conductivities [1, 2] as well as the unique optical, catalytic and electrochemical properties of noble metal nanoparticles [3–5].

Controlling the shape and nanostructure of two components is an important strategy to define the composite the properties [6, 7]. Recently, noble metal/PPy composites with various morphologies and nanostructures, such as silver–polypyrrole coaxial nanocables [8], gold nanocrystal-coated polypyrrole nanotubules [9], core-shell Ag@PPy-CS [10], gold nanoparticls/PPy composites [11] have been fabricated by chemical or electrochemical approaches.

Herein, we report a facile way to prepare Ag/PPy composite by the silver mirror reaction. Compared with the ingenious approach, this method does not require complex process. In this method, the PPy doped with PSSA were immersed first in $Al(NO_3)_3$ solution for desired time. Subsequently, a fresh $Ag(NH_3)_2OH$ solution contacted with PPy. The $[Ag(NH_3)_2]^+$ were reduced to 2D silver nanosheets on the surface of PPy and formed Ag/PPy composite ultimately.

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Experimental

Materials

Poly(4-styrene sulfonic acid) (18 wt% aqueous solution) (PSSA) was purchased from Aldrich. Pyrrole (Chinese Army Medical Institute) was distilled under reduced pressure before use. Silver nitrate (99.8%) was purchased from Beijing Chemical Plant (Beijing, China). Ammonia (25%) was bought from Tianjing 3rd Chemical Reagent Plant (Tianjing, China). Glucose monohydrate (99%) was purchased from Beijing Yili Fine Chemical Corporation (Beijing, China). Aluminum nitrate nonhydrate(99%) was bought from Tianjing Fuchen Chemical Reagent Plant (Tianjing, China). All the reagents were used as received without further purification.

Preparation

The growth of the PPy microstructures were carried out at ambient temperature in a one-compartment cell with the use of a model 283 potentiostal/galvanostat (E.G&G Princeton Applied Research) under computer control. The working and counter electrodes were two stainless steel sheets (AISI 321), each with a surface area of 0.5 cm^2, placed 0.5 cm apart. All potentials were referred to a Ag/AgCl electrode, which was immersed directly in the electrolyte. The electrolyte was an aqueous solution of 0.5 M pyrrole and 0.5 M repeat units of PSSA.

Silver/PPy composites were prepared as follows. The PPy microstructures were immersed into $Al(NO_3)_3$ solution (1 mol L^{-1}) for 24 h. Ammonia was dropped into 10 mL silver nitrate solution (0.12 mol L^{-1}) until the precipitation just disappeared. Subsequently, 15.0 mL glucose solution (0.56 mol L^{-1}) was added into $Ag(NH_3)_2OH$ solution. The

PPy pretreated with $Al(NO_3)_3$ solution were immersed into the above-mentioned solution for 1 h to form silver/PPy composites. Finally, the silver/PPy composites were rinsed with deionized water and dried with pure flowing nitrogen.

Characterization

Scanning electron microscopy (SEM) images and Energy-dispersive X-ray analysis were recorded with a KYKY2800 (Beijing Scientific Instruments Co., China) or a S530 (Hitachi) SEM equipped with an energy-dispersive X-ray detector. The X-ray diffraction data of the Ag/PPy was collected on a D8-advance X-ray diffractometer (Bruker, Germany).

Results and discussion

The SEM images of PPy microstructure and relevant Silver/PPy composites are shown in Fig. 1. With an increase in the potential from 0.8 to 1.4 V, the microstructures

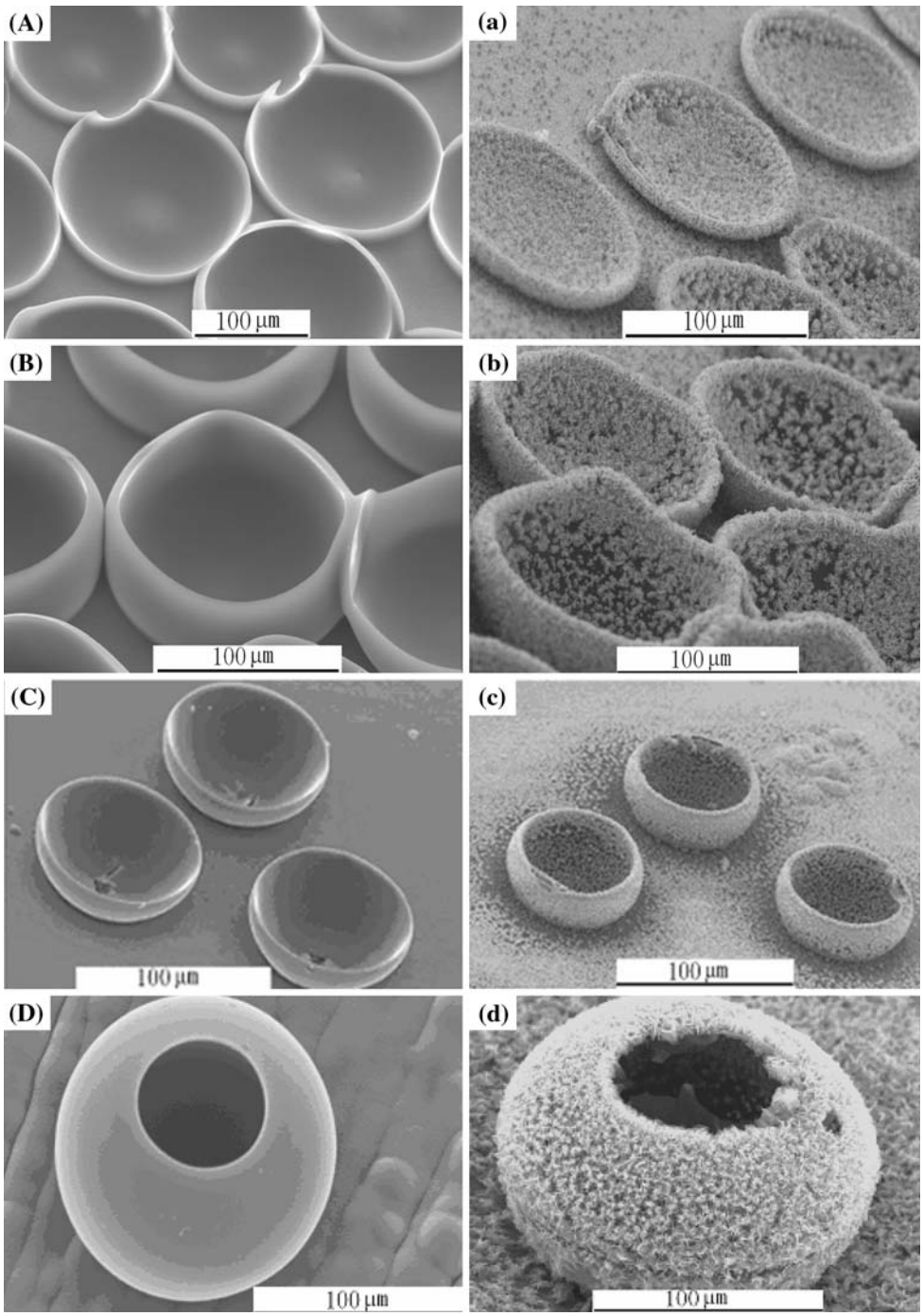

Fig. 1 SEM images of PPy and relevant silver/PPy composites. **A** plate-like PPy, **a** silver/plate-like PPy composite; **B** cup-like PPy, **b** silver/cup-like PPy composite; **C** bowl-like PPy, **c** silver/bowl-like PPy composite; **D** crock-like PPy, **d** silver/crock-like PPy composite

gradually grew higher and their shapes changed from a plate-like (Fig. 1A) to cup-like (Fig. 1B), to bowl-like (Fig. 1C), to crock-like (Fig. 1D). The PPy microstructures show smooth surfaces with the diameter of about 150 μm. The synthesized mechanism of PPy microstructures has been reported in our previous studies [12, 13]. After the PPy microstructures contact with the solution of silver mirror reaction for 1 h, the obtained silver/PPy composites were shown in Fig. 1a, b, c, and d, respectively. The SEM images showed that the surfaces of microstructures have been almost covered with silver.

A magnified view of Fig. 1c was illustrated in Fig. 2, which showed the 2D silver nanosheets were generated on the external surface of PPy microstructure. The silver nanosheets as layers stocking, unaligned on top of each other and their sizes ranged from hundreds of nanometers to several micrometres. The morphologies of silver on the top (Fig. 2b) were similar to those of silver on outer wall of PPy (Fig. 2c). However, the irregular silver nanostructures were also found on the interior bottom of the PPy microstructure in Fig. 2d, and their amount was few and could not cover the interior bottom of PPy. It may be attributed to the solution of silver mirror reaction could not entirely enter into the inside of PPy microstructures due to their shapes, and which led to the silver nanoparticles grew defectively.

The EDX analysis on the silver/PPy composite clearly shows a major peak of silver (Fig. 3a), which implied the surface of the PPy microstructure was almost covered by silver nanosheets. Figure 3b presents X-ray diffraction (XRD) pattern of as-prepared composite. Three sharp diffraction peaks were assigned to (111), (200), (220) planes

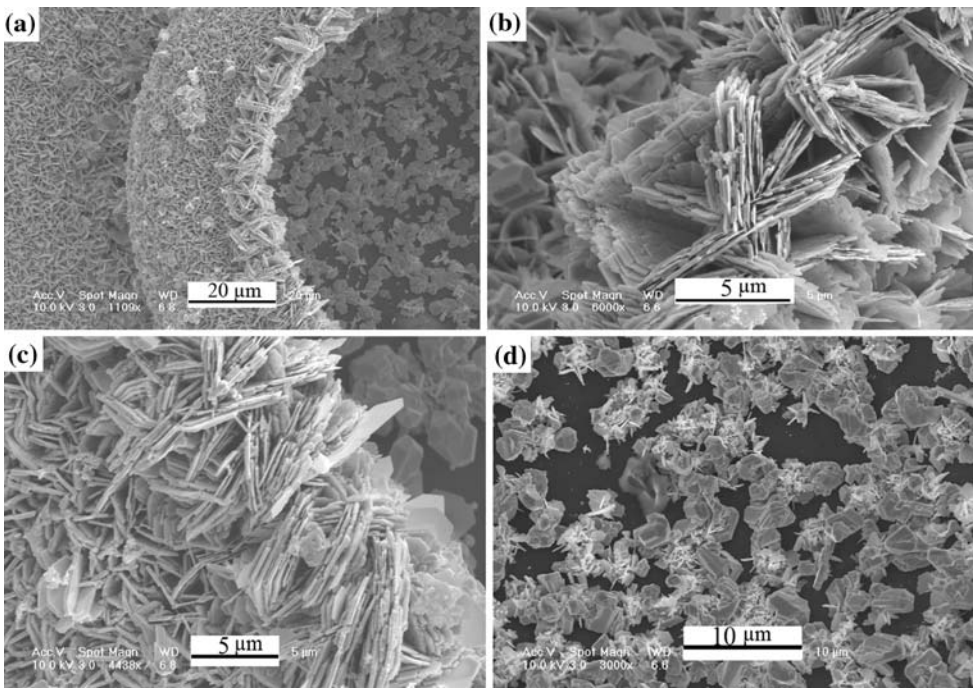

Fig. 2 SEM images of silver/bowl-like PPy composite. **a** A full view of silver/PPy composite. **b**, **c**, **d** silver nanostructure on the top, outer well and interior bottom of the PPy microstructure, respectively

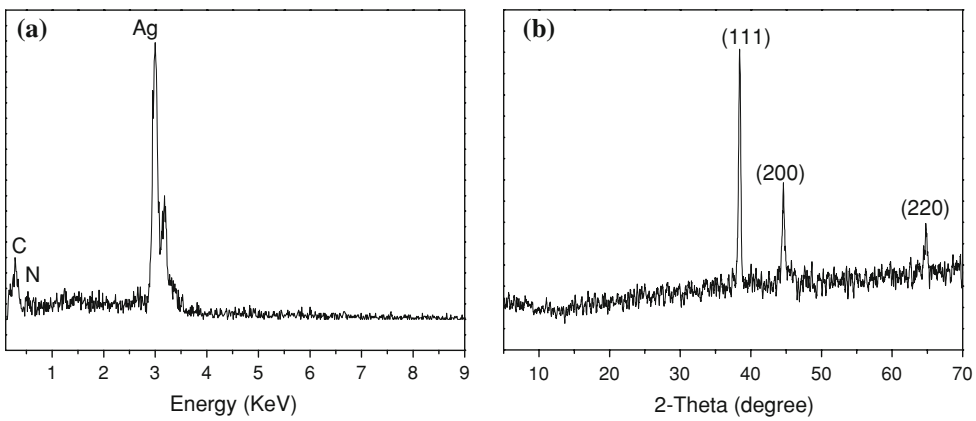

Fig. 3 EDX spectrum (**a**) and XRD pattern (**b**) of the silver/PPy composite

of fcc silver, indicating the formation of highly crystalline silver.

Conclusions

Silver/PPy composites have been prepared by the simple silver mirror reaction. The results indicated that two-dimensional silver nanosheets could be deposited on the surface of the PPy. The obtained silver/PPy composites may have many potential applications in chemistry and physics and the facile method also be extended to fabricate silver/other polymer composite.

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