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Silver–polypyrrole composites: Facile preparation and application in surface-enhanced Raman spectroscopy

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ABSTRACT

A facile method to prepare silver–polypyrrole composite (Ag–PPy) by a modified silver mirror reaction is reported. PPy films pretreated by $Al(NO_3)_3$ solution were immersed into the silver ammonia with glucose. Silver ammonia ions were reduced to two-dimensional staggered silver nanosheets which immobilized on the surface of polypyrrole. The silver nanosheets with different morphologies and sizes can serve as active-substrates for surface-enhanced Raman spectroscopy (SERS). Using 4-mercaptopyridine (4-Mpy) as probe molecules, the as-prepared composites exhibited excellent surface-enhanced Raman scattering.

1. Introduction

Incorporation metal nanoparticles into conducting polymer is of interest due to the strong electronic interaction between the metal and conducting polymer. Such metal-conducting polymer composites have attracted growing attention because of their potential applications in biotechnology, electro-catalysis, sensors, microelectronic devices [1–4], and as substrates for surface-enhanced Raman spectroscopy (SERS) [5].

Surface-enhanced Raman spectroscopy is a powerful surface diagnostic technique because of its extremely high surface sensitivity [6–8]. Among the SERS-active metals, Ag nanostructure had been widely studied [9,10] and the relevant results exhibits the shapes of Ag nanostructures influenced the SERS [11–14]. However, most of the methods are too laborious and expensive to fabricate in large quantities.

Herein, we describe a facile way to fabricate novel silver–polypyrrole (Ag–PPy) composite as SERS-active substrate. By the modified silver mirror reaction, the small size, large surface area, and plate-like structure of the silver nanosheets were deposited on the surface of PPy. The obtained Ag–PPy substrate is very stable, inexpensive, and exhibits excellent SERS enhancement ability.

2. Experimental

2.1. Materials

Poly(4-styrene sulfonic acid) (PSSA) (18 wt.% aqueous solution) and 4-mercaptopyridine (4-Mpy) were 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.

2.2. Synthesis

2.2.1. Electrochemical synthesis of polypyrrole film

The growth of the PPy films were carried out at ambient temperature in a one-compartment cell with the used of a model 283 potentiostat/galvanostat (EG&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 1.5 cm apart. All potentials were referred to Ag/AgCl electrode, which was immersed directly in the electrolyte. A typical electrolyte was an aqueous solution of 0.5 M pyrrole and 0.5 M repeat units of PSSA.

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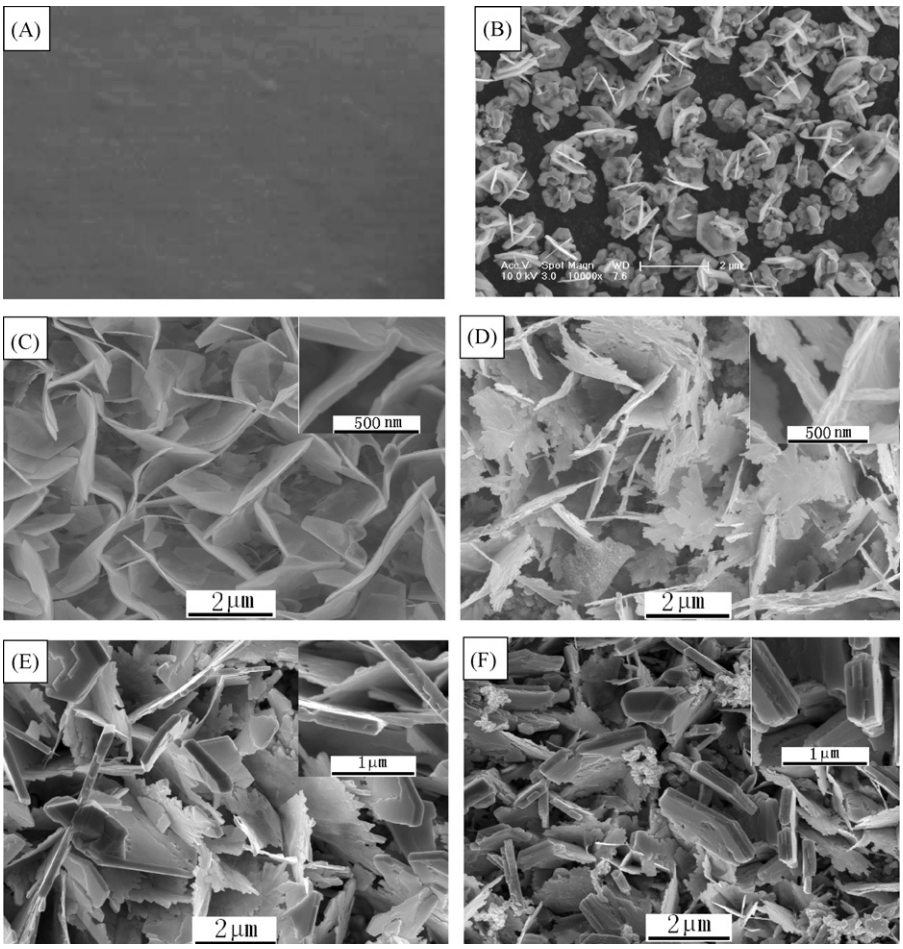

Fig. 1. SEM images of silver nanosheets deposited on PPy for different time: (A) 0 min, (B) 1 min, (C) 5 min, (D) 15 min, (E) 30 min, and (F) 60 min. Inset of part (C–F): a magnified view.

2.2.2. Preparation of silver–PPy composites

Silver–PPy composites were prepared by the silver mirror reaction. The typical experiment: the PPy film 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 by $Al(NO_3)_3$ solution were immersed into the as-prepared solution for different times to deposited silver on the surface of PPy. The silver–PPy composites were rinsed with deionized water and dried with pure flowing nitrogen.

2.2.3. Preparation of SERS-active substrate

The silver–PPy composites were dipped into 4-Mpy solution (10^{-7} M) for desired time. Subsequently, these substrates were

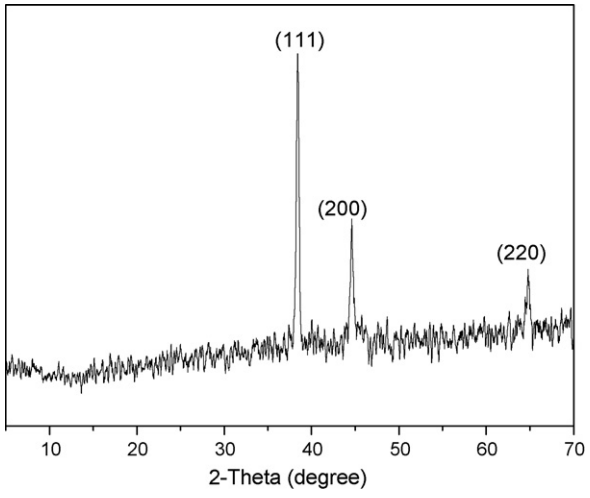

Fig. 2. Typical XRD of the silver–PPy composite. A typical X-ray diffraction (XRD) pattern of as-prepared composites is presented in Fig. 2. Three sharp diffraction peaks are assigned to (1 1 1), (2 0 0), and (2 2 0) planes of fcc silver, respectively.

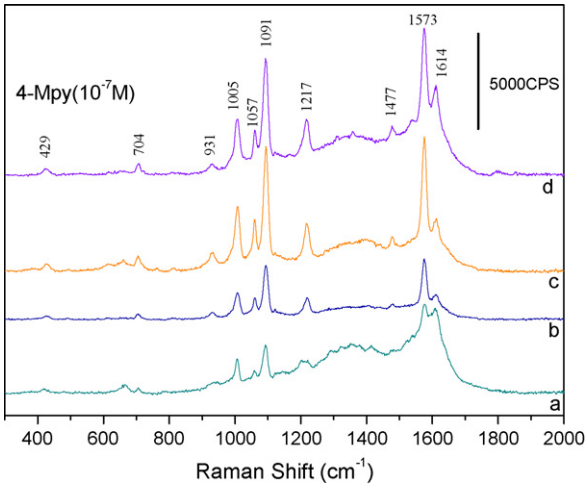

Fig. 3. SERS spectra of 4-Mpy on different silver–PPy substrates. Silver deposited on the PPy film for different time: (a) 5 min, (b) 15 min, (c) 30 min, and (d) 60 min.