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Facile preparation and electrochemical characterization of self-assembled core-shell diamond-polypyrrole nanocomposites

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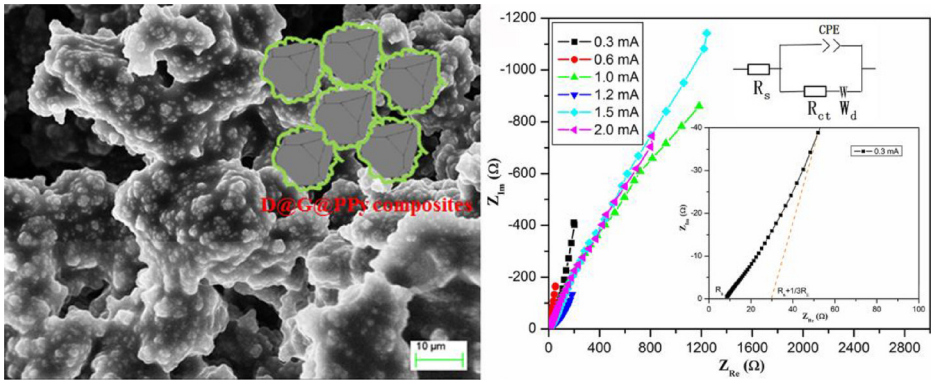
GRAPHICAL ABSTRACT



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ABSTRACT

The fabrication of graphitized diamond covered with polypyrrole (D@G@PPy) core-shell nanocomposites has been achieved by using a superficial electrochemical polymerization and self-assembly strategy. The conductivity of the core-shell nanocomposites was influenced by polymerization time, current as well as the concentration of ions. The obtained excellent conductivity appeared with the current of 0.6 mA and the duration time of 1 h. In addition, the corresponding enhanced electrochemical performance of polypyrrole grown on graphitized diamond substrate is demonstrated compared with pristine polypyrrole. The morphologies of the obtained composites were illuminated through scanning electron microscopy (SEM) and the conductivity was demonstrated by electrochemical impedance spectroscopy (EIS). The characteristic peaks of polypyrrole and qualitative analysis of surface elements have been investigated by Raman spectra and X-ray photoelectron spectroscopy (XPS). The present research could demonstrate a new aspiration for the design and preparation of novel polypyrrole core-shell composites materials.

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1. Introduction

For charge storage, conducting polymers have become promising functional materials due to their low cost and excellent capacitance contribution. As one eye-catching material, polypyrrole (PPy) has received lots of attention originated from excellent charge-storage nature with wide and good potential window as well as eco-friendly property [1]. By using two ordinary methods, we can get polypyrrole. One is chemical polymerization while another is electrochemical polymerization, in which electrochemical polymerization is the main method to prepare conductive polypyrrole. It was found that the electrode substrate had great influence on the electrochemically grown PPy nanoarchitectures [2]. Thus people can obtain flexible, smooth and highly conductive polypyrrole film through regulating the polymerization conditions of polymerization. For instance, with an electrochemical technology treatment PPy nanowires anchored vertically on the surfaces of palladium nanoisland-modified Nafion materials with pyrrole and p-toluenesulfonylsodium. As a result, it enhanced the property of direct methanol fuel cells [3,4]. Huang et al. prepared a similar well-organized PPy nanowires on gold nanoisland-modified platinum plate, which also exhibited a well specific performance about 566 F/g at 1.10 A/g [5].

On the other hand, diamond seemed well known among scientists and technologists for its excellent thermal conductivity, well mechanical properties, and special chemical/electrochemical stability as well as tunable nanostructures [6–9]. As it is well known that diamond has a unique nature, such as high hardness, excellent thermal conductivity and other distinctive characteristics, which make it plays a unique role in a variety of industries, such as in the mechanical, military, semiconductor and medical and other high-tech applications. However, diamond is not conductive, pristine diamond is even a kind of insulator. So the diamond surfaces have been modified with graphite or graphene from all-carbon-based composite materials for subsequent applications. For examples, Wang et al. prepared a kind of surface graphitized nanodiamond (GND) which has a diamond core coated with a graphitic carbon shell. In detail, the brief progress is that a nanodiamond was annealed in high vacuum and temperature of 1300 °C with the support of PtNi electrocatalysts [10]. In addition, diamond/graphene composites have been also prepared by electron-beam (E-beam) irradiation or annealing in a vacuum at high temperatures [11–13]. Hence, we can use graphitized diamonds instead of pristine diamonds to fabricate more composite materials.

However, as far as we know, there is no report about PPy growth on a diamond substrate. Thus we try to fabricate diamond-PPy composite with core-shell structure, which can combine the advantages of PPy and diamond components. The used diamonds were graphitized to enhance the electroconductibility and interfacial reactive sites. Herein we report the electrochemical fabrication of PPy growth on graphitized diamond mainly due to the mighty π-π interactions between graphitized diamond and pyrrole molecules, which can effectively boost the formation of nucleation sites during electrochemical polymerization of pyrrole. Then we did a series of characterizations to investigate the nanostructures of the obtained composites, which demonstrated that the prepared composites showed elevated conductivity and electrochemical performances compared with either pristine polypyrrole or graphitized diamond.

2. Experimental method

2.1. Materials

All of the chemicals we used were purchased from Aladdin Reagent (Shanghai, China) and used as received, apart from pyrrole, which was distilled before use. Microdiamond powders were supplied by Element Six Ltd (Henan, China).

2.2. Preparation of polypyrrole (PPy) nanocomposite

To fabricate PPy on graphitized diamond, we used an electropolymerization strategy. The electrolyte is a solution of 0.2 M phosphate buffer with 0.02 M p-toluenesulfonate acid (TsOH) and 0.145 M pyrrole. We used a glassy carbon electrode, a SCE and platinum as the working reference and counter electrodes, respectively. After polymerization the working electrode was douched thoroughly in ultrapure water and the production was lyophilized. To illustrate the impact of the current on the progress of PPy fabrication, the electropolymerization was executed in a constant current of 0.3, 0.6, 1.0, 1.2, 1.5 mA/cm^2, respectively for 30 min, 1 h and 2 h, respectively. Pyrrole was also directly polymerized on glassy carbon electrode for 30 min and 1 h at different currents with/without graphitized diamond to investigate the differences of composite preparation.

2.3. Characterization

A vibrational spectrum of the sample was used a Spectrum One Fourier transform infrared spectroscopy (FT-IR, PerkinElmer, USA). We used the scanning electron microscope (SEM) Field Emission Gun FEI QUANTA FEG 250 (FEI Corporate, Hillsboro, OR, USA) to investigate the morphologies of the specimens. The frequency of electrochemical impedance spectroscopy (EIS) was measured in the range of 40 mHz to 50 kHz at an open-circuit potential. And the Raman spectra were measured by a microscopic confocal Raman spectrometer (Renishaw PLC., RM 2000) and the laser beam was 632.8 nm and using 20× objectives and accumulated for 30 s to record the spectra. X-ray photoelectron spectroscopy (XPS) was from ESCALAB 250Xi XPS (Thermo Fisher Scientific, San Jose, CA, USA) with 200 W monochromated Al Kα radiation. Both survey scans and individual high-resolution scans for characteristic peaks were recorded. A Si plate was used as the XPS testing substrate which was purchased from Aladdin Reagent (Shanghai, China). A ST-2722 multifunction digital four-probe tester was used to evaluate the electrical conductivity, which outfitted with a SZT-D semiconductor powder resistivity tester (Shenzhen Jingge Electronic Co., Ltd., China). The prepared material was placed in a hemispherical hole directly which around 5 mm in diameter for the tester. Then, the powder sample was pressed slowly through the valve on the tester. Simultaneously, the values of electrical conductivity in different pressures were recorded automatically.

3. Results and discussion

The process of the polymer fabrication was shown schematically in Fig. 1. Firstly, the diamond agglomerate was carried out by the vacuum spark plasma sintering (SPS) for 15 min at the temperature of 1500 °C. Then, the synthesized diamond@graphite (abbreviated as D@G) powder was obtained by grinding the agglomerates. Furthermore, the D@G powder was dissolved in deionized water then put in a water-bath supersonic device for 30 min. In addition, the suspension liquid was dropped in the working electrode with natural withering. After that, the working electrode was immersed in the solution of pyrrole. At the same time, the TsOH anions and pyrrole monomer were absorbed by the graphite result from the influence of π-π interactions among aromatic rings of pyrrole, TsOH and the sp^2 carbon. In consequence, there are sufficient exposed nucleation sites for the formation of PPy due to these π-π interactions. As the report before, the TsOH anions which doped in the oligomers of PPy can avoid random growth of polymer. Then PPy was polymerized on the tips of the nuclei under the influence of the external electric field [5,14]. It is widely speculated that the polymerization of pyrrole contains two steps: nucleation and oriented growth [15–21]. It is because that graphitized diamond act as substrate which can accelerate the progress of nucleation, so the pyrrole we got grown on graphitized diamond is better than which grown on pure glassy carbon electrode.