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More conductive polypyrrole electrodeposited on substrates with close-packed gold nanoparticles

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ABSTRACT

Recently, conductive polymers (CPs) of polypyrrole (PPy) have been widely applied in supercapacitors, gas sensors, photocatalyses and innovative cancer therapies. Chemical and electrochemical oxidation polymerizations are two general pathways for the preparation of PPy. The principal advantage of the electrochemical method is related to the prepared PPy with a better conductivity and its long-term stability. In this work, PPy films are innovatively electrodeposited on Pt substrates modified with Au nanoparticles (NPs) prepared by using sonoelectrochemical deposition-dissolving cycles (SEDDC). The modification of Au NPs demonstrates a catalytic electro-oxidation pathway for the polymerization of PPy. Encouragingly, the conductivity of PPy electrodeposited on this Au NPs-deposited Pt substrate is significantly increased by more than 6-fold of magnitude, as compared with that of PPy electrodeposited on a polished Pt substrate. The increased conductivity of PPy is consistent with its increased oxidation degree, oxidation level and longer conjugating length, and with its dopant ions being more stable during polymerization, which are revealed from analyses of Raman and X-ray photoelectron spectroscopies.

1. Introduction

Electrically conductive polymers (CPs) have attracted considerable attention due to their unique electronic properties. Of all known CPs, polypyrrole (PPy) is the most frequently used one in commercial applications, such as batteries [1,2], supercapacitors [3,4], sensors [5,6], drug carriers [7,8], microwave shielding, and corrosion protection [9,10], because of the fairly good environmental stability and the possibility of forming homopolymers or composites with optimal chemical and physical properties [11,12]. Recently, biocomparable and near infrared (NIR)-adsorbing PPy-based materials were innovatively explored for photothermal treatment of cancer *in vivo* and *ex vivo* [13,14]. Wang et al. [13] reported Fe_3O_4@PPy nanoparticles (NPs) as a multifunctional drug carrier for remotely controlled cancer therapy with synergistic antitumor effect. In preparation clusters of ultrasmall Fe_3O_4 magnetic NPs were coated with the NIR light-absorbing PPy polymer by *in situ* chemical oxidative polymerization, which were then modified with polyethylene glycol (PEG) to acquire water solubility. Yang et al. [15] reported PPy-decorated Ag–TiO_2 nanofibers for exhibiting enhanced photocatalytic activity under visible-light illumination. The proposed PPy–Ag–TiO_2 system exhibits remarkable light absorption in the visible region and high photocurrent. To be named of CPs, therefore, the electrical conductivity, which promises their wide applications, is one of the most concerned properties. This conductivity can be attributed to the electron hopping along and across the polymer chains with conjugating bonds [10,16]. As a result, more positively charged PPy, more electron holes available, longer polymer chains and more coplanarity between interchains, are favorable for PPy with a higher conductivity. The conductivity of oxidized PPy can be increased to a level of 10^3 S cm^{-1}, or higher, depending on the preparation method and the doped ion [17–19]. As reported by Booth et al. [20], low-energy platinum ions were implanted with 15 keV under normal incidence into synthesized conducting PPy films with the aim to improve film conductivity and to demonstrate the use of implanted platinum in a simple sensing design. As reported by Zhang et al. [21], an improved chemical one-step method (ICOSM) was used to

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prepare highly conductive and magnetic PPy/γ-Fe_2O_3 (PPy/γ-Fe_2O_3) nanospheres with 80 nm in diameter.

Chemical and electrochemical oxidation polymerizations are two general pathways for the preparation of PPy. The principal advantages based on the electrochemical method are related to the better conducting properties and the long-term stability of conductivities [22,23]. In our previous study [24], we reported a new pathway for the autopolymerization of pyrrole (Py) monomer on the chlorine- and gold-containing nanocomposites prepared by electrochemical oxidation–reduction cycles (ORC). Conductivity and intensity in Raman spectroscopy of PPy electropolymerized on this electrochemically roughened Au substrate were improved [25]. Recently, we develop a simple pathway to prepare surface-enhanced Raman scattering (SERS)-active substrates with elemental Au NPs by a strategy of sonoelectrochemical deposition-dissolution cycles (SEDDC) [26]. Close packing and even Au NPs islands with Raman activity were observed. The uniformity of Au NPs deposited on a metal substrate is more superior than that obtained from a conventional ORC method. In this work, PPy films are innovatively electrodeposited on Pt substrates with close-packed Au NPs prepared by using SEDDC method. The increased conductivity of prepared PPy is demonstrated and the corresponding explanations are proposed.

2. Experimental section

2.1. Chemical reagents

Py monomer, and electrolytes of KCl and $LiClO_4$ were purchased from Acros Organics. Py monomer was triply distilled until a colorless liquid was obtained and was then stored under nitrogen before use, while electrolytes were used as received without further purification. The experimental solutions were prepared by using deionized 18.2 MΩ cm water provided from a MilliQ system.

2.2. Electrochemical preparation of Au-containing complexes in solution

All the electrochemical experiments were performed in a three-compartment cell at room temperature (23 °C) and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). A sheet of gold with bare surface area of 4 cm^2, a 2 × 4 cm^2 platinum sheet, and KCl-saturated silver-silver chloride (Ag/AgCl) were employed as the working, counter and reference electrodes, respectively. Before the ORC treatment, the gold electrode was mechanically polished (model Minimet 1000, Buehler) successively with 1 and 0.05 μm of alumina slurry to a mirror finish. Then the electrode was cycled in a deoxygenated 0.1 M KCl aqueous solution (40 mL) from −0.28 to +1.22 V vs Ag/AgCl at a scan rate of 500 mV/s for 200 scans. The durations at the cathodic and anodic vertices are 10 and 5 s, respectively. After the ORC treatment, Au- and Cl-containing complexes were produced in the solution, as reported in our previous study [24].

2.3. Sonoelectrochemical preparation of SERS-active Pt substrates with Au NPs

Immediately, the working electrode of gold was replaced by a platinum substrate with a bare surface area of 0.238 cm^2 in the same solution. Here the platinum substrate was chosen because it is inert in the following experiments. Then a cathodic overpotential of 0.6 V and an anodic overpotential of 0.3 V from open circuit potential (OCP) of ca. 0.83 V vs Ag/AgCl were applied in turn under sonication to prepare Au NPs deposited on Pt substrates. The ratio of reaction times of cathodic deposition to anodic dissolution of Au NPs is 0.2. In applying the cathodic overpotential for pulse deposition of Au NPs, the total accumulated deposition times are variables of 20, 40 and 60 s. After this deposition of Au NPs, the platinum substrate was rinsed throughout with deionized water, and finally dried in a dark vacuum-dryer for 1 h at room temperature for subsequent use. The ultrasonic treatment was performed by using an ultrasonic generator (model XL2000, Microson) and operated at 20 kHz with a barium titanate oscillator of 3.2 mm diameter to deliver a power of 80 W. The distance between the barium titanate oscillator rod and the electrode is kept at 5 mm.

2.4. Electrodeposition of polypyrrole on Pt substrates with Au NPs

The electrochemical polymerization of PPy on the Au NPs-deposited Pt substrate was carried out at a constant anodic potential of 0.90 V vs Ag/AgCl in a deoxygenated aqueous solution containing 0.1 M Py and 0.1 M $LiClO_4$. For comparison, PPy was also electrodeposited on the polished Pt substrate without Au NPs by using the same polymerization conditions.

2.5. Characteristics of Au NPs-deposited Pt substrates and electrodeposited PPy

Before conductivity measurements, the PPy films were stripped from the electrodes with insulating Scotch tape and had a mechanical stability that made them well suited for the measurements. Then the conductivities of PPy films were determined by using a commercial instrument (Model RG-7B, Napson) applying a four-probe technique with a direct current (DC) measurement at room temperature. In this measurement, a film thickness of 10 μm, according to a correlation between thickness and charge passed [27], was used. The duration for every measurement of conductivity is 2 s. Surface morphologies of Au NPs-deposited Pt substrates and electrodeposited PPy films were examined by using a scanning electron microscope (SEM, model S-4700, Hitachi). For high resolution X-ray photoelectron spectroscopy (HRXPS) measurements, a ULVAC PHI Quantera SXM spectrometer with monochromatized Al Kα radiation, 15 kV and 25 W, and an energy resolution of 0.1 eV was used. To avoid the interferential signals from the substrate, an arrangement of tilt 15° geometry between X-ray and samples was used in measurements. To compensate for surface charging effects, all HRXPS spectra are referred to the C 1s neutral carbon peak at 284.8 eV. Raman spectra were obtained (Renishaw InVia Raman spectrometer) by using a confocal microscope employing a diode laser operating at 785 nm with an output power of 1 mW on the sample. A 50×, 0.75 NA Leica objective was used to focus the laser light on the samples. The laser spot size is ca. 1–2 μm. A thermoelectrically cooled charge-coupled device (CCD) 1024 × 256 pixels operating at −60 °C was used as the detector with 1 cm^{-1} resolution. All spectra were calibrated with respect to silicon wafer at 520 cm^{-1}. In measurements, a 180° geometry was used to collect the scattered radiation. A holographic notch filter was used to filter the excitation line from the collected light. The acquisition time for each measurement was 10 s. Replicate measurements of five times on different areas were made to verify the spectra were a true representation of each sample. The relative standard deviation is within 10% based on the strongest band intensity of PPy on the Raman spectrum. For different experimental requirements, the charges used in electrodepositing PPy on substrates were 5000, 1, 1 and 1 mC cm^{-2} for the experiments of conductivity, Raman, HRXPS and SEM, respectively.