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Poly(ionic liquid) functionalized polypyrrole nanotubes supported gold nanoparticles: An efficient electrochemical sensor to detect epinephrine

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ABSTRACT

Poly(ionic liquids) (PILs) have been applied as the linkers between Au nanoparticles (NPs) and polypyrrole nanotubes (PPyNTs) for the synthesis of Au/PILs/PPyNTs hybrids. Due to the presence of PILs, high-density and well-dispersed Au NPs have been deposited on the surface of PILs/PPyNTs by anion-exchange with Au precursor and the in-situ reduction of metal ions. The obtained Au/PILs/PPyNTs hybrids can be used as a good steady electrode material for sensitively and selectively detecting epinephrine (EP). The catalytic oxidation peak currents obtained from differential pulse voltammetry (DPV) increased linearly with increasing EP concentrations in the range of 35–960 μM with a detection limit of 298.9 nM according to the criterion of a signal-to-noise ratio = 3 (S/N = 3), respectively, which showed the excellent electrocatalytic activity towards this significant hormone in human life.

1. Introduction

Noble metal nanoparticles (NPs), such as Au, Ag, Pt, Pd, Ru and their alloys, have stimulated much interest over the past decades due to their unique electric, magnetic, optical, and catalytic properties, which showed great difference from those of the bulk materials depending on the particle size, morphology and specific surface area [1–5]. They displayed various applications in many fields, including electronics [6], photonics [7], catalysts [8], biotechnology [9], medicine [10], electrochemical detection and sensing [11]. In order to accurately control particle size and prevent agglomeration resulting from van der Waals attractions [12], many synthetic routes have been developed to prepare stable and monodisperse noble metal NPs capped with a certain stabilizer (surfactants [13] and nucleotides [14]) or supported on certain substrates, especially micro-/nanomaterials (carbon nanotubes [15], polymer microspheres [16], porous membrane [17] and metal oxides nanomaterials [18]) always by gentle reduction.

In the family of various micro-/nanomaterials, conducting polymers with one-dimensional (1D) nanostructures have received a tremendous amount of attentions due to their long conjugation length and controllable conductivity resulted from their smaller dimension structures and high surface area [19–23]. In particular, 1D conducting polymers can be further oxidized due to their reversible oxidation/reduction chemical properties by several strong oxidants (including $HAuCl_4$, H_2PdCl_4, H_2PtCl_6, $AgNO_3$) as the precursors for preparing noble metal NPs. Therefore, 1D conducting polymers can act as templates for the dispersion and stabilization of noble metal NPs, and the obtained new composites will be potentially exploited in some particular application because of the electron transfer between the two components [24–26].

Recently, many kinds of 1D conducting polymers nanocomposites with noble metal NPs have been successfully fabricated via an in-situ redox reaction between noble metal precursors and conducting polymers or suitable reducing agent, which might be exploited in the application to nonvolatile plastic digital memory device [27], semi-heterogeneous catalyst in water [28], direct methanol fuel cells [29], high-efficiency nanoelectrocatalysts for electrochemical devices [30], etc. It's worth noting that ionic liquids (ILs) with excellent ion-exchange capability have been involved in the surface modification of polypyrrole nanotubes (PPyNTs) and applied as the linkers for the synthesis of platinum nanoparticles/ionic liquids/polypyrrole nanotubes (Pt/ILs/PPyNTs) hybrids, which exhibited high electrocatalytic activity in electrocatalytic oxidation of methanol [31]; Au/ILs/PPyNTs hybrids synthesized by such method can be used as efficient electrocatalyst for oxygen reduction and catalytic reduction of 4-nitrophenol [32]. The existence of ILs has contributed to the deposition of high-density and well-dispersed Pt or Au NPs on the surface of PPyNTs and optimized the performance of the obtained hybrids.

Herein, poly(ionic liquids) (PILs) with both unique properties of ILs together and the intrinsic polymer properties have been applied as the linkers between Au NPs and PPyNTs for the synthesis of Au/PILs/PPyNTs hybrids. In our previous research [33], the excellent electrochemical

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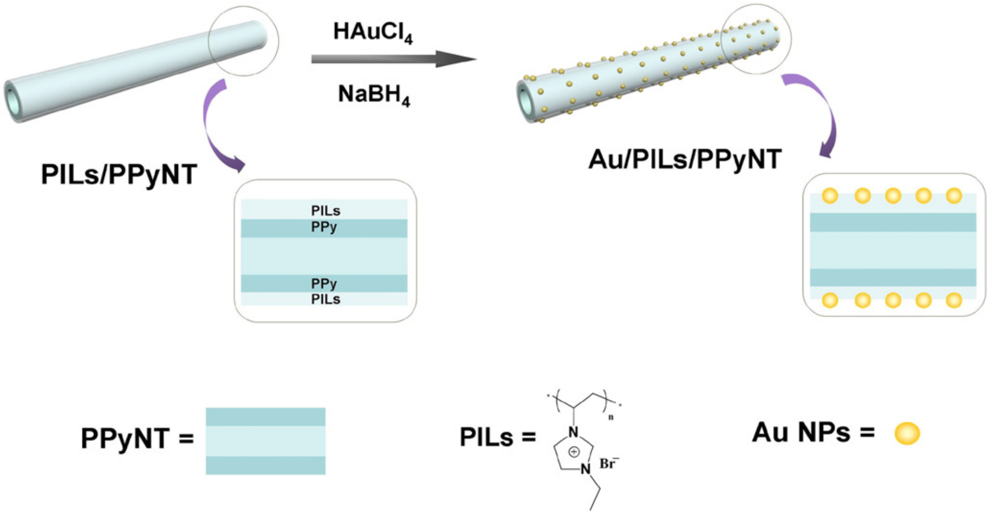

Scheme 1. The reaction procedure for the preparation of Au/PILs/PPyNTs. High-density and well-dispersed Au NPs could be deposited on the surface of PILs/PPyNTs by anion-exchange of PILs with Au precursor and the in-situ reduction of the metal ions, due to the presence of PILs.

catalytic activities towards dopamine (DA) and ascorbic acid (AA) were achieved by PILs functionalized PPyNTs (PILs/PPyNTs) modified glassy carbon electrode (GCE), which exhibited excellent sensitivity and good stability for the simultaneous detection of both basic life substances. Noble metal NPs possess excellent electrocatalytic activity towards many hormones as well as basic life substances and may effectively improve the electron transfer rate, which are usually used in electrochemical detection and sensing [11]. Therefore, the obtained Au/PILs/PPyNTs hybrids can be used as a good steady electrode material for sensitively and selectively detecting epinephrine (EP), which showed the excellent electrocatalytic activity towards this significant hormone in human life.

2. Experimental section

2.1. Materials

Pyrrole (Py) (≥98.0%) and bromoethane (Sinopharm Chemical Reagent Co. Ltd. (Shenyang, Liaoning province, China), ≥98.0%) are chemical grade. *N*-vinyl imidazole was purchased from Yancheng Medical Chemical Factory (Yancheng, Jiangsu province, China), which were distilled under vacuum before use. All the other reagents were analytical grade, and used without further purification, including methyl orange (MO) (IND) and ethanol (≥99.7%) (Tianjin Damao Chemical Factory, Tianjin, China); $FeCl_3 \cdot 6H_2O$ (≥99.0%), KOH (≥85.0%), NaCl (≥99.5%), chloroform (≥98.0%), glucose (≥99.5%), citric acid (≥99.5%), uric acid (UA) (≥99.0%), sodium borohydride ($NaBH_4$) (≥96.0%) and $HAuCl_4 \cdot 4H_2O$ (content of Au ≥ 48.7%) (Sinopharm Chemical Reagent Co. Ltd.); 1,4-dibromobutane (≥98.0%), 2,2-azobisisobutyronitrile (AIBN) (≥98.0%) and (±)-epinephrine hydrochloride (EP) (≥98.0%) (Aladdin reagent Co., Ltd., Shanghai, China); dimethyl formamide (DMF) (Tianjin Beilian Fine Chemicals Development Co., Ltd. (Tianjin, China), ≥99.5%), D-fructose (Beijing Biotopped science & technology Co., Ltd. (Beijing, China), ≥99.0%), sucrose (Tianjin Kemiou Chemical Reagent Co., Ltd. (Tianjin, China), ≥99.5%), dopamine hydrochloride (DA) (Alfa Aesar (Shanghai, China), ≥99.0%), L-ascorbic acid (AA) (≥99.7%), Na_2HPO_4 (≥99.0%) and NaH_2PO_4 (≥99.0%) (Tianjin Yongda Chemical Reagent Co., Ltd., Tianjin, China).

2.2. Preparation of Au/PILs/PPyNTs

Firstly, PILs/PPyNTs were synthesized by a covalent method as our previous report [33], for instance, they were obtained by a polymerization of 1-vinyl-3-ethylimidazole bromide (VEIB) on the surface of imidazolium-type ILs modified PPyNTs with polymerizable vinyl groups, which were pre-prepared by bonding 1,4-dibromobutane and *N*-vinyl imidazole to PPyNTs in sequence in DMF containing KOH. Then, Au/PILs/PPyNTs were prepared by the in-situ growth of Au NPs on the surface of PILs/ PPyNTs (Scheme 1), similarly to the previous report [32]. In a typical procedure, 10 mg of PILs/PPyNTs were well dispersed in 18 mL of deionized water by ultrasonic processing in an ultrasonic bath (40 kHz, 200 W, SB-5200DTN, Ningbo Ultrasound Co. Ltd., Ningbo City, China) for 10 min. $HAuCl_4$ aqueous solution (0.5 mL, 30 mM) was then added in the above mixture. After the mixture was stirred at room temperature for 3 h, $NaBH_4$ aqueous solution (2.5 mL, 0.04 M) was added into the reaction mixture and further stirred at room temperature for 12 h until the Au precursor was reduced completely, which was determined by the fact that no Au ion can be

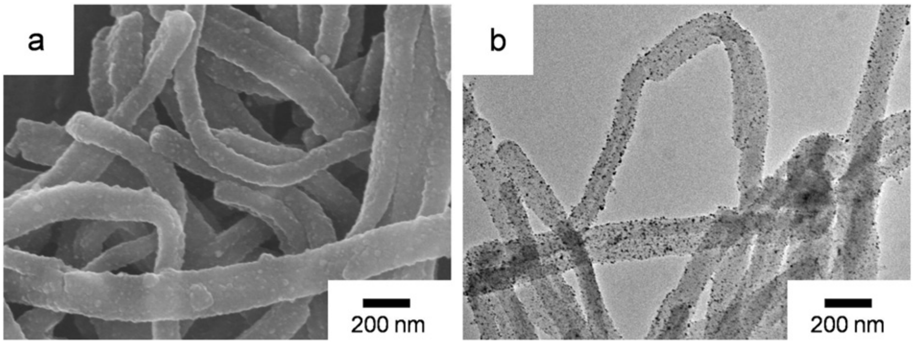

Fig. 1. (a) SEM and (b) TEM images of Au/PILs/PPyNTs. Au NPs in the diameter range of 13–16 nm are densely and uniformly distributed on the surface of PILs/PPyNTs.