Hollow, Spherical, Poly(3,4-ethylenedioxythiophene)-Bearing Methanethiol as a Gold Stabilizer for High-Efficiency Electrochemical Sensors

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Conducting polymers decorated with noble metals are good electrochemical sensors for biological species. In this work, we developed a polymer of methanethiol-grafted poly(3,4-ethylenedioxythiophene) hollow spheres (Poly(EDOT-MeSH)) using SiO2 nanospheres as a hard template. The Poly(EDOT-MeSH) spheres were used as both a reductant and stabilizer to decorate gold nanoparticles (Au NPs). FTIR, XRD, EDX, SEM and TEM analyses were used to characterize the Poly(EDOT-MeSH)/Au hollow spheres. The chemical bond between S and Au was confirmed by XPS. The electrochemical performance of the Poly(EDOT-MeSH)/Au hollow spheres was determined by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The results revealed that the Poly(EDOT-MeSH)/Au hollow sphere-based electrochemical sensor possesses an excellent conductivity and high redox reversibility with detection limits (S/N = 3) of 5.3, 0.04 and 0.12 μM in the linear ranges of 50–320 μM, 0.05 μM, 780 μM and 0.8 μM — 250 μM for the determination of AA, DA and UA, respectively. These results will further the development of this type of electrochemical sensor for biological species.

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Small biological species usually coexist in physiological fluids, which are very important for maintaining the functions of organisms.1,2 As typical biological species, dopamine (DA), uric acid (UA) and ascorbic acid (AA) are important components of the neural system and play significant roles in physiological functions.3,4 DA is a natural neurotransmitter that plays an important role in controlling the central nervous system and coordinating normal cardiovascular, renal, and hormonal functions.5,6 The UA concentration in blood and urine is usually related to diseases such as Lesch-Nyhan syndrome, hyperuricemia, gout and kidney stones.7,8 Therefore, the ability to detect and quantify these biological species is very important. Several analytical techniques, such as liquid chromatography,9 ultraviolet visible spectroscopy,10 capillary electrophoresis,11,12 chemiluminescence13,14 and spectrometry15 have been used to detect single or multiple biological species. However, most of these techniques require specialized, expensive instruments and can be utilized only for individual determination. In the last few years, electrochemical techniques have attracted attention for the determination of multiple components due to their simplicity, low cost, minimal analysis time, high sensitivity, good selectivity and simple instrumentation.16–18 However, the electrochemical oxidation of DA and UA is difficult to observe with conventional electrodes, such as glassy carbon, gold and platinum electrodes, because the oxidation products cause electrode surface fouling.19–21 In addition, AA co-exists with DA and UA in most biological fluids, and the AA concentration is higher than that of DA and UA (100–1000 times higher than that of DA).20 The AA oxidation peak often overlaps with the DA and UA peaks because their oxidation potentials on conventional electrodes are nearly equal.21,22 To solve this problem, novel sensing materials must be developed. The ineffectiveness of conventional electrodes can be improved by modifying them with electrochemically active materials, such as carbon-based nanomaterials,23,24 metal nanoparticles,25 polymeric materials26,27 and nanocomposites.28,29 Among these materials, noble metals (gold (Au), platinum (Pt), and palladium (Pd)) have been widely used for electrode modification due to their remarkable electronic, optic, catalytic and size-dependent properties. In particular, Au nanoparticles (NPs) have wide applications as “electron antennae” due to their high electron kinetics, good conductivity, high surface area and biocompatibility. However, their reproducibility, stability and ability to sense low concentrations of DA and UA are complicated by their large surface-to-volume ratio and tendency to aggregate.30–32 Studies have shown that electrochemically active materials, including conducting polymers32,33, graphene oxide,34 carbon nanotubes (CNTs),35,36 and some metal oxides,37 are ideal substrates for uniform NPs deposition due to their remarkable conductivities and fast electron kinetics.38,39 In addition, the deposition of Au NPs onto conducting polymers can enhance the electroactive surface area, facilitate the electro kinetics, and enhance the electrode sensitivity and selectivity.40 Among the various types of conducting polymers, PEDOT and its derivatives are typically used as substrates for Au NPs due to the strong attraction between the Au NPs and the S atom in the thiophene ring.41–43 These polymers are also widely used as modifiers because of their excellent redox activity, biocompatibility, high electron transfer capability, and strong absorption of certain analytes.44,45 The physiochemical properties and practical applications of Au NPs strongly depend on their specific size and morphology. Therefore, preparation of Au NPs with a uniform size is still a research focus.46 Recent studies have shown that Au NPs can be effectively stabilized by a thiol group through Au–S bonding,37,47 and the resultant species have extraordinary electrocatalytic activity due to their high dispersivity and size-specific physical and chemical properties. Thus, these species have potential applications in sensing and photodetective devices.48,49 In our previous work, we synthesized PEDOT/Au hollow spheres using PVP as both the soft template and stabilizer,51 and we determined that the spherical, hollow morphology and interaction between the thiophene S and Au results in a uniform distribution with a high surface area. Studies have shown that thiol S atoms can more favorably bind on the Au surface than thiophene S atoms, and the thiol S–Au interaction is more energetically stable than the interaction between a thiophene S atom and Au.52–54

Herein, we report the preparation and electrocatalytic applications of highly dispersible Poly(EDOT-MeSH)/Au hollow spheres using SiO2 nanospheres as the hard template. The PEDOT derivative, i.e., the Poly(EDOT-MeSH) spheres, may act as a substrate and function as both a reductant and stabilizer for the Au NPs. The electrocatalytic studies showed that the Poly(EDOT-MeSH)/Au-modified electrode exhibited a high sensitivity and selectivity for AA, DA and UA.
Experimental

Chemicals and reagents.—3,4-Dioxythiophene, 3-chloro-1,2-propanediol, chlorauric acid hydrate (HAuCl₄ • 4H₂O), ammonium persulfate ((NH₄)₂S₂O₈) and polyvinyl pyrrolidone (PVP) (molecular weight of ~ 40,000) were purchased from Shanghai Aladdin Reagent Company (China).

Monomer synthesis.—As shown in Fig. 1, EDOT-MeSH was synthesized through a three-step reaction based on a literature report. First, a mixture of 3,4-dimethoxythiophene (1.64 g, 5.7 mmol), 3-chloro-1,2-propanediol (2.6 g, 12 mmol), toluene (28 mL) and p-toluene sulfonic acid monohydrate (0.16 g, 0.42 mmol) were placed in a two-neck flask and magnetically stirred at 90 °C for 24 h under a nitrogen atmosphere. Then, 2.6 g (12 mmol) of 3-chloro-1,2-propanediol was added to the solution, and the solution was refluxed for an additional 5 h at 90 °C. A yellow oil (yield 56%) of chloromethyl-EDOT was obtained by column chromatography (silica gel, volume ratio of hexane/dichloromethane = 8:2) after evaporation of toluene. (The 1H-NMR data for EDOT-MeCl are shown in Fig. S1(A).)

Second, chloromethyl-EDOT (1.20 g, 3.1 mmol) and the thioacetic acid s-potassium salt (1.08 g, 4.7 mmol) were added to N,N-dimethylformamide (DMF, 6 mL) and refluxed for 16 h at 50 °C. The reaction mixture was then cooled to room temperature and extracted with dichloromethane (30 mL) by replacing the water three times. The organic phase was dried using anhydrous magnesium sulfate, and the EDOT-methanethioester was obtained as orange oil after evaporation (yield 70%). (The 1H-NMR data for the EDOT-methanethioester are shown in Fig. S1(B).)

Third, the thioester-EDOT (1.0 g, 2.2 mmol) and sodium methoxide (1.2 M in methanol, 8.0 mL) were added to distilled THF (80 mL), and stirred at room temperature for 5 h. The mixture was treated with 5 M HCl before evaporation. The organic phase was washed three times with water. An orange oil of EDOT-methanethiol was obtained after evaporation (yield 75%). (The 1H-NMR data for EDOT-MeSH are shown in Fig. S1(C).)

Modification of the SiO₂ spheres.—The prepared SiO₂ nanospheres (0.3 g) were added to a polyvinylpyrrolidone (PVP, 1.6 M, Mw ~ 40,000; the concentration was calculated based on the repeating unit) solution. The mixture was stirred for 4 h at 100 °C to load PVP on the surface of the SiO₂ nanospheres, and then, the mixture was cooled to room temperature.

Poly(EDOT-MeSH)/SiO₂ spheres synthesis.—As shown in Fig. 2, PVP-modified SiO₂ nanospheres (0.3 g) and EDOT-MeSH monomer (110 μL) were dispersed in 5 mL of CHCl₃ and ultrasonicated for 15 min to facilitate absorption of the monomer onto the surface of the PVP-modified SiO₂ spheres. Then, the CHCl₃ was evaporated at room temperature, and the remaining mixture was dispersed in 20 mL of distilled water. (NH₄)₂S₂O₈ (0.69 g) and 1.5-NSA (0.1 g) were added to the EDOT-MeSH-absorbed SiO₂ sphere dispersion, and the mixture was stirred for 24 h at room temperature. Finally, the product was centrifuged at 6000 rpm for 20 min and washed with trichloromethane and ethanol. The hollow and de-doped Poly(EDOT-MeSH) spheres were obtained using 0.1 M NaBH₄ (aq) at 60 °C for 6 h.

Poly(EDOT-MeSH)/Au hollow spheres synthesis.—The Poly(EDOT-MeSH) hollow spheres (0.3 g) were dispersed in deionized water (20 mL) in an ice bath with magnetic stirring. An HAuCl₄ aqueous solution (0.017 mM, 10 mL) was added dropwise to the suspension (~ drip/10 s), and the system was stirred for 16 h. Finally, the products were washed with deionized water and ethanol and dried under vacuum at 60 °C for 24 h.
Figure 3. (A): FTIR, (B): XRD and (C): EDX spectra of Poly(EDOT-MeSH) and Poly(EDOT-MeSH)/Au hollow spheres.

Structural characterization.—The FTIR spectra of the samples were recorded using an FTIR spectrometer (BRUKER- QEuinox-55) and KBr pellets. Energy dispersive X-ray spectroscopy (EDS) was obtained with a scanning electron microscope (Hitachi, S-4800, operating voltage, 5 kV, Japan). X-Ray photoelectron spectroscopy (XPS) images were collected on a JEM-1230 transmission electronic microscope (JEOL, model 2100). X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 diffractometer with a monochromatic Cu-Kα radiation source (λ = 0.15418 nm), and the scan range (2θ) was 5° to 70°.

Electrocatalytic activity measurements.—An electrochemical workstation, CHI 660C (ChenHua Instruments Co., Shanghai, China) was used to perform the electrochemical experiments. A three-electrode system was employed to study the electrochemical performance of the composites. A Pt electrode was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode. A Poly(EDOT-MeSH)/Au hollow sphere-modified GCE (glassy carbon electrode, diameter = 4 mm) was used as the working electrode. The working electrode was pretreated by placing 5 μL of a 0.5 mg/mL Poly(EDOT-MeSH)/Au suspension (included 2 μL of Nafion) on a bare GCE surface, and drying the solution for 20 min at room temperature. Differential pulse voltammetry (DPV) was performed in 0.1 M N2-saturated PBS (pH 7.0).

Results and Discussion

Materials characterization.—Fig. 3A presents the FTIR spectra of the Poly(EDOT-MeSH) and Poly(EDOT-MeSH)/Au hollow spheres. As shown in Fig. 3A, the bands at ~1023, ~940, ~760, ~1384, ~1355, ~1480 and ~1645 cm⁻¹ are typical, characteristic vibrations of PEDOT.51 The bands at ~3117, ~3012 and ~2930 cm⁻¹ are due to the out-plane deformation vibrations of C-H, C-H-C and C-H₂-C, respectively, in the long chain of the fatty acid.48 The broad band at 3200–3700 cm⁻¹ is due to the vibrations of OH and S-H. The vibrations of the Poly(EDOT-MeSH) and Poly(EDOT-MeSH)/Au hollow spheres were approximately the same because Au NPs do not absorb in the infrared region. After the Au NPs were stabilized on the surface of the Poly(EDOT-MeSH) hollow spheres, the intensity of the vibration band at 3200–3700 cm⁻¹ was weaker for Poly(EDOT-MeSH)/Au than Poly(EDOT-MeSH). These results suggest that the interaction between Au and S-H weakens the vibration band at 3200–3700 cm⁻¹.

The presence of Au NPs was confirmed by the powder XRD patterns, which are shown in Fig. 3B. Poly(EDOT-MeSH) shows a broad characteristic peak at 2θ = 29.15°, which is associated with intermolecular π-π* stacking and is attributed to the (020) reflection of the polymer backbone.31 In addition to the characteristic peak of Poly(EDOT-MeSH), four strong diffraction peaks for Au NPs appear at 2θ = 37.80°, 43.95°, 64.20° and 77.25°, and are correspond to the (111), (200), (220) and (311) planes of Au, respectively.31 These results provide good evidence for the successful formation of Au NPs on Poly(EDOT-MeSH).

Fig. 3C shows the energy dispersive X-ray spectrometry (EDX) spectra of the Poly(EDOT-MeSH)/Au hollow spheres. The EDX
spectra show peaks for C (37.21 wt%), O (17.71 wt%), S (14.79 wt%), and Au (30.29 wt%). Furthermore, the results confirm that the chemical state of the gold incorporated into the Poly(EDOT-MeSH) hollow spheres was metallic gold, and the Au NPs were stabilized on the polymer backbone through Au–S bonding.

To evaluate the chemical bond formation between S and the Au NPs, an XPS analysis was performed. The wide-scan XPS spectrum of Poly(EDOT-MeSH)/Au showed sharp peaks at 87, 164, 285 and 532 eV, which correspond to the signals of Au 4f, S 2p, C 1s and O 1s, respectively (Fig. 4A). The high-resolution XPS spectra of the Poly(EDOT-MeSH) and Poly(EDOT-MeSH)/Au hollow spheres are shown in Figs. 4B, 4C and 4D. As shown in Fig. 4B, the Au 4f7/2 and Au 4f5/2 peaks at 84.2 and 87.9 eV, respectively, for the Poly(EDOT-MeSH)/Au hollow spheres indicate the presence of Au0.58,59 Generally, the binding energies of the bulk Au 4f levels appear at (4f7/2) 83.8 and (4f5/2) 87.6 eV.60,61 In our case, the Au 4f7/2 and Au 4f5/2 binding energies were slightly higher than the bulk Au 4f levels, which suggested that the Au atoms bond with the S atom in Poly(EDOT-MeSH).62–64 The C 1s spectra of Poly(EDOT-MeSH) and the Poly(EDOT-MeSH)/Au hollow spheres display three peaks at 284.8, 286.1 and 288 eV (Fig. 4C), which correspond to the C-C, C-S and C-O bonds in Poly(EDOT-MeSH), respectively.65–67 The S 2p spectra of Poly(EDOT-MeSH) showed spin-split doublet peaks at 163.7 (S 2p3/2) and 164.9 eV (S 2p1/2), which correspond to unbonded S atoms in Poly(EDOT-MeSH)57,68 (Fig. 4D). In addition, the peaks at 167.4 and 168.7 eV can be attributed to oxidized S,68,69 which represents the S atoms in ammonium persulfate and the camphor-sulfonic acid doping agent. These peaks disappeared after de-doping with NaBH4. For the Poly(EDOT-MeSH)/Au hollow spheres, the S 2p peaks at 163.7 and 164.9 eV slightly shifted to 162.9 and 164.1 eV, respectively, after Au NP decoration, which suggested the formation of the Au–S bond.53,70 Therefore, the XPS characterization of the Poly(EDOT-MeSH)/Au hollow spheres reveals that the Au NPs are attached to the Poly(EDOT-MeSH) surface through S-Au bonds.

The typical morphology of the Poly(EDOT-MeSH) and Poly(EDOT-MeSH)/Au hollow spheres was observed with TEM, and the results are displayed in Fig. 5. The size of prepared SiO2 nanospheres is approximately 350 nm, and which are relatively uniform and highly monodispersed (Fig. 5a). Hence, the SiO2 nanospheres are ideal hard templates for the preparation of uniform, hollow nanospheres. The SiO2 modification plays an important role in the growth of Poly(EDOT-MeSH) on the SiO2 spheres. The SiO2 spheres were modified with PVP (molar ratio of PVP:SiO2 of 10:1) at 100 °C for 3 h before preparing the Poly(EDOT-MeSH)/SiO2 spheres. And the thickness of the PVP layer can be seen in the TEM image (Fig. 5b). Fig. 5c shows the shell/core structure of the Poly(EDOT-MeSH)/SiO2 spheres. It’s clear that surface of the SiO2 spheres uniformly encapsulated by polymer layer after the oxidative polymerization. Hollow and de-doped Poly(EDOT-MeSH) spheres were obtained using a 0.06 g/ml NaBH4 solution. The largest difference between the shell/core Poly(EDOT-MeSH)/SiO2 and Poly(EDOT-MeSH) hollow spheres is that the former has a dark core with a polymer shell (Fig. 5c) and the latter has a polymer shell with a bright center (Fig. 5d). Furthermore, the shell thickness of the polymer is uniform, indicating uniform growth of Poly(EDOT-MeSH) on the surface of the SiO2 spheres. After decorated with Au NPs, the Au NPs were clearly
uniformly distributed on the hollow Poly(EDOT-MeSH) (Figs. 5e and 5f) due to the interaction between the Au NPs and the functional groups (−SH) on the Poly(EDOT-MeSH) hollow sphere surfaces. When the redox reaction happens, Au nuclei will grow on the surface of the Poly(EDOT-MeSH) hollow spheres, and Au will attach to the thiol groups through Au–S bonding.

**Electrochemical activity.**—Metallic NPs can significantly improve the electrochemical properties of composites because of their characteristics, such as a high surface to active area, highly efficient electronic transport and electrocatalytic activity.57 The electrochemical properties of Poly(EDOT-MeSH)/Au-modified electrode (Poly(EDOT-MeSH)/Au/GCE) were measured by CV in a 0.3 mM DA in PBS (pH 7.0) solution, and compared with those of bare GCE and Poly(EDOT-MeSH)-modified electrode (Poly(EDOT-MeSH)/GCE). (Fig. 5A). Well-defined oxidation peaks of DA were observed in all the CV curves. In order to understand the role of polymer supports and −SH group during the oxidation process of DA, the PEDOT/Au/GCE (PEDOT/Au HNs prepared by similar method with that of Poly(EDOT-MeSH) HNs) and AuNPs/GCE (particle size ~ 10 nm) also performed. It’s clear that the strongest oxidation peak of DA appears at polymer supported Au NPs/GCE. Besides that, Poly(EDOT-MeSH)/Au/GCE possess highest peak current, which suggested the polymer and −SH groups plays critical role during the electrochemical reaction. Furthermore, the uniform distribution of Au NPs provides a high specific area with excellent conductivity, and the superior electron transfer property of Poly(EDOT-MeSH) results in a composite with better electrocatalytic activity.

**Detection of DA.**—To evaluate the electrochemical sensing ability of the modified electrodes, different concentrations of DA were detected. First, the effect of the accumulation time was investigated, and the results showed that the anodic peak current of DA rapidly increased up to approximately 120 s of accumulation time. Then, the increase in the peak current was less prominent. Thus, 120 s was chosen as the optimal accumulation time to obtain a high sensitivity in the following experiments. Besides that, effect of the pH toward the oxidation of DA also performed. Fig. S2 shows the CV of DA at the Poly(EDOT-MeSH)/Au/GCE with different pH condition. It’s obvious that maximum current responses appeared at the pH = 7.0, and the peak current decreases pH value higher or lower than 7.0. Therefore, pH = 7.0 is applied to subsequent electrochemical detection.

Figs. 6B, 6C, 6D shows the DPV results for various DA concentrations with a GCE, Poly(EDOT-MeSH)/GCE and Poly(EDOT-MeSH)/Au/GCE in a PBS buffer solution (pH = 7.0). A calibration plot for the DPV responses of DA was obtained and is shown in Figs. 6B, 6C, 6D (inset)). As shown in Figs. 6A and 6B, the DA linear ranges on the GCE, Poly(EDOT-MeSH)/GCE and Poly(EDOT-MeSH)/Au/GCE were 3.5–25 μmol L⁻¹, 2.0–60 μmol L⁻¹, and 0.05–750 μmol L⁻¹ with regression equations of y = 0.087x + 0.432 (R² = 0.985), y = 0.067x + 2.015 (R² = 0.994), and y = 0.009x + 2.65 (R² = 0.998), respectively. Furthermore, the DA detection limits (S/N = 3) on the GCE, Poly(EDOT-MeSH)/GCE and Poly(EDOT-MeSH)/Au/GCE were 1.63, 0.47 and 0.04 μmol L⁻¹, respectively. Poly(EDOT-MeSH)/Au/GCE has the highest sensitivity and the lowest determination limit. The Au–S bonding allows a uniform distribution of Au NPs on Poly(EDOT-MeSH) hollow spheres and facilitates the composite electron kinetics.

**Simultaneous detection of AA, DA and UA.**—Generally, DA, UA, and AA coexist in biological species, and AA interferes with electrochemical sensing of DA and UA. The simultaneous detection of 150 μM AA, 20 μM DA and 30 μM UA by the bare GCE, Poly(EDOT-MeSH)/GCE and Poly(EDOT-MeSH)/Au/GCE in a 0.1 M PBS (pH = 7.0) solution was investigated using DPV. As illustrated in Fig. 7, the AA, DA and UA oxidation peaks nearly overlap with the GCE and Poly(EDOT-MeSH)/GCE because these electrodes have a lower sensitivity and poor selectivity. The Poly(EDOT-MeSH)/Au/GCE displayed three well-separated oxidation peaks for AA, DA and UA with higher anodic peak currents, which indicated Poly(EDOT-MeSH)/Au/GCE has a faster and stronger accumulation ability than the Poly(EDOT-MeSH)/GCE and bare GCE. The potential differences between AA-DA and DA-UA were 0.21 V and 0.19 V, respectively, and these differences are sufficient for the simultaneous determination of these species.
Figure 6. (A): Cyclic voltammograms of different modified electrodes in a 5.0 mM Fe(CN)$_6^{3-}$/$4-$/0.1 M KCl redox probe solution; DPV results with the (B): GCE (DA: 3.5–25 μM), (B): Poly(EDOT-MeSH)/GCE (DA: 2.0–60 μM), and (C): Poly(EDOT-MeSH)/Au/GCE (DA: 0.05–750) in a PBS solution (pH 7.0).

Simultaneous detections of AA, DA and UA mixtures with the Poly(EDOT-MeSH)/Au/GCE were performed by DPV. As shown in Fig. 8, the concentration of one species was changed while that of the other two species was held constant. The DA peak current increased as the DA concentration (Fig. 8A) increased, and the AA (150 μM) and UA (30 μM) peak currents were stable. The results show that the linear relationship between the peak current and species concentration occurs in the range of 0.05–550 μM for DA, which is lower than the linear range of 0.05–750 μmol L$^{-1}$ for a single species. Furthermore, the UA peak current increased when the UA concentration (Fig. 8B) increased, while the AA (150 μM) and DA (20 μM) peak currents were stable. The linear relationship between the peak current and species concentration occurred in the range of 0.8–270 μM for UA. These results indicate that Poly(EDOT-MeSH)/Au/GCE can be used to determine UA in the presence of multiple species.

Fig. 8C shows the results for the simultaneous detection of various concentrations of AA, DA and UA with Poly(EDOT-MeSH)/GCE. As shown in Fig. 8C, the oxidation peak currents increased as the concentrations of AA, DA and UA increased. The corresponding linear relationships between the peak currents and species concentrations are 50–320 μM (R$^2$ = 0.998), 0.05–600 μM (R$^2$ = 0.998) and 0.8–250 μM (R$^2$ = 0.998) for AA, DA and UA, respectively. Furthermore, the corresponding linear regression equations are y = 0.009x + 2.89, y = 0.008x + 3.05 and y = 0.02x + 3.47 for AA, DA and UA with detection limits of (S/N = 3) 5.3, 0.04 and 0.12 μM, respectively. A comparison of the different modified electrodes is shown in

Figure 7. (a) DPV of the (a) GCE, (b) Poly(EDOT-MeSH)/GCE, and (c) Poly(EDOT-MeSH)/Au/GCE in a PBS solution containing 150 μM AA, 20 μM DA and 30 μM UA (pH 7.0).
Figure 8. DPV curves of Poly(EDOT-MeSH)/Au/GCE in a PBS solution (pH 7.0) containing mixed concentrations of AA, DA and UA. (A): 150 μM AA, 30 μM UA and DA (0.05–550 μM); (B) 150 μM AA, 20 μM DA and UA (0.8–270 μM); (C) AA (50–320 μM), DA (0.05–600 μM), and UA (0.8–250 μM).

Table S1. The high selectivity and sensitivity of the modified electrode are due to the two main characteristics of the Poly(EDOT-MeSH)/Au hollow spheres. First, Poly(EDOT-MeSH) has hydrophobic (reduced) and hydrophilic (oxidized) regions. The hydrophobic regions prefer to interact with DA and UA, while the hydrophilic regions interact with AA. Second, the –SH group acts as a stabilizer and functions as a bridge between Poly(EDOT-MeSH) and the Au NPs, and this bridge, i.e., S–Au bond, can accelerate the composite electron kinetics. It must be noticed that detection of AA was greatly decreased, and the possible reason is that the Nafion layers would inhibit the interaction between AA and the GCE surfaces, resulting in reduced electrochemical oxidation of AA. However, Nafion layers facilitate the electrochemical oxidation of DA, such as electrostatic attraction between positively-charged DA and Nafion layers.
Biosensor reproducibility and stability.—The reproducibility and stability of Poly(EDOT-MeSH)/Au/GCE were investigated. The stability of the prepared sensor was determined by detecting 165 μM AA, 35 μM DA and 30 μM UA with the Poly(EDOT-MeSH)/Au/GCE for 20 runs (Fig. 9A). The relative standard deviation (RSD) of the Poly(EDOT-MeSH)/Au/GCE was 3.1%, which suggested that the modified electrode is stable for the determination of multiple species. The modified electrode reproducibility was examined by detecting 100 μM AA, 75 μM DA and 70 μM UA with five electrodes independently prepared with Poly(EDOT-MeSH)/Au via the same procedure (Fig. 9B), and the RSD was 3.7%. A modified electrode was also stored at room temperature and tested every day. The current response of the modified electrode was 98.2% of the initial value after 10 days and 91.5% after 20 days (Fig. 9C). These results suggest that Poly(EDOT-MeSH)/Au/GCE has a good reproducibility and stability.

Real sample analysis.—To test the practical applications of the modified electrode, Poly(EDOT-MeSH)/Au/GCE was applied for the simultaneous detection of AA, DA and UA in urine samples using a standard addition method. AA, DA and UA were detected in three human urine samples by a standard addition method using DPV. The human urine samples were diluted 100 times with PBS (0.10 M, pH 7.0) before use. The diluted urine samples were added to an electrochemical cell (containing certain amounts of AA, DA and UA). As shown in Table S2, the recoveries for the human urine samples ranged from 97% to 103.5%. Therefore, Poly(EDOT-MeSH)/Au/GCE can be used to detect AA, DA and UA in real samples.

Conclusions

In summary, a novel Gold-decorated Poly(EDOT-MeSH)/Au hollow sphere sensor was synthesized using SiO2 as a hard template and Poly(EDOT-MeSH) as both the reductant and stabilizer. The results confirmed that the Poly(EDOT-MeSH) hollow spheres were successfully decorated with Au NPs through a redox reaction between Poly(EDOT-MeSH) and HAuCl4. The Poly(EDOT-MeSH) and Au NPs link through Au–S bonds, which effectively stabilize the Au NPs and result in a uniform distribution. Therefore, the Poly(EDOT-MeSH) hollow spheres act as a substrate, reductant and stabilizer. Furthermore, the chemical interaction between the Poly(EDOT-MeSH) and Au NPs was confirmed by the determination of DA, UA and AA. The findings confirmed that the excellent conductivity, high sensitivity, and high surface area of the Au NPs and the good selectivity and high electron kinetics of Poly(EDOT-MeSH) result in a composite with a high sensitivity, selectivity and stability.

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Figure 9. DPV curves of Poly(EDOT-MeSH)/Au/GCE for the (A) repeatability (containing 165 μM AA, 35 μM DA and 30 μM UA) and (B) reproducibility (containing 100 μM AA, 75 μM DA and 70 μM UA) tests. (C) Stability curves of Poly(EDOT-MeSH)/GCE and Poly(EDOT-MeSH)/Au/GCE.
