Gold Nanorods (AuNRs) and Zeolitic Imidazolate Framework-8 (ZIF-8) Core–Shell Nanostructure-Based Electrochemical Sensor for Detecting Neurotransmitters

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ABSTRACT: The development of novel electrode materials for rapid and sensitive detection of neurotransmitters in the human body is of great significance for early disease diagnosis and personalized therapy. Herein, gold nanorod@zeolitic imidazolate framework-8 (AuNR@ZIF-8) core–shell nanostructures were prepared by controlled encapsulation of gold nanorods within a ZIF-8 assembly. The designed AuNR@ZIF-8 nanostructures have uniform morphology, good dispersion, a large specific surface area, and an average size of roughly 175 nm. Compared with individual ZIF-8 and AuNR-modified electrodes, the obtained core–shell-structured AuNR@ZIF-8 nanocomposite structure-modified electrode shows excellent electrocatalytic performance in the determination of dopamine (DA) and serotonin (ST). The designed AuNR@ZIF-8 exhibited a wide linear range of 0.1–50 μM and low detection limit (LOD, 0.03 μM, S/N = 3) for the determination of DA, as well as a linear range of 0.1–25 μM and low LOD (0.007 μM, S/N = 3) for monitoring ST. The improved performance is attributed to the synergistic effect of the high conductivity of AuNRs and multiple catalytic sites of ZIF-8. The good electroanalytical ability of AuNR@ZIF-8 for detection of DA and ST can provide a guide to efficiently and rapidly monitor other neurotransmitters and construct novel electrochemical sensors.

INTRODUCTION

Dopamine (DA) and serotonin (ST) are among the most important monoamine neurotransmitters in the central nervous system. Dopamine is the most abundant catecholamine neurotransmitter in the brain, and it plays a key role in the function of the human central nervous system.1,2 However, the abnormal release of dopamine may cause a series of physical and psychological diseases. For example, an excessively high level of DA may cause neurological diseases such as hypertension, rapid heart rates, heart failure, and drug addiction. However, an excessively low level of DA can cause Alzheimer’s disease, Parkinson’s disease, and depression.3,4 Serotonin is widely distributed throughout the central nervous system and plays an important role in regulating neural activity and emotion-related behaviors.5 Deficiency in ST levels causes migraines, anxiety, and depression. Extremely high levels of ST can cause noticeable toxicity, thermoregulation, liver regeneration, and irritable bowel syndrome.6 A simple and rapid test to assess the DA/ST levels can be used as an early indicator of disease diagnosis. Therefore, the development of rapid and sensitive DA and ST analysis methods is very important for the clinical field and the management of multiple diseases.7 Up to now, many methods for the determination of DA and ST have been reported, including spectrophotometry,8 fluorescence,9 high-performance liquid chromatography (HPLC),10,11 mass spectrometry,12 capillary electrophoresis,13 and enzyme-linked immune sorbent assay (ELISA).14 However, these methods are expensive, difficult, and time-consuming.15 Compared with these technologies, electrochemical sensors have attracted much attention among researchers due to their low cost, fast response, good stability, and high sensitivity.16,17 As we all know, electrode materials are the key factor affecting the analytical performance of electrochemical sensors.18 Therefore, it is very important to develop suitable electrode materials to enhance the current response signal to a specific target analyte.19–21 Various types of materials have been used to construct electrochemical sensors, such as noble metal nanomaterials,
inorganic semiconductor nanomaterials, and carbon-based nanomaterials.\textsuperscript{22}−\textsuperscript{25} Among them, the emerging metal−organic frameworks (MOFs) materials have attracted widespread attention and obtained explosive development due to their ordered structure, large internal surface area, uniform but adjustable cavity, and tailorable chemical properties.\textsuperscript{4,26,27} They have been widely used in various applications, such as catalysis,\textsuperscript{28,29} gas storage/adsorption,\textsuperscript{30,31} drug delivery,\textsuperscript{32,33} and electrochemical sensing.\textsuperscript{34,35} Zeolitic imidazolate framework-8 (ZIF-8) is a typical MOFs material, which is constructed from Zn\textsuperscript{2+} ions and 2-methylimidazolate. It has the advantages of easy preparation, a simple crystal structure, good chemical stability, and high loading capacity.\textsuperscript{36} However, the direct applications of most MOFs in electrochemical sensing are still severely limited by their poor conductivity and weak electrocatalytic ability. In order to solve this problem, high conductivity and electroactive materials are usually introduced into MOFs, especially noble metal nanoparticles with special optical and electronic properties.\textsuperscript{37} The addition of these electrochemically active substances not only provides sufficient defects of MOFs but also effectively improves the conductivity of the constructed sensor, making the detection of DA and ST more efficient and sensitive.\textsuperscript{37}

Gold nanorods (AuNRs) have general properties just as gold nanomaterials, such as a high active surface area, excellent conductivity, high stability, and good biocompatibility.\textsuperscript{38,39} In addition, AuNRs have several advantageous features over the spherical gold nanoparticles, such as good electron transfer, a higher surface area, higher adsorption cross sections, and stronger light scattering properties.\textsuperscript{40,41} Such intrinsic properties of the AuNRs were believed to be favorable for the electrochemical analysis of biomolecules.\textsuperscript{42} Herein, we prepared a novel core−shell nanostructure of the gold nanorod@zeolite imidazolate ester framework (AuNR@ZIF-8) by growing a ZIF-8 shell in situ on the surface of the gold nanorods. Gold nanorods can increase the conductivity by facilitating the flow of electrons. ZIF-8 was used as a backbone to provide large adsorption sites.\textsuperscript{19,35} Therefore, the combination of AuNRs and ZIF-8 significantly enhanced the electrochemical performance of each component, enabling trace detection of DA and ST. The electrochemical test proved that the sensor constructed by AuNR@ZIF-8 has high sensitivity and selectivity and was not affected by the adsorption interference of serum proteins, indicating that this new type of sensor might have great potential in clinical sample detection.

\section*{RESULTS AND DISCUSSION}

Characterization of AuNR@ZIF-8. Figure 1a describes the preparation of the AuNR@ZIF-8 core−shell nanostructure. First, CTAB and 5-bromosalicylic acid-stabilized AuNRs were pre-prepared using the seed-mediated method. Transmission electron microscopy (TEM) showed that the as-synthesized AuNRs were well dispersed with an average size of $\sim 14 \times 58$ nm (width $\times$ length) (Figure S1a,c,d). Figure S1b shows that the as-synthesized AuNRs had a strong localized surface plasmon resonance (LSPR) peak at $\sim 800$ nm. Subsequently, the surface of the AuNRs was modified with PVP. The PVP adsorbed on the surface of the nanoparticles not only stabilizes the nanoparticles in the reaction solution but also provides the nanoparticles with an enhanced affinity to coordination-polymer spheres through weak coordination interactions between pyrrolidone rings (C\textsuperscript{=}O) and zinc atoms in ZIF nodes.\textsuperscript{43} Then, PVP-stabilized AuNRs were added to 2-MIM under gentle stirring. After that, a solution of Zn(NO\textsubscript{3})\textsubscript{2}·6H\textsubscript{2}O in methanol was added into the mixed solution, and the mixture solution was placed at room temperature without stirring for 1 h. Afterward, AuNR@ZIF-8 core−shell nanostructures were obtained. Surface plasmon resonance (SPR) is the most typical feature of noble metal nanoparticles.
According to the shape, position, and intensity of the SPR band, the shape and size of the nanoparticles can be judged. Therefore, the structural characteristics of the synthesized nanocomposites were first characterized by UV-vis. As seen from Figure 1b, the AuNR@ZIF-8 core–shell nanostructure shows a broad LSPR absorption centered at ~820 nm. Compared with pure AuNRs, due to the coating of the ZIF-8 shell, it exhibits a small bathochromic shift (~20 nm), which is consistent with the previously reported theoretical result.\(^4\)

The inset image in Figure 1b is the picture of AuNRs and AuNR@ZIF-8. The color of the solution changes from a transparent deep red to a colloidal pink after the ZIF-8 is coated, indicating the successful synthesis of AuNR@ZIF-8.

The morphology of the synthesized materials was investigated by SEM and TEM analyses. ZIF-8 nanocrystals have a regular dodecahedron shape with a relatively uniform size (Figures S2a and S3). SEM and TEM images show that the AuNR@ZIF-8 nanocomposite has a typical core–shell structure with an average particle size of 175 nm (Figure S2b and Figure 1c–e). The high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image clearly shows the core–shell structure of AuNR@ZIF-8, and energy-dispersive X-ray (EDX) elemental mapping further shows that Au is located in the core while Zn of ZIF-8 is distributed within the shell, revealing that a single AuNR core was surrounded by a uniform ZIF-8 shell (Figure 1f). In addition, the chemical composition of the AuNR@ZIF-8 was tested by energy-dispersive X-ray (EDX) spectrum analysis (Figure S4), confirming the presence of Au and Zn elements. Moreover, the dynamic light scattering (DLS) test demonstrates that the hydrodynamic particle size of AuNR@ZIF-8 is about 242.7 nm and the PDI is 0.176 (Figure S5), indicating a good colloidal dispersibility.

The structure of AuNR@ZIF-8 nanocomposites was further characterized by FTIR and XRD analyses. Figure 2a shows the FTIR spectra of ZIF-8, AuNR, and AuNR@ZIF-8 samples. The peak in the 1100–1400 cm\(^{-1}\) region corresponds to the C–N adsorption bond and the peak at 421 cm\(^{-1}\) is associated with the Zn–N stretching mode, which indicated the formation of ZIF-8 and AuNR@ZIF-8. The crystal structure and phase composition of AuNR@ZIF-8 core–shell nanostructures were characterized by X-ray diffraction (XRD). The XRD pattern of the as-synthesized AuNR@ZIF-8 core–shell nanostructure (Figure 2b) is similar to that of a ZIF-8 single crystal, except for the diffraction peaks at 38.18, 44.39, 64.58, 77.55, and 81.72° corresponding to the (111), (200), (220), (311), and (222) crystal facets of Au (JCPDS 00-004-0784), which is in agreement with previous reports.

A large surface area and high porosity are the most prominent features of MOFs, thus the Brunauer–Emmett–Teller (BET) measurements of ZIF-8 and AuNR@ZIF-8 were conducted. The N\(_2\) adsorption–desorption isotherms of ZIF-8 and AuNR@ZIF-8 both were a typical type I isotherm, which indicated that ZIF-8 and AuNR@ZIF-8 nanocomposites were dominated by a microporous structure, as presented in Figure S6a. The BET surface areas of ZIF-8 and AuNR@ZIF-8 were 1056 and 985 m\(^2\)/g, and pore volumes were 0.43 and 0.48 cm\(^3\)/g, respectively, revealing that the AuNR@ZIF-8 nanostructure maintains the distinguishing properties of ZIF-8. Moreover, the porosity distribution curve (Figure S6b) shows that the pore sizes in ZIF-8 and AuNR@ZIF-8 are in the range of 1–2 nm, demonstrating that ZIF-8 and AuNR@ZIF-8 mainly contains micropores. The above-analyzed results implied that the high specific surface area and unique porous nanostructure of AuNR@ZIF-8 nanocomposites may provide more active sites for the adsorption of DA and ST, which will contribute to improving the electrocatalytic performance of the modified electrode.

X-ray photoelectron spectroscopy (XPS) was used to determine the element composition and chemical status of AuNR@ZIF-8. Figure 2c shows the survey scan spectrum, confirming the presence of elements C, N, O, Zn, and Au in the as-prepared AuNR@ZIF-8, which is consistent with the EDX report. AuNR@ZIF-8 was further studied by high-resolution Au4f–Zn3p and Zn2p scans (Figure 2d,e). The Au4f–Zn3p peak is resolved into four separated peaks, Au4f\(_{7/2}\) (83.8 eV), Au4f\(_{5/2}\) (87.4 eV), Zn3p\(_{3/2}\) (88.7 eV), and Zn3p\(_{1/2}\) (91.6 eV), which are consistent with a Au–Zn alloy.\(^47\) Binding energies at 1021.6 and 1044.7 eV in the Zn 2p region can be ascribed to the Zn+\(^2\).\(^49\) These results indicate that AuNRs were successfully coated in ZIF-8.

**Electrochemical Behaviors of Different Modified Electrodes.** The electrochemical behaviors of the AuNR@ZIF-8-modified electrode, AuNR-modified electrode, ZIF-8-modified electrode, and bare electrode were checked by cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS). Figure S7a shows the CV curves of different modified electrodes in 30 mM potassium ferricyanide solution. A pair of redox peaks appears on the bare electrode, and the peak potential difference (\(\Delta E_p\)) is 73 mV. It can be seen that the redox peak current value of the ZIF-8/GCE is lower than that of the bare electrode, which is caused by the poor conductivity of ZIF-8, but its advantages should still be recognized and are worth discussing. The introduction of highly conductive AuNRs significantly improves the current response of the modified electrode and provides a higher redox peak current. In particular, the composite co-modified electrode of ZIF-8 and AuNR shows the highest current...
response due to their synergistic effect. The AuNR improves the electric conductivity, while ZIF-8 provides a larger specific surface area, contributing more active sites on the electrode surface.

Figure S7b shows the electrochemical impedance spectra of AuNR@ZIF-8/GCE, AuNR/GCE, ZIF-8/GCE, and GCE, respectively. This experiment was carried out at open-circuit potential (OCP) in the frequency range from 100 kHz to 0.01 Hz. According to a Randle-equivalent circuit, the circuit includes solution resistance \( (R_s) \), double-layer capacitance \( (C_{dl}) \), charge transfer resistance \( (R_{ct}) \), and Warburg impedance \( (Z_w) \). The initial point of the semicircle indicates the solution resistance \( (R_s) \), the diameter of the semicircle indicates the charge transfer resistance \( (R_{ct}) \), and the linear line indicates the diffusional process. A lower semicircle diameter means a smaller charge transfer resistance \( (R_{ct}) \). Obviously, the AuNR@ZIF-8-modified electrode has the smallest semicircle diameter in the high-frequency region, indicating that the AuNR@ZIF-8-modified electrode has the highest charge transfer rate and the lowest resistance, which is beneficial to promote the interface electrochemical reaction.\(^{51}\) Due to the poor conductivity of ZIF-8, the semicircle diameter of ZIF-8/GCE is the largest, indicating that it has the largest resistance, while the resistance of the bare electrode is lower than the former. Remarkably, the \( R_s \) value of the AuNR@ZIF-8/GCE is lower than that of AuNR/GCE and bare electrodes, which strongly proves that ZIF-8 has the advantages of high porosity and an orderly structure. In addition, the Nyquist diagram of the AuNR@ZIF-8-modified electrode shows a larger slope in the low-frequency region than the AuNR/GCE and the bare electrode, which means that the diffusion and mass transfer speed of the AuNR@ZIF-8/GCE is faster.\(^{52}\)

Subsequently, the prepared modified electrode was used to analyze DA and ST. First, cyclic voltamogram was used to investigate the electrochemical behavior of different modified electrodes in 0.1 M PBS (pH = 7.4) containing 25 \( \mu M \) DA, and the results are shown in Figure 3a. The bare electrode did not show obvious redox peaks. It is worth noting that, compared with the ZIF-8/GCE and the AuNR/GCE, the AuNR@ZIF-8/GCE exhibits the largest electrochemical signal and the highest peak current, which is mainly due to the high conductivity of AuNRs and the large surface area of ZIF-8. In addition, similar to the experimental phenomenon obtained by measuring DA, the AuNR@ZIF-8/GCE also shows the largest electrochemical signal and the highest peak current in 0.1 M PBS (pH = 7.4) containing 25 \( \mu M \) ST (Figure 3b). These results strongly indicate that the AuNR@ZIF-8-modified electrode has excellent electroanalytical performance in the determination of DA and ST.

**Effects of pH and the Scan Rate.** Generally, pH plays an important role in electrochemical processes. The effect of pH on the AuNR@ZIF-8/GCE was investigated using CV analysis with 25 \( \mu M \) DA in 0.1 M PBS with a pH between 6.0 and 8.0 at a 100 mV/s scan rate. Figure 4a shows that the anodic peak potential of DA oxidation gradually shifts negatively with the decrease of hydrogen ions and the increase of the pH value in the solution, indicating that protons participate in the electrochemical oxidation reaction of DA.\(^{53}\) In addition, the high current response was observed at pH 7.4 from Figure 4b, indicating that the AuNR@ZIF-8/GCE has the highest electrochemical activity at pH 7.4. Same as the DA measurement conditions, pH 7.4 was selected as the optimal pH for the sequent experiments toward the determination of ST in the pH range of 6.0–8.0 based on the experimental results shown in Figure S8a,b.

In order to study the possible kinetic mechanisms, we further tested the CV curves of the AuNR@ZIF-8/GCE at different scan rates. As shown in Figure 4c, the anodic oxidation peak current \( (I_{pa}) \) and cathodic reduction peak current \( (I_{pc}) \) increase gradually with the increment of the scan rate from 50 to 400 mV/s\(^{1/2}\). The linearity of the square root of the scan rate \( (\nu^{1/2}) \) and the redox peak current intensities are shown in Figure 4d. The linear regression equations are determined as follows: \( I_{pa} (\mu A) = 0.2116 \nu^{1/2} - 0.4817 \) \( (R^2 = 0.9643) \) and \( I_{pc} (\mu A) = -0.2964 \nu^{1/2} + 1.2930 \) \( (R^2 = 0.9760) \), where \( \nu \) and \( \nu^{1/2} \) mean the peak current and scan rate, respectively. These results indicate that the redox process of DA is diffusion controlled. Similarly, the AuNR@ZIF-8/GCE also shows a linear relationship between the scanning speed and the oxidation peak current during the ST detection process, indicating that the electroanalysis of ST is also a
diffusion control process (Figure S8c,d). It is worth noting that these oxidation processes mainly occur on the surfaces of AuNR@ZIF-8 for the determination of DA and ST. Due to the large surface area and a large number of open metal active sites of the AuNR@ZIF-8 catalyst, the electrocatalytic activity is significantly improved.

**Analytical Performance.** In order to demonstrate the sensitivity and detection limits of the modified electrode, under the optimal experimental conditions, the electrochemical responses of DA and ST on the AuNR@ZIF-8/GCE were determined by the CV method. As shown in Figure 5a, the oxidation peak current increases as the DA concentration increases from 0.1 to 50 μM. In addition, the peak current intensity has a good linear relationship with the DA concentration (Figure 5b). The linear regression equation is

\[ I_p = 0.0472c (\mu M) + 0.3609 \ (R^2 = 0.9994) \]

The limit of detection (LOD) is calculated to be 0.03 μM using the equation LOD = 3b/S, where S stands for the standard deviation of the blank and b is the slope of the linear equation of the concentration vs peak current. Figure 5c shows the CV response to the continuous addition of ST in 0.1 M PBS (pH 7.4). The AuNR@ZIF-8-modified GCE shows a rapid and sensitive response to the change in ST concentration, and the anode peak current increases significantly with the increase in ST concentration. In addition, the peak current intensity has a good linear relationship with the DA concentration (Figure 5d). The linear relationship between them can be fitted in two concentration ranges. When the ST concentration is in the range of 0.1–5 μM, the linear equation is fitted as follows: \( I (\mu A) = 0.0472c (\mu M) + 0.3609 \ (R^2 = 0.9955) \), the LOD is 0.007 μM; when the ST concentration is in the range of 5–25 μM, the linear equation is fitted as follows: \( I (\mu A) = 0.0818c (\mu M) + 0.8823 \ (R^2 = 0.9885) \), the LOD is 0.018 μM. The two linear regions appearing in the fitted curve in the two concentration ranges may be due to the following reasons. When the ST concentration is low, the electrochemical process is mainly an adsorption process. When the concentration increases, the influence of the diffusion process becomes more important and cannot be ignored. In addition, the sensitivity of the second linear range is lower than that of the first. The main reason is that as the ST concentration increases, the diffusion layer becomes thicker and the mass transfer resistance increases, resulting in a decrease in sensitivity. Compared with various electrochemical sensors reported in other literature studies for detecting DA and ST, the performances of our sensor based on the AuNR@ZIF-8-modified electrode herein is comparable and even better, and the results are presented in Table 1.

**Stability and Anti-Interference Ability of the AuNR@ZIF-8/GCE.** Stability and anti-interference ability are also important parameters for evaluating sensor capabilities. In order to investigate the stability of AuNR@ZIF-8, 40 continuous cycles were performed at a scan rate of 100 mV s⁻¹ in PBS (pH 7.4) containing DA or ST, respectively. As shown in Figure S9, the electrocatalytic current displays only a marginal decrease after 40 times of CV tests, indicating that the AuNR@ZIF-8-modified electrode has good electrochemical detection stability. Next, the anti-interference performance of the AuNR@ZIF-8/GCE was studied. In real samples, DA and ST often coexist with other electroactive molecules; thus, it is

### Table 1. Comparisons of the Analytical Parameters for the Determination of DA and ST with Different Electrode Materials

| Electrode materials | DA (μM) | ST (μM) | DA (μM) | ST (μM) | Ref. |
|---------------------|---------|---------|---------|---------|------|
| Naion/ni(OH)₂/MWCNTs | 0.05–25 | 0.008–10 | 0.015 | 0.003 | 7 |
| rGO-Ag:Se | 0.1–15 | 0.0296 | 16 |
| AuNPs/AuNRTs-rGO-Naf | 3–1000 | 0.387 | 18 |
| UiO-66-NH₂@P(ANI-co-ANA) | 10–110 | 0.3 | 35 |
| COF-NH₂-MWCNTs/Au | 0.4–108 | 0.21 | 37 |
| P-Arg/ErGO/AuNP | 0.001–0.05 | 0.001 | 0.03 | 54 |
| AuaAg-GR | 1–50 | 1–10 | 1.0–50 | 0.0027–4.82 | 55 |
| f-MWCNTs/AuNPs | 0.01–10 | 0.012 | 57 |
| H-ZIF | 0.25–590 | 0.03 | 0.007 | This work |
| AuNR@ZIF-8 | 0.1–50 | 0.1–25 | 57 |

*MWCNTs: multiwalled carbon nanotubes. rGO: reduced graphene oxide. AuNRTs: Au-nanorattles. P-Arg: poly(L-arginine). GR: graphene.
necessary to study the effects of some common interferents on the current signal in DA or ST determination. Since the oxidation peak positions of DA and ST are very close, the electrochemical signals will interfere with each other. First, the mutual influence of DA and ST was tested. Figure 6a gives the differential pulse voltammetric (DPV) curves of the AuNR@ZIF-8/GCE obtained in 0.1 M PBS (pH 7.4) containing 25 μM DA before and after (magenta) adding 25 μM ST; (b) anti-interference ability of the AuNR@ZIF-8/GCE to various inorganic ions and organic species. \( I_p \) and \( I_{50} \), respectively, represented the peak currents of DA and ST with and without the interference.

\[ \text{Figure 6. (a) DPV curves of the AuNR@ZIF-8/GCE obtained in 0.1 M PBS (pH 7.4) containing 25 \( \mu \)M DA before (blue) and after (magenta) adding 25 \( \mu \)M ST; (b) anti-interference ability of the AuNR@ZIF-8/GCE to various inorganic ions and organic species. \( I_p \) and \( I_{50} \), respectively, represented the peak currents of DA and ST with and without the interference.} \]

Figure 6a shows that the AuNR@ZIF-8-modified electrode has good electrochemical performance for DA and ST detection, with wide linear ranges (0.1–50 μM for DA and 0.1–25 μM for ST) and low detection limits (0.03 μM for DA and 0.007 μM for ST). These excellent performances resulted from the synergistic effect of the loose porosity and high specific surface area of the ZIF-8 with good conductivity and catalytic activity of AuNRs. In addition, the sensor also shows good electrochemical stability and anti-interference ability. These excellent characteristics provide potential applications for AuNR@ZIF-8 as a sensing material.

**Effect of Human Serum Albumin (HSA) on the AuNR@ZIF-8-Modified Electrode.** Serum, including proteins, electrolytes, antibodies, antigens, hormones, and the like, is used in numerous diagnostic tests. Since serum contains a large amount of albumin (40–55 g/L), its effects cannot be ignored in the testing of clinical serum samples. Therefore, we studied the effect of serum albumin on the sensing performance of the material by simulating the environment of human serum. Fifty-five milligrams of HSA with a fluorescein isothiocyanate isomer (FITC) was dissolved in 20 mL of PBS (pH 7.4) to prepare an HSA-FITC solution of 2.75 mg/mL. This ratio is 20 times diluted according to the 55 g/L albumin content in human serum. First, the CV curve of the AuNR@ZIF-8/GCE in 0.1 M PBS (pH 7.4) containing 25 μM DA was tested, then the electrode was incubated in the prepared HSA-FITC solution for 1 h, and the CV response of the electrode after incubation was tested. As shown in Figure 7a, the CV curves of the AuNR@ZIF-8/GCE are unchanged before and after the incubation. In the same way, the ST was also tested, and the result is shown in Figure 7b. The detection effect of the electrode on ST before and after the incubation is unchanged. The AuNR@ZIF-8/GCE before and after the incubation does not affect the ST detection. Next, we took the AuNR@ZIF-8/GCE before (Figure 7c) and after (Figure 7d) incubation to be observed under a fluorescence microscope and found that there was fluorescence on the surface of the electrode after incubation, indicating that AuNR@ZIF-8 adsorbed HSA-FITC molecules, but it did not affect the sensing performance of the electrode. The above research shows that the AuNR@ZIF-8-modified electrode has good application potential in the detection of clinical serum samples.

**CONCLUSIONS**

In summary, a novel electrode material, AuNR@ZIF-8 core–shell structure, was successfully synthesized in this work. The electrode material has a facile preparation process and mild reaction conditions. The electrochemical sensor based on AuNR@ZIF-8 nanocomposite materials can be used to detect DA and ST with high sensitivity and selectivity. We have experimentally demonstrated that the sensor has excellent analytical performance for DA and ST detection, with wide linear ranges (0.1–50 μM for DA and 0.1–25 μM for ST) and low detection limits (0.03 μM for DA and 0.007 μM for ST). These excellent performances resulted from the synergistic effect of the loose porosity and high specific surface area of the ZIF-8 with good conductivity and catalytic activity of AuNRs. In addition, the sensor also shows good electrochemical stability and anti-interference ability. We also studied the effect of human serum albumin on the electrode material, and the results showed that although a small amount of protein was adsorbed, it did not affect the detection of DA and ST. This research provides a new high-efficiency electrocatalyst for the design of electrochemical biosensors based on a conductive nanoparticles@MOFs heterostructure.

**EXPERIMENTAL SECTION**

**Reagents.** Gold(III) chloride trihydrate (H\(\text{AuCl}_3\cdot3\text{H}_2\text{O}\), 99%), cetyltrimethylammonium bromide (CTAB), 2-methylimidazole (2-MIM, 99%), zinc nitrate hexahydrate (Zn(NO\(_3\))\(_2\)·6\(\text{H}_2\text{O}\), 99%), polyvinylpyrrolidone (PVP, K30), and methanol (AR grade, 99.9%) were purchased from Shanghai Macklin.
Biochemical Co., Ltd. Silver nitrate, ascorbic acid, and sodium borohydride were bought from Sinopharm Chemical Reagent Co., Ltd. 5-Bromosalicylic acid was supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. All the chemicals were used as received without further purification. Ultrapure water (Millipore Milli-Q grade) with a resistivity of 18.2 MΩ was used in all the experiments.

**Characterization.** UV−vis−NIR absorption spectral values were measured on a SPECTORD 200 PLUS spectrophotometer (Analytik Jena AG). Scanning electron microscopy (SEM) measurements were performed using a JSM-7800F (JEOL, Japan). Transmission electron microscopy (TEM) images were obtained using an HT-7700 (JEOL, Japan) system. High-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) imaging and energy-dispersive X-ray spectroscopy (EDX) elemental mapping were performed by a JEM-2200FS electron microscope operated at 200 kV. Powder X-ray diffraction (XRD) patterns were recorded on a D8 DISCOVER with Cu Kα radiation (λ = 1.542 Å) operating at 50 kV and 300 mA. Fourier transform infrared spectroscopy (FTIR) was recorded on a spectrometer (Nicolet 6700) by a KBr tablet method, and the spectra were scanned in the range of 400−4000 cm⁻¹ at a resolution of 4 cm⁻¹. Nitrogen adsorption−desorption isotherms were measured with a Micrometrics instrument (ASAP 2460, USA) at 77 K. X-ray photoelectron spectroscopy (XPS) analysis was carried out on an ESCALAB 250XI electronic spectrometer (ThermoFisher, USA). Particle size distribution was measured by dynamic light scattering (DLS) on a Malvern Zetasizer Nano ZS (Malvern Instruments Ltd., Worcestershire, U.K.). Electrochemical measurements were carried out on a model DH7000 electrochemical workstation (Jiangsu Donghua Analysis Instrument, China). A conventional three-electrode system was adopted, including a modiﬁed glassy carbon electrode (GCE, diameter: 3 mm) as the working electrode, a platinum wire as the auxiliary electrode, and a saturated calomel electrode (SCE) as the reference electrode. The ﬂuorescence images were acquired using a Leica DM4 B microscope.

**Synthesis of Gold Nanorods.** Synthesis of AuNRs was performed according to the classical seed mediated growth method as described below. 38, 58 Briefly, the seed solution was made by adding a freshly prepared, ice-cold aqueous solution of NaBH4 (0.6 mL, 0.01 M) into a mixture solution composed of HAuCl4·3H2O (0.025 mL, 0.1 M) and CTAB (10 mL, 0.1 M). The solution was stirred vigorously (1000 rpm) for 2 min and aged at room temperature for 30 min before use.

The growth solution was prepared by dissolving CTAB (3.6 g) and 5-bromosalicylic acid (0.44 g) in 100 mL of warm water (55 °C). AgNO3 (1.92 mL, 0.01 M) was added to this solution, and after keeping undisturbed at room temperature for 15 min, 100 mL of 1 mM HAuCl4·3H2O solution was added. After gentle mixing of the solution for 15 min, 0.512 mL of 0.1 M ascorbic acid was added with vigorous stirring for 30 s until the mixture became colorless. At this point, 0.32 mL of seed solution was added to the entire growth solution. The mixture was stirred for 30 s and left undisturbed at 27 °C for 12 h.

**Preparation of PVP-Capped AuNRs.** Sixty milliliters of CTAB and 5-bromosalicylic acid-stabilized AuNRs were taken out and centrifuged twice at 10,000 rpm. After removing the supernatant, 20 mL of PVP methanol solution (0.75 g, K30) was added to the AuNR suspension, stirred at room temperature for 2 h, and then ultrasonicated into a homogeneous solution. Then, PVP-stabilized AuNRs were collected by centrifugation at 8000 rpm for 20 min. The sample was dispersed in 10 mL of methanol.

**Synthesis of AuNR@ZIF-8 Core–Shell Nanostructures.** ZIF-8 and AuNR@ZIF-8 were synthesized according to the previous report. 39 At room temperature, 2 mL of methanol solution of the PVP-stabilized AuNRs and 4 mL of methanol solution of 2-MIM (7.125 mg) were mixed and stirred for 2 min. Then, 4 mL of methanol solution of Zn(NO3)2·6H2O (15.191 mg) was added into the mixed solution. After standing for 1 h at room temperature, the ﬁnal product was collected by centrifugation at 5000 rpm for 10 min, washed with methanol twice, and ﬁnally dispersed in 0.5 mL of methanol to obtain AuNR@ZIF-8 nanoparticles. Pure ZIF-8 was synthesized under the same reaction conditions but without adding the concentrated aqueous solution of PVP-AuNRs.

**Electrochemical Measurements.** The AuNR@ZIF-8-modiﬁed glassy carbon electrode (GCE) was prepared as follows. First, the glassy carbon electrode was thoroughly polished with alumina powder and then cleaned with water and ethanol in an ultrasonic bath. 60 Second, 5 μL of the prepared dispersion was dropped onto a pre-treated GCE and dried at room temperature. After it was dried, 5 μL of Nanoﬁltration ethanol solution (0.5 wt %) was dropped on the modiﬁed electrode and dried in air. All of the samples were made in the same process to keep the same loading. Electrochemical measurements were carried out at room temperature. The AuNR@ZIF-8-modiﬁed electrode, the saturated calomel electrode (SCE), and the platinum wire were used as the working electrode, reference electrode, and counter electrode, respectively. 61, 62 With the same process, the AuNR and ZIF-8-modiﬁed GCE were also prepared.

## ASSOCIATED CONTENT

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c05529.

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TEM image, UV−vis−NIR spectrum, statistical data of the length and the diameter of AuNRs; SEM images of ZIF-8 and AuNR@ZIF-8; TEM image and statistical data of the diameter of ZIF-8; EDX of AuNR@ZIF-8; particles size distribution of AuNR@ZIF-8; nitrogen adsorption−desorption isotherms and the corresponding pore size distribution of ZIF-8 and AuNR@ZIF-8; cyclic voltammograms and nyquist plots of bare GCE, ZIF-8/GCE, AuNR/GCE, and AuNR@ZIF-8/GCE; CV curves of AuNR@ZIF-8-modified GCE; CV curves of AuNR@ZIF-8-modiﬁed GCE in 0.1 M PBS containing 25 μM ST by varying the pH values from 6.0 to 8.0 at 100 mV s⁻¹ and the corresponding plots of the oxidation peak currents vs the pH values; CV curves of AuNR@ZIF-8-modiﬁed GCE in 0.1 M PBS (pH 7.4) containing 10 μM ST at different scan rates (20, 50, 100, 150, 200, 250, 300, and 350 mV s⁻¹) and dependence of peak currents vs the square root of the scan rate; cyclic voltammetric stability of AuNR@ZIF-8-modiﬁed GCE in 0.1 M PBS (pH 7.4) containing DA or ST at a scan rate of 100 mV s⁻¹.
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Notes
The authors declare no competing financial interest.

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References
(1) Cernat, A.; Ştefan, G.; Tertis, M.; Cristea, C.; Simon, I. An Overview of the Detection of Serotonin and Dopamine with Graphene-Based Sensors. Bioelectrochemistry 2020, 136, 107620.
(2) Emran, M. Y.; Shenashen, M. A.; Morita, H.; El-Salify, S. A. 3D-Ridge Stocked Layers of Nitrogen-Doped Mesoporous Carbon Nanosheets for Ultrasensitive Monitoring of Dopamine Released from PC12 Cells under K+ Stimulation. Adv. Healthcare Mater. 2018, 7, 1701459.
(3) Liu, X.; Liu, J. Biosensors and sensors for dopamine detection. Viewpoint 2021, 2, 20200102.
(4) Geng, W. Y.; Zhang, H.; Luo, Y. H.; Zhu, X. G.; Di Xie, A.; Wang, J.; Zhang, D. E. Facile fabrication of carbon-loaded covalent-organic framework composites with enhanced electrochemical performance for dopamine determination. Microporous Mesoporous Mater. 2021, 323, 111186.
(5) Sharma, S.; Singh, N.; Tomar, V.; Chandra, R. A review on electrochemical detection of serotonin based on surface modified electrodess. Biosens. Bioelectron. 2018, 107, 76–93.
(6) Selvarajran, S.; Suganthi, A.; Rajarajan, M. A novel highly selective and sensitive detection of serotonin based on Ag/polypropylene/Ca3O nanocomposite modified glassy carbon electrode. Ultrason. Sonochim. 2018, 44, 319–330.
(7) Babaei, A.; Taheri, A. R. Nafion/Ni(OH)2 nanoparticles-carbon nanotube composite modified glassy carbon electrode as a sensor for simultaneous determination of dopamine and serotonin in the presence of ascorbic acid. Sens. Actuators B 2013, 176, 543–551.
(8) Prashanth, K. N.; Basavaiah, K.; Raghu, M. S. Spectrophotometric Determination of Zolmitriptan in Bulk Drug and Pharmaceuticals Using Vanillin as a Reagent. ISRN Anal. Chem. 2013, 2013, 1–7.
(9) Azuaje, J.; López, P.; Iglesias, A.; De La Fuente, R. A.; Pérez-Rubio, J. M.; García, D.; Stepniewski, T. M.; García-Mera, X.; Brea, J. M.; Selent, J.; et al. Development of Fluorescent Probes that Target Serotonin 5-HT1A Receptors. Sci. Rep. 2017, 7, 1–16.
(10) Saraji, M.; Shahvar, A. Selective micro solid-phase extraction of epinephrine, norepinephrine and dopamine from human urine and plasma using aminophenylboronic acid covalently immobilized on magnetic nanoparticles followed by high-performance liquid chromatography-fluorescence detection. Anal. Methods 2016, 8, 830–839.
(11) Tekes, K. HPLC determination of serotonin and its metabolites from human platelet-rich plasma; shift to 5-hydroxytryptophol formation following alcohol consumption. J. Chromatogr. Sci. 2008, 46, 169–173.
(12) De Jong, W. H. A.; Wilkens, M. H. L. I.; De Vries, E. G. E.; Kema, I. P. Automated mass spectrometric analysis of urinary and plasma serotonin. Anal. Bioanal. Chem. 2010, 396, 2609–2616.
(13) S. M. PDMS/glass hybrid device with a reusable carbon electrode for on-line monitoring of catecholamines using microdialysis sampling coupled to microchip electrophoresis with electrochemical detection. Electrophoresis 2018, 39, 462–469.
(14) Nichkova, M. I.; Huisman, H.; Wynveen, P. M.; Marc, D. T.; Olson, K. L.; Kellermann, G. H. Evaluation of a novel ELISA for serotonin: Urinary serotonin as a potential biomarker for depression. Anal. Bioanal. Chem. 2012, 402, 1593–1600.
(15) Geng, X.; Zhang, M.; Long, H.; Hu, Z.; Zhao, B.; Feng, L.; Du, J. A reusable neurotransmitter aptasensor for the sensitive detection of serotonin. Anal. Chim. Acta 2021, 1145, 124–131.
(16) Panneer Selvam, S.; Yun, K. A self-assembled silver chalcogenide electrochemical sensor based on rGO-Ag2Se for highly selective detection of serotonin. Sens. Actuators B 2020, 302, 127161.
(17) Lee, J.; Kang, Y.; Chang, J.; Song, J.; Kim, B. K. Determination of Serotonin Concentration in Single Human Platelets through Single-Entity Electrochemistry. ACS Sens. 2020, 5, 1943–1948.
(18) Mahato, K.; Purohit, B.; Bhardwaj, K.; Jaiswal, A.; Chandra, P. Novel electrochemical biosensor for serotonin detection based on gold nanorattles decorated reduced graphene oxide in biological fluids and in vitro model. Biosens. Bioelectron. 2019, 142, 111502.
(19) Chen, Y.; Huang, W.; Chen, K.; Zhang, T.; Wang, Y.; Wang, J. Facile fabrication of electrochemical sensor based on novel core-shell...
(37) Guan, Q.; Guo, H.; Xue, R.; Wang, M.; Zhao, X.; Fan, T.; Yang, W.; Xu, M.; Yang, W. Electrochemical sensor based on covalent organic frameworks-MWCNT-NH2/AuNPs for simultaneous detection of dopamine and uric acid. J. Electroanal. Chem. 2021, 880, 114932.

(38) Alagiri, M.; Rameshkumar, P.; Pandikumar, A. Gold nanorod-based electrochemical sensing of small biomolecules: A review. Microchem. Acta 2017, 184, 3069–3092.

(39) Feng, Y. G.; Wang, X. Y.; Wang, Z. W.; Wang, A. J.; Mei, L. P.; Luo, X.; Feng, J. J. A label-free electrochemical immunosensor based on encapsulated signal molecules in mesoporous silica-coated gold nanorods for ultrasensitive assay of proclacitinon. Bioelectrochemistry 2021, 140, 107753.

(40) Rao, D.; Zhang, J.; Zheng, J. A novel electrochemical sensor based on gold nanorods and Nafion-modified GCE for the electrocatalytic oxidation of nitrite. J. Iran. Chem. Soc. 2016, 13, 2257–2266.

(41) Parab, H. J.; Jung, C.; Lee, J. H.; Park, H. G. A gold nanorod-based optical DNA biosensor for the diagnosis of pathogens. Biosens. Bioelectron. 2010, 26, 667–673.

(42) Deng, C.; Chen, J.; Yang, M.; Nie, Z.; Si, S. Electrochemical determination of dopamine in the presence of ascorbic acid based on the gold nanorods/carbon nanotubes composite film. Electrochim. Acta 2011, 56, 8851–8866.

(43) Lu, G.; Li, S.; Guo, Z.; Farha, O. K.; Hauser, B. G.; Qi, X.; Wang, Y.; Wang, X.; Han, S.; Liu, X.; Duchene, J. S.; Zhang, H.; Zhang, Q.; Chen, X.; Ma, J.; Loo, S. C. J.; Wei, W. D.; Yang, Y.; Hupp, J. T.; Hsu, F. Imparting Functionality to a Metal-Organic Framework Material by Controlled Nanoparticle Encapsulation. Nat. Chem. 2012, 4, 310–316.

(44) Zhang, Z.; Wang, L.; Wang, J.; Jiang, X.; Li, X.; Hu, Z.; Ji, Y.; Wu, X.; Chen, C. Mesoporous Silica-Coated Gold Nanorods as a Light-Mediated Multifunctional Theranostic Platform for Cancer Treatment. Adv. Mater. 2012, 24, 1418–1423.

(45) Cai, W.; Wang, J.; Liu, H.; Chen, W.; Wang, J.; Du, L.; Hu, J.; Wu, C. Gold Nanorods@Metal–Organic Framework Core–Shell Nanoscale as Contrast Agent for Photoacoustic Imaging and Its Biocompatibility. J. Alloys Compd. 2018, 748, 193–198.

(46) Chen, L.; Peng, Y.; Wang, H.; Gu, Z.; Duan, C. Synthesis of Au@ZIF-8 Single- or Multi-Core–Shell Structures for Photocatalysis. Chem. Commun. 2014, 50, 8651–8654.

(47) Cheng, Y.; Lu, S.; Xu, W.; Wen, H.; Wang, J. Fabrication of Superhydrophobic Au-Zn Alloy Surface on a Zinc Substrate for Rolldown Self-Cleaning and Anti-Corrosion Properties. J. Mater. Chem. A 2014, 3, 16774–16784.

(48) Yang, Y.; Wang, S. Q.; Wen, H.; Ye, T.; Chen, J.; Li, C. P.; Du, M. Nanoporous Gold Embedded ZIF Composite for Enhanced Electrochemical Nitrogen Fixation. Angew. Chem., Int. Ed. 2019, 58, 15362–15366.

(49) Chai, C.; Gao, J.; Zhao, G.; Li, L.; Tang, Y.; Wu, C.; Wan, C. In-Situ Synthesis of Ultrasmall Au Nanoparticles on Bimetallic Metal–Organic Framework with Enhanced Electrochemical Activity for Estrone Sensing. Anal. Chim. Acta 2021, 1152, 338242.

(50) Su, P.; Pei, W.; Wang, X.; Ma, Y.; Jiang, Q.; Liang, J.; Zhou, S.; Zhao, J.; Liu, J.; Lu, G. Q. Exceptional Electrochemical HER Performance with Enhanced Electron Transfer between Ru Nanoparticles and Single Atoms Dispersed on a Carbon Substrate. Angew. Chem., Int. Ed. 2021, 116023, 16044–16050.

(51) Su, J.; Ge, R.; Jiang, K.; Dong, Y.; Hao, F.; Tian, Z.; Chen, G.; Chen, L. Assembling Ultralarge Copper-Doped Ruthenium Oxide Nanocrystals into Hollow Porous Polyhedra: Highly Robust Electrocatalysts for Oxygen Evolution in Acidic Media. Adv. Mater. 2018, 30, 1801351.

(52) Ji, L.; Wang, J.; Wu, K.; Yang, N. Tunable Electrochemistry of Electrolysized Copper Metal–Organic Frameworks. Adv. Funct. Mater. 2018, 28, 1706961.

(53) Fang, J. J.; Yang, N. N.; Gao, E. Q. Making Metal–Organic Frameworks Electron-Deficient for Ultrasensitive Electrochemical Detection of Dopamine. Electrochem. Commun. 2018, 89, 32–37.
Khan, M. Z. H.; Liu, X.; Tang, Y.; Zhu, J.; Hu, W.; Liu, X. A glassy carbon electrode modified with a composite consisting of gold nanoparticle, reduced graphene oxide and poly(L-arginine) for simultaneous voltammetric determination of dopamine, serotonin and L-tryptophan. *Microchim. Acta* **2018**, *185*, 1.

Thanh, T. D.; Balamurugan, J.; Van Hien, H.; Kim, N. H.; Lee, J. H. A novel sensitive sensor for serotonin based on high-quality of AuAg nanoalloy encapsulated graphene electrocatalyst. *Bioelectroch.* **2017**, *96*, 186–193.

Poudyal, D. C.; Satpati, A. K.; Kumar, S.; Haram, S. K. High sensitive determination of dopamine through catalytic oxidation and preconcentration over gold-multiwall carbon nanotubes composite modified electrode. *Mater. Sci. Eng. C* **2019**, *103*, 109788.

Dong, Y.; Liu, J.; Zheng, J. A sensitive dopamine electrochemical sensor based on hollow zeolitic imidazolate framework. *Colloids Surf., A* **2021**, *608*, 125617.

Zheng, Z.; Tachikawa, T.; Majima, T. Single-Particle Study of Pt-Modified Au Nanorods for Plasmon-Enhanced Hydrogen Generation in Visible to near-Infrared Region. *J. Am. Chem. Soc.* **2014**, *136*, 6870–6873.

Li, Y.; Jin, J.; Wang, D.; Lv, J.; Hou, K.; Liu, Y.; Chen, C.; Tang, Z. Coordination-Responsive Drug Release inside Gold Nanorod@metal-Organic Framework Core–Shell Nanostructures for near-Infrared-Induced Synergistic Chemo-Photothermal Therapy. *Nano Res.* **2018**, *11*, 3294–3305.

Berbeč, S.; Žolądek, S.; Jabłońska, A.; Pahys, B. Electrochemically Reduced Graphene Oxide on Gold Nanoparticles Modified with a Polyoxomolybdate Film. Highly Sensitive Non-Enzymatic Electrochemical Detection of H2O2. *Sens. Actuators, B* **2018**, *258*, 745–756.

Zhao, L.; Wang, Y.; Zhao, X.; Deng, Y.; Li, Q.; Xia, Y. Green Preparation of Ag-Au Bimetallic Nanoparticles Supported on Graphene with Alginate for Non-Enzymatic Hydrogen Peroxide Detection. *Nanomaterials* **2018**, *8*, 507.

Yang, B.; Bin, D.; Zhang, K.; Du, Y.; Majima, T. A Seed-Mediated Method to Design N-Doped Graphene Supported Gold-Silver Nanothorns Sensor for Rutin Detection. *J. Colloid Interface Sci.* **2018**, *512*, 446–454.