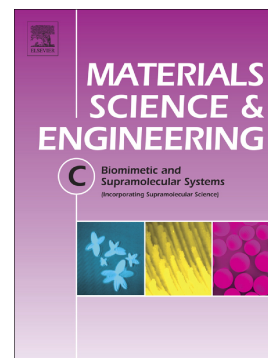


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PII: S0928-4931(19)30070-0

DOI: <https://doi.org/10.1016/j.msec.2019.110490>

Reference: MSC 110490

To appear in: *Materials Science & Engineering C*

Received date: 8 January 2019

Revised date: 30 October 2019

Accepted date: 23 November 2019

Please cite this article as: H.Y. Yue, H.J. Zhang, S. Huang, et al., Highly sensitive and selective dopamine biosensor using Au nanoparticles-ZnO nanocone arrays/graphene foam electrode, *Materials Science & Engineering C* (2018), <https://doi.org/10.1016/j.msec.2019.110490>

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Highly sensitive and selective dopamine biosensor using Au nanoparticles-ZnO nanocone arrays/graphene foam electrode

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Abstract

Based on the Au nanoparticles-ZnO nanocone arrays/graphene foam electrode, a novel dopamine biosensor was successfully developed. Graphene foam was synthesized by chemical vapor deposition, ZnO nanocone arrays were grown on its surface by a hydrothermal method and Au nanoparticles with carboxyl groups were self-assembled onto the ZnO nanocone arrays to obtain Au nanoparticles-ZnO nanocone arrays/graphene foam electrode. The result indicates that the prepared electrode has a high sensitivity ($4.36 \mu\text{A } \mu\text{M}^{-1}$) and low limit of detection ($0.04 \mu\text{M}$, $S/N=3$) for the detection of dopamine. The prepared electrode also exhibits an excellent selectivity under the interference of uric acid, good repeatability and stability. The prepared sensor has been successfully applied in real samples and has a great potential to be used in the field of medical and health.

Keywords: ZnO nanocone arrays; Graphene foam; Au nanoparticles; Dopamine

1. Introduction

Dopamine (DA), a main member of catecholamine group, is widely found in the nervous system, kidneys and cardiovascular ^[1, 2]. In the human body, a variety of diseases will appear if the content of DA is not in the normal range ^[3-5]. For example, Parkinson's disease afflicts millions of elderly people due to insufficient dopamine levels ^[6]. Therefore, accurate detection of DA in human body has vital significance for the treatment and prevention of diseases.

Recently, various techniques have been employed for the determination of DA, such as high performance liquid chromatography, fluorescence spectrometry and flow-injection chemiluminescence. However, longer pretreatment time and expensive equipment are not conducive to rapidly detect DA. Electrochemical method is a biomolecule detection method with fast, simple and high sensitivity. It is well known that it contains not only DA but also uric acid (UA) in human body ^[7-9]. Due to the close oxidation peak potential of DA and UA ^[10, 11], it is very important to avoid the effect of UA to the detection of DA. Some novel nanomaterial modified electrodes have been used to electrochemically detect DA. But low sensitivity and high limit of detection are associated with these modified electrodes, and the interference of other biomolecules should be researched more accurately. 3-dimensional graphene foam (GF) is the integration and assembly of 2D graphene ^[12-16], which not only inherits the excellent properties of graphene but also prevents the agglomeration of graphene. GF prepared by chemical vapor deposition (CVD) has attracted much attention due to its excellent properties (better stability and high conductivity) ^[17, 18], which make it a

good biosensor substrate material.

However, the contact area of the GF with the solution is still small, which seriously affects the electrochemical properties the electrode material. It is also a major problem to limit the development of biosensors. Zinc oxide (ZnO) has received a wide attention due to its high catalytic performance, biocompatibility and good chemical stability under physiological conditions. Our previous research also proved that the combination of graphene and ZnO can achieve excellent electrochemical performance ^[17-20]. In different structure of ZnO, the ZnO nanocone arrays (NCAs) can provide more active sites for electrodes to adsorb biomolecules due to its well-defined and highly ordered structure, thereby exhibiting more excellent electrochemical performance ^[17]. However, the wide band gap (3.37 eV) limits its electrochemical performance ^[19-23]. Au nanoparticles with small-size effect, quantum-size effect, surface effect and enhanced electrochemical signal function become a hot topic in the fields of materials science and sensors ^[24-26]. Combining it with ZnO NCAs is expected to solve the problem of poor conductivity of ZnO and obtain excellent electrode materials.

In this paper, a novel Au-ZnO NCAs/GF composite electrodes are designed for biosensor application. Firstly, nickel foam is used as a substrate to synthesize GF by CVD. Subsequently, ZnO NCAs were grown on its surface through hydrothermal synthesis. Finally, the Au nanoparticles are evenly self-assembled onto the ZnO NCAs surface to form Au-ZnO NCAs/GF electrode. The combination of Au nanoparticles, ZnO NCAs and GF has high conductivity and electrocatalysis properties, increases

contact area with the solution, and provides more active sites, thereby improving the electrochemical performance of the biosensor. Therefore, the Au-ZnO NCAs/GF electrode exhibits excellent sensitivity, reliable selectivity and stability for the determination of DA.

2. Methods

2.1 Reagents

All argents were analytical grade and without further purification. Zinc acetate ($\text{Zn}(\text{CH}_3\text{COO})_2$), methanol (CH_3OH), hexamethylenetetramine (HMTA), zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were bought from Tianli Chemical Reagent (<http://www.tianli-tj.com/>). Au nanoparticles with carboxyl groups preserved in sodium citrate, potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$), UA, DA and phosphate buffered saline (PBS) were bought from Sigma-Aldrich (<https://www.sigmaaldrich.com/>). Deionized (DI) water was obtained by a Water Purifier. ITO glass for preparation of electrodes was purchased from Zhuhai Kaivo Electronic Company.

2.2 Fabrication of the Au-ZnO NCAs/GF electrode

Nickel foam was used as a skeleton for the preparation of GF and the detailed process is shown in the previous report ^[27]. ZnO NCAs were grown on the GF by a hydrothermal method. Firstly, ITO glass is ultrasonically cleaned with ethanol, acetone and deionized water, respectively. GF with a size of $\sim 1 \text{ cm} \times 1 \text{ cm}$ was transferred onto its surface. $\text{Zn}(\text{CH}_3\text{COO})_2$ was completely dissolved in the methanol solution to prepare a seed layer solution (0.01M). Subsequently, the seed layer

solution was homogeneously dropped onto the surface of GF and calcined at 200°C for 1 h. Secondly, 0.05 M $\text{Zn}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$, 0.05 M HMTA and 0.5 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ were dissolved in DI water (75 mL) to form a transparent hydrothermal solution. After that, the hydrothermal solution and GF covered by the seed layer were transferred to 100 mL autoclave and heated at 100°C for 10 h. After natural cooling to room temperature, it was washed for several times with DI water and heat-treated at 450°C in Argon for 1 h to obtain ZnO NCAs/GF. Finally, 50 μL Au nanoparticles with carboxyl groups were dissolved in 5 mL ethanol solution and uniformly dropped onto the surface of the ZnO NCAs/GF (50 μL per sample). And then, the prepared electrode was dried at 160°C to obtain the Au-ZnO NCAs/GF electrode (Fig. S1a).

2.3 Characterizations

Scanning electron microscope (SEM, JSM 7000F, JEOL) was used to observe the morphologies of the Au-ZnO NCAs/GF. The energy dispersion X-ray spectrum (EDS) was used to investigate the element composition and elemental distribution of the Au-ZnO NCAs/GF. The crystal structure of the Au-ZnO NCAs/GF is analyzed by X-ray diffraction (XRD, Rigaku Rotaflex D/MAX diffractometer). At room temperature, the Raman spectrum (excited at 514 nm) was obtained from the micro-Raman system (Renishaw, RM-1000 In via).

2.4 Electrochemical properties

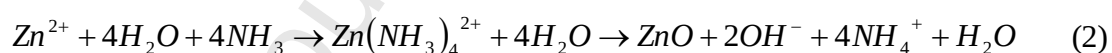
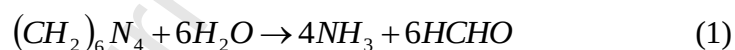
All electrochemical tests in this experiment were performed on an electrochemical workstation (VMP3, France) and the test was carried out in an electrochemical cell (Fig. S1b). Using a traditional three-electrode system, the

electrochemical performance of the prepared electrode was analyzed by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Electrochemical tests were performed in 0.01 M PBS solution at room temperature (pH=7.5). The measured plane area of the Au-ZnO NCAs/GF electrode was 0.7 cm².

3. Results and discussion

3.1 Fabrication process and structural characterisations of the Au-ZnO NCAs/GF

Figure 1 shows the synthesis process schematic of the Au-ZnO NCAs/GF electrode and redox reactions of DA and UA on the electrode surface. GF was fabricated by CVD (Fig. 1a and d), and ZnO NCAs were grown on the GF by hydrothermal method (Fig. 1b and e). Afterwards, the Au nanoparticles with carboxyl groups dispersed in the ethanol were dropped onto the surface of the ZnO NCAs/GF to form the Au-ZnO NCAs/GF electrode (Fig. 1c and f). Based on previous reports^[28, 29], the reaction process of ZnO NCAs is as follows:



The surface of ZnO NCAs prepared by hydrothermal synthesis carries a large amount of hydroxyl groups^[30-32]. The combination of ZnO NCAs with hydroxyl groups and Au nanoparticles with carboxyl groups is shown in Fig. S2. The electrochemical reactions of DA and UA at the Au-ZnO NCAs/GF electrode are displayed in Fig. 1g.

The SEM images and EDS results of the Au-ZnO NCAs/GF are exhibited in Figure 2. Fig. 2a-c show the SEM images of the prepared Au-ZnO NCAs/GF

electrode with different magnifications. It can be seen that the average pore size of the Au-ZnO NCAs/GF electrode is $\sim 300\ \mu\text{m}$. The surface of GF is uniformly covered by ZnO NCAs with the length of $\sim 500\ \text{nm}$. The prepared electrode contains C, O, Zn and Au elements (Fig. 2d). To further study the elemental distribution of electrode materials, elemental mapping is used (Fig. 2e-i). According to the elemental map, it is observed that the Au nanoparticles are homogeneously distributed on the ZnO NCAs/GF surface.

Figure 3 exhibits the Raman spectrum of GF and XRD pattern of the Au-ZnO NCAs/GF electrode. Fig. 3a shows the Raman spectrum of GF prepared by CVD. It can be obviously observed that two main peaks are located at ~ 1582 and $\sim 2725\ \text{cm}^{-1}$, which are consistent with G and 2D bands of graphene. No obvious D band indicates that the prepared GF has few defects and high quality. The intensity ratio of the G band to the 2D band indicates that GF is composed of multilayered graphene. Fig. 3b shows XRD pattern of the Au-ZnO NCAs/GF electrode. There are obvious diffraction peaks at $2\theta=26.4^\circ$ and 54.6° , which can be indexed as crystal planes of (002) and (004) of graphite (JCPDS No. 75-1621). The crystal planes of (222), (400), (441) and (622) correspond to those of ITO (JCPDS card No. 39-1058). The rest of the diffraction peaks are consisted with those of ZnO (JCPDS No. 36-1451). The Au nanoparticles content is small in the electrode, so they cannot be detected by XRD. Based on the above results, we can conclude that the Au-ZnO NCAs/GF electrode are successfully prepared.

3.2 The Au-ZnO NCAs/GF electrode for electrochemical detection of DA and UA

DA and UA detections of the bare ITO electrode and the Au-ZnO NCAs/GF electrode by CV are shown in the Figure 4. The oxidation peak potentials of DA and UA are located at ~ 0.2 and 0.3 V, respectively. Compared with the bare electrode, the oxidation peak current of the Au-ZnO NCAs/GF electrode obviously improved. The possible reasons are as follows: (1) After uniformly droplet coating of Au nanoparticles with carboxyl groups, the Au-ZnO NCAs/GF electrode has a high electrical conductivity (Fig. S3) and electrocatalytic properties. (2) The Au-ZnO NCAs/GF electrode has a large electrochemical active area of 6.82 cm^2 (Fig. S4). (3) The synergistic effect of Au nanoparticles, ZnO NCAs and GF further improves the electrochemical performance of the prepared electrode.

The effect of different scan rates on the CV voltammograms of the Au-ZnO NCAs/GF electrode in $50 \text{ }\mu\text{M}$ DA and UA was investigated, as shown in Figure 5. It can be seen that with the increase of scan rate ($10\text{-}100 \text{ mV s}^{-1}$), the redox peak currents of DA and UA increase (Fig. 5a and c). The equation of $I_{DA} = (-2.29 \pm 3.47) + (1.65 \pm 0.05)\nu$ ($R^2=0.9953$) and $I_{UA} = (6.16 \pm 1.68) + (0.64 \pm 0.03)\nu$ ($R^2=0.9928$) indicates the linear relationship between the oxidation peak current of UA and DA and scan rate (ν), respectively (Fig. 5b and d). So both the electrochemical oxidation reactions of DA and UA are adsorption-controlled processes.

Compared with CV, the charging current of DPV has little influence on background current^[33, 34], so DPV was chosen to investigate the effect of pH value on the electrochemical properties and obtain the sensitivity of the electrode more

accurately.

Figure 6 shows the influence of pH value of PBS solution for the detection of DA biomolecules. In order to obtain the best pH value for detecting DA, the PBS solution containing 30 μM DA was investigated. NaOH and H_3PO_4 was used to adjust the pH value of the PBS solution. It shows that with the increase of pH value from 4.5 to 8.5, and the oxidation peak current initially increases and later decreases (Fig. 6a-b). And the current response of the electrode is best at the pH value of 7.5, which is related to the biological activity. So all tests were performed at this pH value. Moreover, the oxidation peak potential of DA is negatively shifted with the increase of pH value. This indicates that protons have been involved in the electrode reaction. The linear fitting equation for pH value and oxidation peak potential of DA is as follows: $E_p = 0.329 - 0.024\text{pH}$ ($R^2=0.9925$) (Fig. 7c). This result indicates that the number of protons and electrons transferred are same during the oxidation process^[12, 35].

Figure 7 exhibits the DPV curves of the Au-ZnO NCAs/GF electrode in DA with a series of concentrations. With the improvement of DA concentration (0-80 μM), the oxidation peak current of DA increases (Fig. 7a). And the linear equation is $I_{DA} = (23.21 \pm 6.05) + (4.36 \pm 0.14)C_{DA}$ ($R^2=0.9934$) (Fig. 7b). According to linear regression equation, we can conclude that the sensitivity of the Au-ZnO NCAs/GF electrode is 4.36 $\mu\text{A } \mu\text{M}^{-1}$. The limit of detection (LOD) of the electrode is calculated according to formula of $LOD = 3S_b/m$, where S_b (Fig. S5) stands for the standard deviation of blank signals and m stands for the analytical sensitivity, the calculated

LOD of the Au-ZnO NCAs/GF electrode is 0.04 μM ($S/N=3$). As shown in Table 1 [36-41], the performance of the Au-ZnO NCAs/GF electrode are more excellent than that of the previous report. This can be explained that the large surface area with mesoporous ZnO NCAs and high conductivity 3D graphene foam to facilitate ion diffusion and transfer easily, and high active catalytic sites of Au nanoparticles on ZnO surface for high selectivity.

Because human body fluid contains both DA and UA, so it is important to verify the selectivity of the prepared electrode in our experiment. Figure 8 reveals the DPV curves of the Au-ZnO NCAs/GF electrode in DA with a series of concentrations in the presence of 40 μM UA. It can be seen the oxidation peak current of DA increases linearly with increasing its concentration (Fig. 8a). The linear regression equation is $I_{DA} = (10.54 \pm 6.09) + (4.29 \pm 0.14)C_{DA}$ ($R^2=0.9931$) (Fig. 8b). It means that the presence of UA has no obvious effect on the detection of DA.

3.3 Reproducibility and stability analysis

Excellent reproducibility and stability are important performance indicators for biosensors. In this experiment, 40 μM DA was selected for research. Reproducibility of the Au-ZnO NCAs/GF electrodes was analyzed by relative standard deviation (RSD). According to the results of seven duplicative measurements, the RSD was only 0.73%, which indicated that the prepared electrode had a good reproducibility (Fig. 9a). The stability of the Au-ZnO NCAs/GF electrode was measured by the DPV experiment every two days in 40 μM DA. (Fig. 9b). Two weeks later, 98% of its original oxidation peak current of DA was retained, which indicated that the electrode

had a long-term stability.

3.4 Analysis of real sample

To investigate the application of the prepared electrode in real samples, human urine samples were used. Before measurement, urine was diluted 100-fold with 0.01 M PBS. Table 2 shows the results of the experiment. The recovery of the prepared electrode ranges from 100.2% to 110.4%. The RSD ranges from 0.97% to 1.03%. The experimental results confirm that the Au-ZnO NCAs/GF electrode can be used for the detection of DA in actual human urine.

4. Conclusions

To sum up, we have successfully prepared the Au-ZnO NCAs/GF electrodes. ZnO NCAs with the length of ~ 500 nm were uniformly grown on the surface of porous GF with the pore size of ~ 300 μm . Au nanoparticles are homogeneously distributed on the ZnO NCAs. The sensitivity and LOD of the electrode for the detection of DA are $4.36 \mu\text{A} \mu\text{M}^{-1}$ and $0.04 \mu\text{M}$, respectively. Besides, the selectivity, repeatability and stability of the electrode are excellent. All of these advantages make the electrode possible to be used in the field of medical and health.

Acknowledgements

We acknowledge the financial support from the fundamental research foundation for University of Heilongjiang province (LGYC2018JQ012) and the foundation for selected overseas Chinese Scholar, Ministry of personal of Heilongjiang province (2018383).

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72-81.

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Table 1. Summary of the previously published results for individual detection of DA using different electrodes

Table 2. Determination of DA level in real urine samples using the Au-ZnO NCAs/GF electrode by DPV. (n = 5)

Table 1. Summary of the previously published results for individual detection of DA using different electrodes

Electrodes	LDR (μM)	LOD (μM)	Sensitivity ($\mu\text{A}/\mu\text{M}$)	Ref.
CuO	5-40	0.11	1.28	35
$\text{Co}_3\text{O}_4@\text{NiO}$	1-20	1.21	0.04	36
N-rGO/MnO/GCE	10-180	3	0.09	37
β -CD/CQDs/GCE	4-220	4	0.31	38
PABSA-rMoS ₂	1-50	1	0.22	39
Nickel oxide NPs	2-100	1.04	0.06	40
Au-ZnO NCAs/GF	0-80	0.04	4.36	ours

LDR: linear dynamic range; LOD: limit of detection

$\text{Co}_3\text{O}_4@\text{NiO}$: Co_3O_4 @NiO core-shell nanotubes

N-rGO/MnO/GCE: nitrogen-doped graphene/manganese monoxide composites/glassy carbon electrode

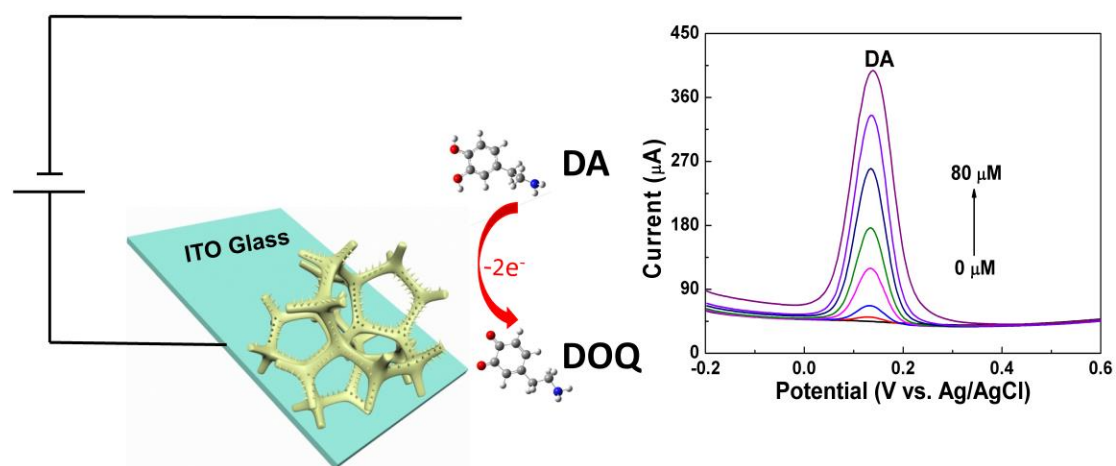
β -CD/CQDs/GCE: poly (β -cyclodextrin) (β -CD)/carbon quantum dots (CQDs) composite modified glass carbon electrode

PABSA-rMoS₂: poly(m-aminobenzenesulfonic acid)-reduced MoS₂ nanocomposites modified carbon paste electrode

Nickel oxide NPs: functionalized nickel oxide nanoparticles

Table 2. Determination of DA level in real urine samples using the Au-ZnO NCAs/GF electrode by DPV (n = 5)

Samples	Spiked (μM)	Found (μM)	Recovery (%)	RSD (%)
urine	10	10.43	104.3	1.03
	20	22.08	110.4	0.89
	40	40.06	100.2	0.97



Graphical abstract

Highlights

1. A highly sensitive and selective dopamine biosensor based on the Au-ZnO NCAs/GF electrode.
2. The optimal pH value of PBS solution for detection of DA is 7.5.
3. The Au-ZnO NCAs/GF electrode shows a high sensitivity of $4.36 \mu\text{A} \cdot \mu\text{M}^{-1}$ and lower limit of detection of $0.04 \mu\text{M}$ for detection of dopamine.
4. The Au-ZnO NCAs/GF electrode also shows an excellent selectivity, reproducibility and stability.

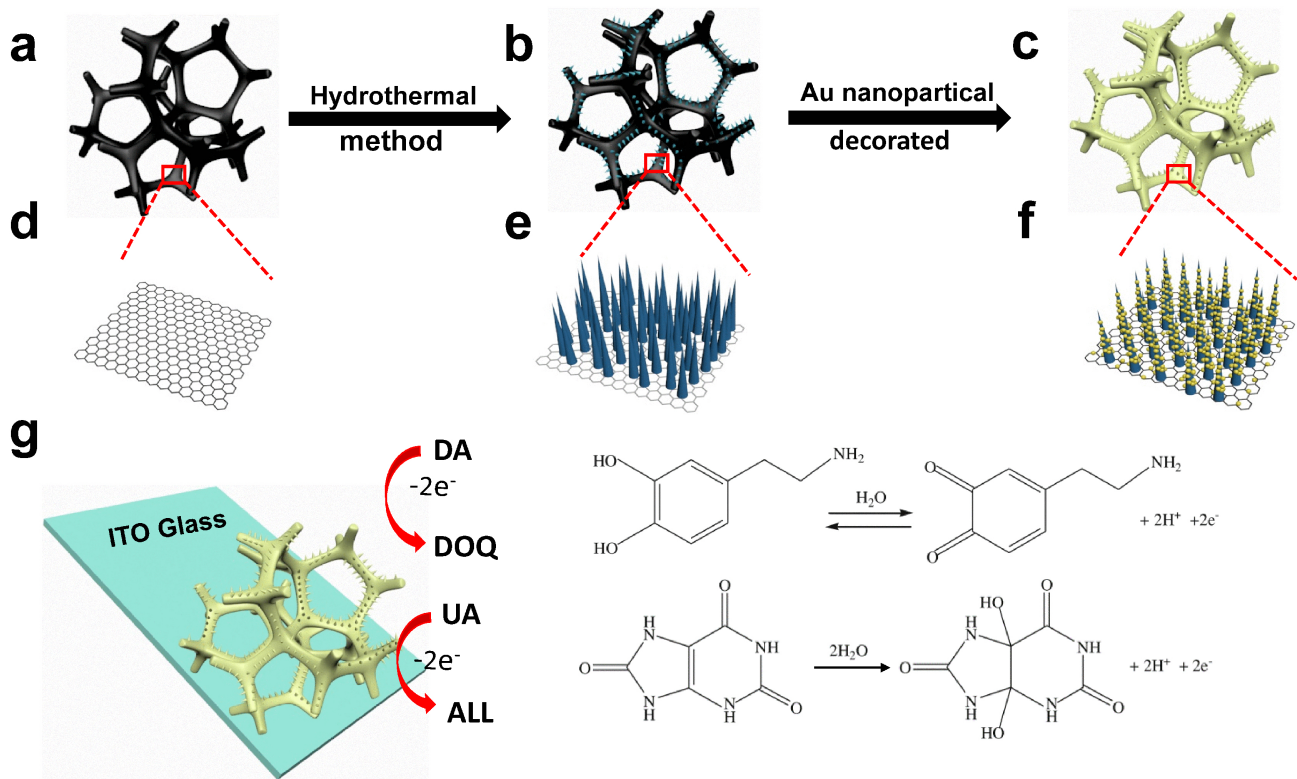


Figure 1

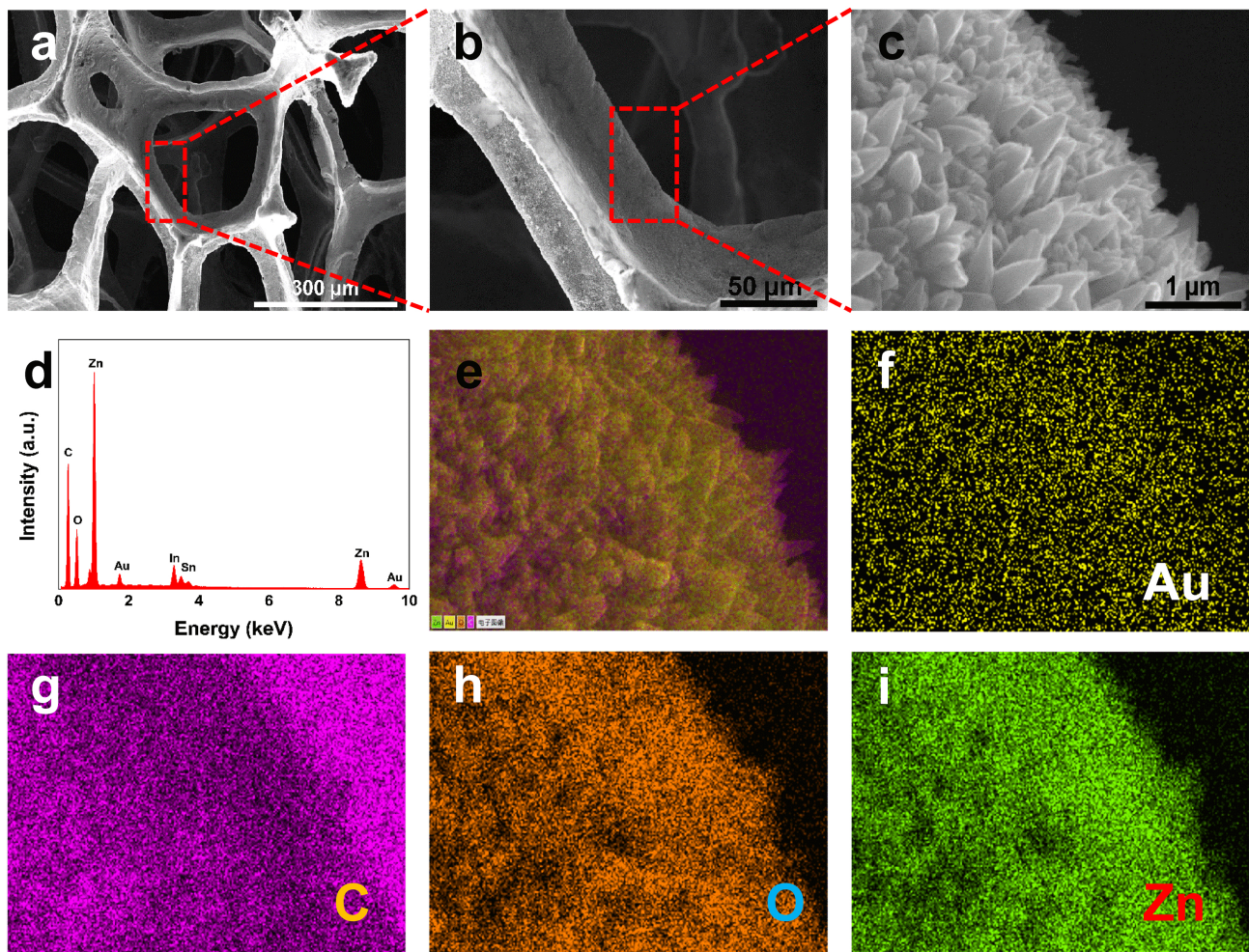


Figure 2

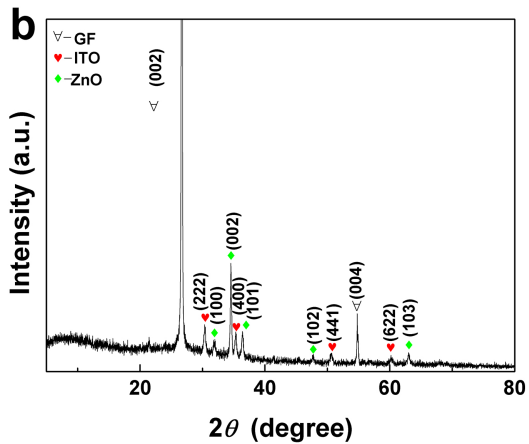
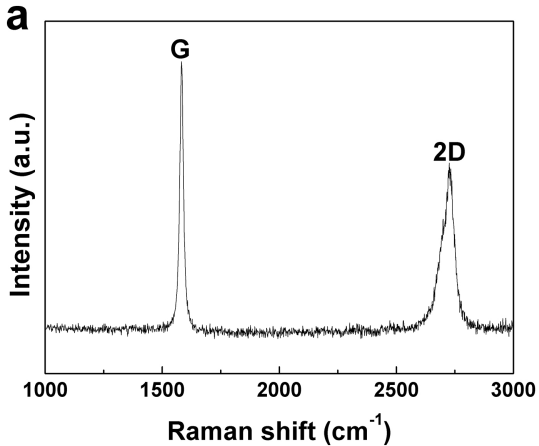


Figure 3

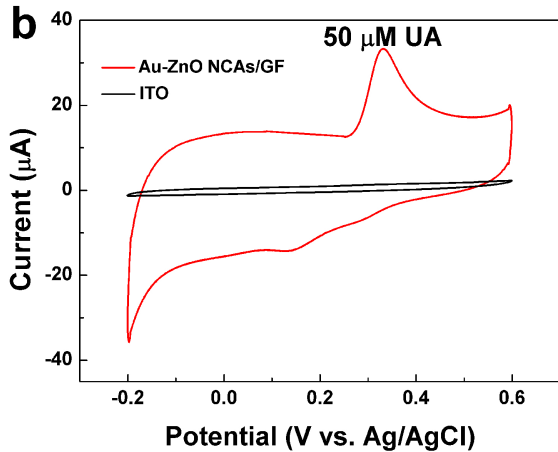
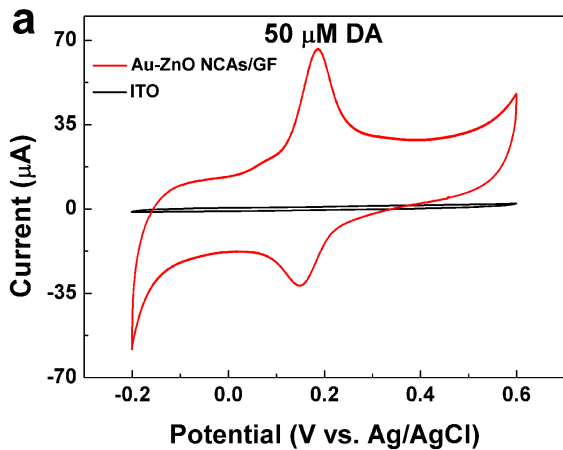


Figure 4

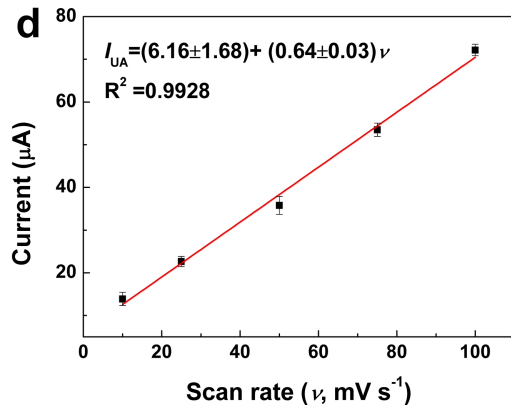
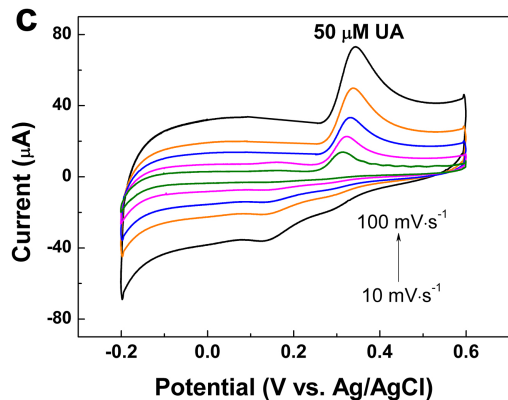
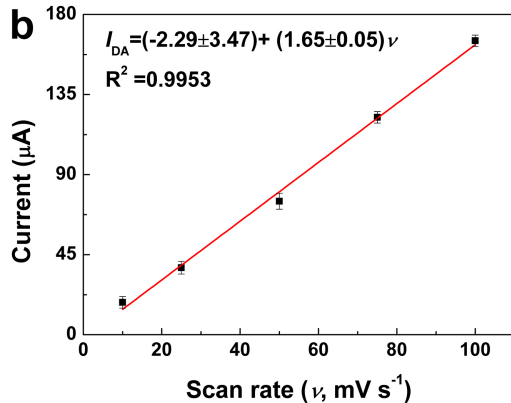
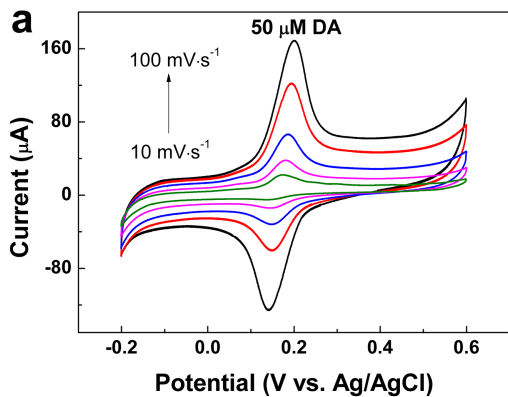


Figure 5

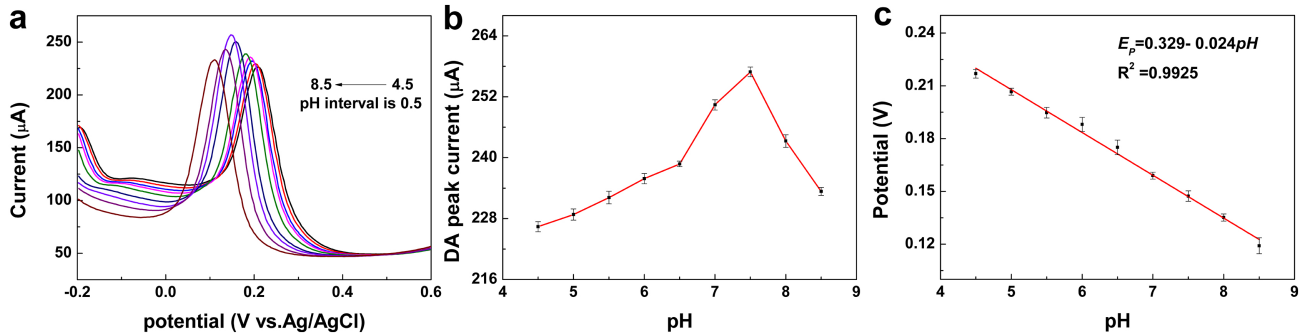


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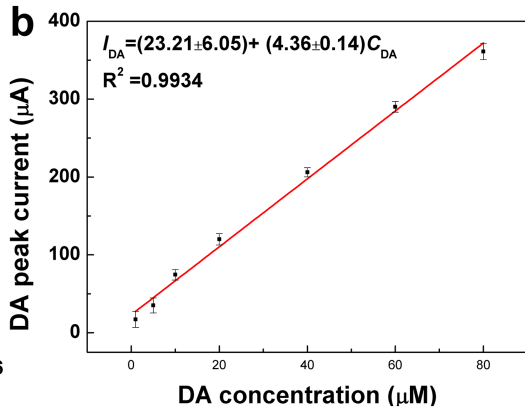
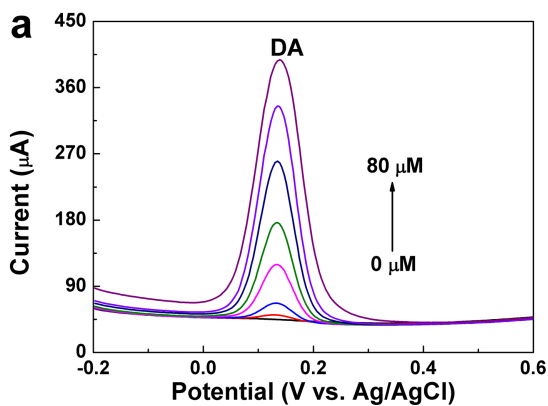


Figure 7