Indium tin oxide-coated glass modified with reduced graphene oxide sheets and gold nanoparticles dopamine sensing

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Possibly the most important catecholamine, the neurotransmitter DA (4-(2-aminoethyl)benzene-1,2-diol) plays an indispensable part in the central nervous, renal, hormonal and cardiovascular systems of animals. DA has been associated with important brain functions and pathological process of neurodegenerative diseases such as Parkinson’s disease.1 High concentration of DA can lead to abnormally high pulse and blood pressure. DA is also one kind of widespread ‘lean meat powder’ added to feed to help animal stocks build muscle rather than fat as an adrenergic neural stimulant. Use of DA in animal feed has been banned in most countries, and it is essential to prevent its illegal use. Therefore detecting the presence of DA in physiological or biological samples is of great significance for both diagnostics and therapeutics. Current approaches for detecting DA include but not limit to UV-vis spectrometry, fluorescence,2, capillary electrophoresis,3 and chemiluminescence.1 Electrochemical detection offers several advantages over these methods in its easiness, high sensitivity, environment-friendliness, rapidity, capability to be used in turbid or colored fluids, suitability for both in vitro and in vivo detection and most importantly, the portability to be carried out of labs with a hand-held analyzer.

Herein we report a facile and green approach at room temperature to reduce graphene oxide (GO) without using any chemical reducing agent and the following in situ synthesis of AuNPs in the carbon network. The reduction of GO is highly effective and rapid with oxygenated defect sites removed and electronic properties improved. Further modification of reduced graphene oxide sheets (rGOS) with AuNPs can enhance their electrical conductivity and electrocatalytic activity, in an electrochemically controllable process. The size, density, and even appearance of AuNPs can be easily controlled by varying deposition conditions such as potential, time, and precursor concentrations. Our as-synthesized AuNPs-rGOS-ITO sensor showed extraordinary electrocatalytic activity against DA. Also, owing to its low cost, easy fabrication and miniature size, this sensor can be designed as one-time-use disposable sensors by microfabrication, hence eliminating complicated and laborious cleaning steps needed while using common solid electrodes. This sensor is also compatible for some lithographic approaches and has the potential in microfluidic applications for DA detection.

A typical SEM image of rGOS (Fig. 2A) exhibited the characteristic wrinkled and folded sheet structure of graphene. Apart from being wrinkled and folded, the rGOS sheets appeared flat and parallel to ITO substrate surface, indicating good film-forming ability with large surface coverage on substrate. The rug-like interconnecting network formed as well as the decrease in defects and oxygen content after reduction favored the conduction pathways for charge transport. The SEM of the AuNPs-modified rGOS showed that AuNPs were evenly distributed in the rGOS network, providing larger surface area, good biocompatibility, electrocatalytic activity and enhanced conductivity with additional conducting pathways for fast electron transfers

The presence of a number of different oxygen functionalities in GO was confirmed the successful oxidation of graphite (Fig. 2B) a broad and intense band centered at 3400 cm\(^{-1}\) of O-H stretching vibration (intercalated water), another overlapping broad and strong band at 3200 cm\(^{-1}\) of O-H coupling stretching vibration (carboxylic acid), a sharp peak at 1740 cm\(^{-1}\) of C=O stretching vibration (carbonyl), a weak band at 1420 cm\(^{-1}\) of O-H deformation vibration (carboxyl), a weak band at 1220 cm\(^{-1}\) for C-OH stretching vibration (alcohol), and a shoulder band at 1060 cm\(^{-1}\) of C-O stretching vibration (epoxy or alkyl), similar to those previously reported.4 The C=C band at 1620 cm\(^{-1}\) was caused by skeletal vibrations of unoxidized graphitic domains. After reduction, bands of O-H stretching at 3400 cm\(^{-1}\) [due to the hydrophobicity of rGOS], O-H deformation at 1420 cm\(^{-1}\), and C-O stretching at 1060 cm\(^{-1}\) completely disappeared in rGOS while intensities of bands of O-H stretching at 3200 cm\(^{-1}\) and C-O stretching vibration 1740 cm\(^{-1}\) greatly decreased, suggesting GO was efficiently reduced with most oxygenated groups eliminated. Moreover, the C=C skeletal vibrations of unoxidized graphitic bands increased in intensity and shifted to lower wavenumbers, indicating that the resulting rGOS has high purity.

An excellent correlation (R=0.997) was found between the AuNPs-rGOS-ITO sensor and UV-vis spectrophotometry (Fig. 3A). Therefore, this sensor can serve as a supplement or a substitute for the conventional UV detection, especially for dilution-free high DA concentrations and in presence of UV-vis absorbing species in biological or physiological samples at wavelengths nearby. In the presence of DA, a well-defined sharp peak centered around +0.20 V can be seen at AuNPs-rGOS-ITO. A linear relationship of peak current and DA concentration (Fig. 3B inset) can be established from 10-1000 μM, with sensitivity of 62.74 μA mM\(^{-1}\) cm\(^{-2}\). The detection limit (DL) is determined to be 6.0x10\(^{-8}\) M (at signal/noise=3).

Fig. 1: Fabrication of AuNPs-rGOS-ITO dopamine sensor with a disposable working electrode.

Fig. 2: (A) SEM image and (B) ATR-FTIR of AuNPs-rGOS-ITO.

Fig. 3: (A) Correlation of electrochemical sensor to UV-vis detection (B) DPV detection of DA and calibration curve.

References