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# Long-term stability of Au nanoparticle-anchored porous boron-doped diamond hybrid electrode for enhanced dopamine detection

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ABSTRACT

A porous boron-doped diamond (pBDD) was made for immobilizing gold nanoparticles on BDD facets by a special process, wherein methods of magnetron sputtering and thermal catalytic treatment were utilized. Au nanoparticles are seated in the pores of pBDD facets and could be more stable during electrochemical tests. This hybrid structure significantly improved the electrochemical properties due to the introduction of Au nanoparticles and pores, which could increase the specific surface area. The cyclic voltammetry oxidation peak current of the Au/pBDD electrode decreased with an average daily loss of 0.02 μA and maintained approximately 90.1% of its initial value after detecting dopamine once per two days for 30 days, showing an excellent long-term electrochemical stability. In addition, the Au/pBDD electrode exhibited excellent sensitivity for the detection of DA, and the limit of detection was 0.06 μM in a linear concentration range of 0.1 μM–1 mM. This work indicates that the Au/pBDD is an appropriate material for detecting DA in a long-term tests.



## 1. Introduction

It is well known that the neurotransmitter dopamine (DA) in the central nervous systems plays an important role in the regulation of physiological events such as movement, behaviour and stress [1]. Some neurological diseases such as schizophrenia, epilepsy and Parkinson's disease are linked with the abnormal concentrations of dopamine [2,3]. Therefore, detecting the levels of DA accurately is crucial, and considerable research efforts have been made currently towards DA detection [4–9].

Electrochemical techniques have been commonly applied for the detection of DA due to their high sensitivity and low-cost, as well as the capability of in vivo monitoring of DA in the human body [10–12]. A common problem in electrochemically monitoring DA in vivo is electrode fouling. The oxidation products of DA can trigger the formation of an insulating polymer on the electrode surface, which will reduce the reusability and reproducibility of the electrode and damage the long-term stability of the electrode [13–16]. In addition, the stability of the structure and material of the electrode is also vital because it is related to the reusability of the electrode. Damage to electrode material and structure is disadvantageous to the accuracy of the electrochemical results and the life-time service of the electrode.

Boron-doped diamond (BDD) is recognized to be a promising electrode material due to its unique electrochemical properties, such as wide potential windows, low background currents, excellent electrochemical stability as well as a good resistance to biofouling [17–20]. Several biological substances (such as glucose, dopamine, etc.) have been detected successfully using BDD electrodes [21–24]. In contrast, the as-grown BDD electrode with terminated hydrogen always shows the tendency of chemical inertness, which leads to a limitation in electrochemical detection [25,26]. Therefore, improving the sensitivity of a pure BDD

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electrode remains an issue.

Until now, many researchers have studied a lot in order to improve the electrochemical sensitivity of BDD electrode [27–31]. The method of surface modification by using metal nanoparticles is commonly recognized as an efficient approach to improve its electrochemical performance [32–34]. Metal nanoparticles, especially gold nanoparticles, exhibit electronic and catalytic properties that are different from those of bulk materials in electrochemical processing. In terms of gold nanoparticle-modified BDD electrodes, electrochemical reactions occur relatively easily on the surroundings of individual gold nanoparticle with high electrochemical activities, namely, at electrochemical active sites [35]. Therefore, a lot of research has been done to improve the specific surface area of gold nanoparticles on the surface of a substrate electrode. Carbon materials, such as graphene, carbon nanotubes, glassy carbon and graphite, possess superior electronic conductivities and high specific surface area, which is thought to be a perfect substrate to support gold nanoparticles. These gold nanoparticle-modified carbon electrodes always showed good electrochemical performance towards dopamine detection, including high sensitivity, good selectivity and low limit of detection [36–39]. Song et al. prepared a Au nanoparticles/overoxidized-polyaniline-modified BDD complex electrode, in which the oxidation peaks for DA shifts from 0.4 V for the PANIox/BDD electrode to 0.27 V, indicating that Au nanoparticles possessed very strong catalytic activity for DA oxidation [40]. Weng, J. et al. showed that the gold nano-sized cluster-modified BDD electrode exhibited significantly improved current response and a low limit of detection (LOD) of 0.1 μM for DA, and the modified electrode possessed a higher activity for DA oxidation than ascorbic acid [41].

Until now, different methods to deposit gold nanoparticles on the BDD surface have been reported, and electrochemical deposition is considered a useful and simple method [42,43]. Generally, the size of the gold nanoparticles shows a significant effect on the catalytic activity [44]. In the traditional method of electrochemical deposition, the size distribution and the diameters of nanoparticles are both difficult to control precisely due to the predomination of crystal growth rather than nucleation, resulting in the formation of large clusters. The magnetron sputtering method is a good way to obtain a uniform gold layer on the BDD surface. Thereafter, through catalytic treatment at high temperature, uniform gold nanoparticles distributed on the BDD surface can be achieved, since this coupled method can effectively separate the nucleation and particle growth [45]. However, the wettability between gold nanoparticles and BDD substrate is not good enough because of a simple physical link between them. During the process of long-term electrochemical detection, gold nanoparticles weakly adhered on the BDD surface tend to fall off, which can weaken the reusability and reproducibility of the electrode and is not ideal for DA detection, as mentioned before. Therefore, a coupled method of magnetron sputtering and thermal catalytic treatment is put forward to obtain a uniform distribution of gold nanoparticles on the porous BDD surface, and this composite electrode is expected to show excellent long-term stability towards electrochemical detection.

In detail, based on previous work, we first fabricated a porous BDD substrate through a thermal catalytic etching treatment using nickel as the catalyst, as reported in previous studies [46–49]. Then, a uniform gold layer was deposited on the porous BDD surface by the method of magnetron sputtering. During the catalytic treatment at high temperature, the layer of gold atoms aggregated to form small gold clusters in a stable state at high temperature. Meanwhile, these aggregated small clusters might migrate on the BDD surface and sink into the pores, stopping in some sites of the pores with a relatively low energy. As a consequence, the Au nanoparticles inside the pores would be in a low-energy state and be strongly immobilized, leading to an improvement in the stability of Au nanoparticles on the BDD surface. Electrochemical measurement results demonstrating that the Au nanoparticle-anchored porous BDD hybrid electrode possessed enhanced long-term stability, high sensitivity and a wide detection range towards DA oxidation have also been achieved.

## 2. Material and methods

### 2.1. Reagents

Analytical grade potassium hydroxide and potassium chloride were purchased from Shanghai Macklin Biochemical Co., Ltd. Analytical grade potassium ferricyanide was purchased from Tianjin Recovery Fine Chemical Research Institute. Analytical grade dopamine was purchased from Sigma Aldrich (Shanghai, China). Analytical grade perchloric acid was purchased from Beijing Chemical Company.

### 2.2. Preparation of the electrodes

A p-type silicon wafer was cut into $4 \times 4$ mm$^2$ pieces as substrates. The BDD layer was deposited on the substrates using the hot filament chemical vapour deposition method, as described in detail in the literature [50]. Before the deposition, the substrates were ultrasonically cleaned with acetone, ethanol and deionized water for 10 min individually, and then the substrates were ultrasonically treated in the suspension of diamond nano-powder and deionized water for 30 and 2min, respectively. In BDD deposition, the mixture gases of $CH_4$ (2 sccm), $H_2$ (98 sccm) and $B_2H_6$ (0.8 sccm) was introduced into a stainless-steel chamber. The pressure was kept at 3.0 kPa while the temperatures of a tungsten filament and the substrate were maintained at 2200 and 750 °C, respectively, during the12-hours deposition. The porous BDD (pBDD) was obtained by a thermal catalytic etching (TCE) process, which includes: 1) sputtering a nickel layer on the BDD, 2) heat treating the Ni/BDD and 3) removing remaining Ni. The details of the TCE were given in our earlier work [48]. The electrodes of Au/BDD and Au/pBDD were respectively prepared by using a similar special process, which included a sputtering of Au (99.99%) target in 5.0 Pa Ar atmosphere for 2 min, and then a vacuum heat treatment in a quartz tube of 1 kPa for 1 h at 800 °C. The procedure of preparing the samples is illustrated in Fig. 1.

### 2.3. Apparatus

Scanning electron microscopy (SEM) (FEI, Nova NanoSEM 230) was used for the surface morphologic characterization. The structure and composition of the prepared electrodes were characterized using Raman spectroscopy (HORIBA, LabRAM HR800; 488 nm, 10 mW) and Energy Dispersive X-ray (EDX) analysis.

### 2.4. Electrochemical analysis

Electrochemical analysis (EA) was performed using the electrochemistry workstation (Shanghai CH Instruments, China). In the EA the prepared electrodes of the BDD, Au-BDD, pBDD and Au-pBDD were used as the working-electrodes. An Ag/AgCl electrode and a platinum plate ($10 \times 10 \times 3$ mm$^3$) were used as the reference- and counter-electrodes, respectively. Before EA, all prepared electrodes were pretreated in 1 M KOH solution with a potential of 1.2 V for 5 min. The measurement of electrochemical impedance spectra (EIS) of the electrodes was performed over a frequency range of $10^{-2}$ -$10^6$ Hz. The DA detection was performed in 0.1 M $HClO_4$