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공학석사 학위논문

**Au nanoparticle-graphene quantum
dot-Nafion modified electrode for
voltammetric determination of
dopamine**

금 나노입자-그래핀 양자점-나피온 복합체
수식전극으로 도파민의 전기화학적 검출연구

2018년 2월

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Au nanoparticle-graphene quantum dot-Nafion modified electrode for voltammetric determination of dopamine

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이 논문을 공학석사 학위논문으로 제출함
2018 년 2 월

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Abstract

Au nanoparticle-graphene quantum dot-Nafion modified electrode for voltammetric determination of dopamine

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In this work, glassy carbon electrode was modified by gold nanoparticle-graphene quantum dots-Nafion (Au-GQDs-Nafion) nanocomposite and used for voltammetric determination of trace dopamine. The properties of the as-prepared material were characterized by UV-vis spectrometry, Fluorescence spectrometry, and TEM. The Au-GQDs-Nafion composite showed the excellent synergistic effect for electrochemical detection of dopamine (DA).

Under optimum conditions, the differential pulse voltammetric (DPV) peak current and the concentration of DA displayed a linear range from 2 μM to 50 μM with the detection limit of 0.84 μM . Furthermore, the as-

prepared electrode also showed selectivity toward DA detection in the existence of uric acid (UA) and ascorbic acid (AA). The interference experiments showed that most of the ions did not show obvious influence on the detection of DA. The modified electrode presented reasonable stability and reproducibility in voltammetric sensing of DA, and also was applied to human urine samples.

Keywords: Graphene Quantum dots, Gold nanoparticles, Nafion, Dopamine, Voltammetry

Student Number: 2016-26026

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1. Introduction

1.1 Dopamine and its conventional detection method

Dopamine(DA) works as an important neurotransmitter in the central nervous system and significantly contributes to the neurological control of emotion, movement, perception, and motivation.^[1] In biological environments, transfer of the signal to the brain and other organs is usually regulated by DA.^[2] However, the abnormal level of DA has been implicated in neurological disorders such as schizophrenia, Parkinson's and Huntington's diseases.^[3-5] Thus, it is quite essential to quantify and detect the concentration of dopamine under biological conditions. In the literature, Dopamine (DA) has been monitored by chromatography-mass spectroscopy^[6, 7], and fluorescence methods.^[8] Compared to these described methods, electrochemical methods have drawn great interests due to their beneficial characteristics of simplicity, rapid response, cost-effectiveness and high sensitivity.^[9, 10]

Dopamine is an electroactive material, which can be oxidized into dopamine-quinone (DAQ). When a potential is applied to the electrode, DA is oxidized to form DAQ after the interchange of 2 electrons and 2 protons. These electrons are transferred to the electrode, and then a faradaic current is produced.^[11]

Generally, conventional electrochemical methods were widely used for the determination of DA. However, the electron-transfer was sluggish and

also poor response signals were observed at the bare glassy carbon electrode. ^[12] Moreover, DA (dopamine), AA (Ascorbic acid) and UA (Uric acid) show overlapping of the oxidation peaks at conventional electrodes, which makes it difficult to selectively detect DA. ^[13] Additionally, these substances require high over-potentials to go through electrochemical reaction at the bare electrode surface and the unmodified electrode undergoes fouling effects, which also makes it hard to detect DA due to the accumulation of oxidation products. ^[14] Therefore, the selective determination of DA has been a major aim of many studies. ^[15]

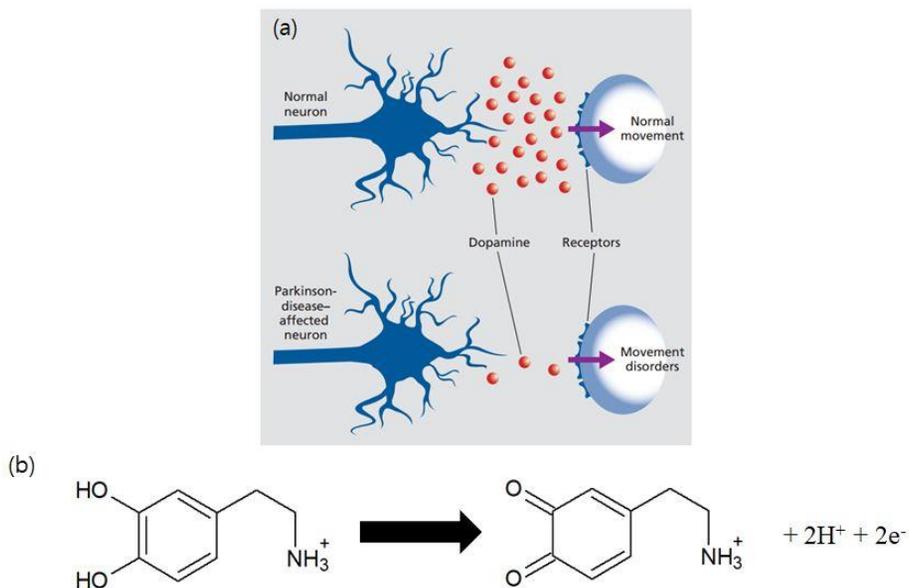


Figure 1. (A) Dopamine levels in a normal and Parkinson disease-affected neuron. Adapted from Ref [5] (P.C. Tiwari, R. Pal, *Dialogues Clin, Neurosci*, **2017**, *19*,71.) (B) Electrochemical oxidation of dopamine mechanism.

1.2 Graphene-based electrochemical sensors

Graphene is a carbon-based two-dimensional nanomaterial, which consists of sp^2 -bonded carbon networks that are densely packed in a honeycomb lattice. ^[16] Its pronounced properties include strong mechanical strength, exceptional electrical conductivity, charge mobility, large surface area and thermal conductivity. ^[17] Especially, Graphene has been employed for electrochemical sensing and bio-sensing materials due to biocompatibility, lack of metallic impurities, cost-effectiveness, more uniform and greater electroactive size distribution, large surface area. ^[18] More specifically, Graphene-based materials, such as graphene ^[19], graphene-gold ^[20], graphene-tin oxide ^[21], and graphene-chitosan ^[22], have been widely used to modify the working electrode for the selective determination of dopamine (DA). The reason is that π - π interaction between the phenyl moiety of DA and π -conjugation graphene structure enables the electron transfer. ^[23, 24] These materials contribute to the selective determination of dopamine. Nevertheless, they exhibit limited detection sensitivity and also involved complicated synthetic procedures.

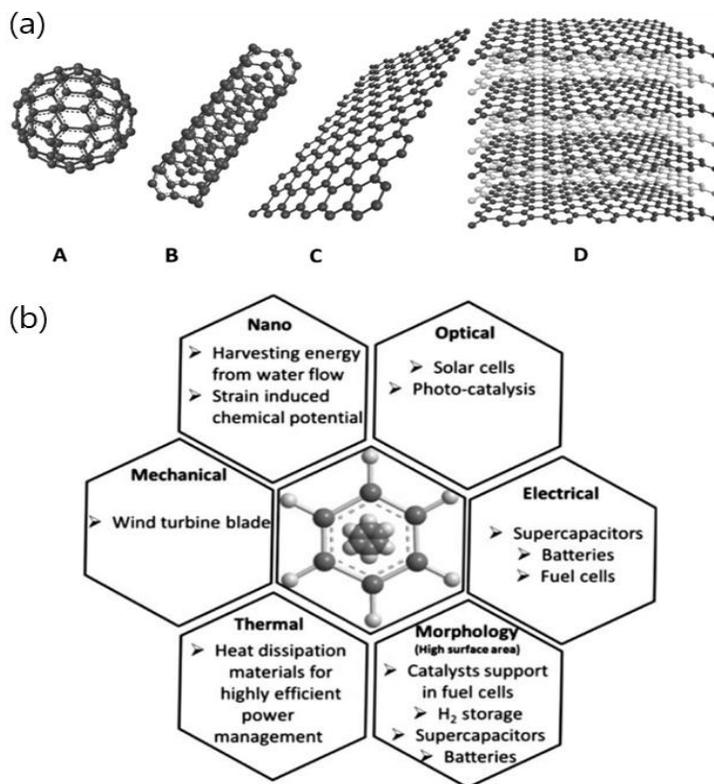


Figure 2. (A) Forms of sp^2 – hybridized carbons: Fullerene, single-walled carbon nanotubes, graphene, and graphite. Reprinted with permission from Ref [18] (M. Pumera, A. Ambrosi, A. Bonanni, E.L.K. Chng, H.L. Poh, *TrAC-Trends Anal. Chem.* 2010, 29, 954.) (B) Relationship between graphene properties and their applications. Reprinted with permission from Ref [17] (D. Wei, J. Kivioja, *Nanoscale.* 2013, 5, 10108.)

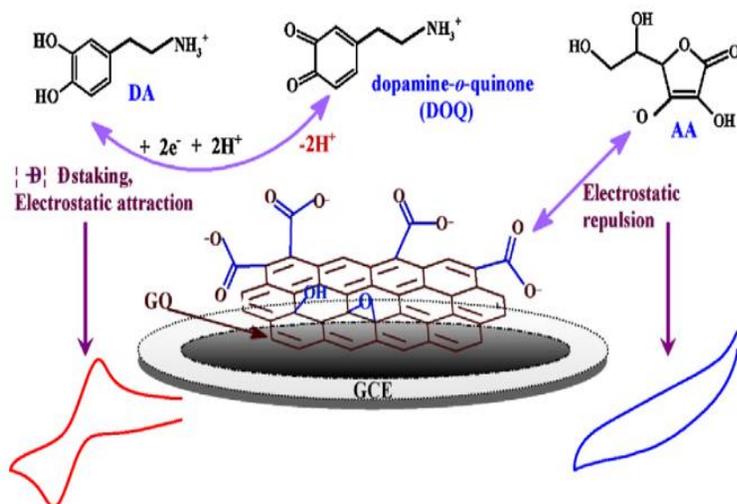


Figure 3. Electrochemical detection of dopamine on the graphene-based working electrode. Reprinted with permission from Ref [23] (F. Gao, X. Cai, X. Wang, C. Gao, S. Liu, F. Gao, Q, *Sensors Actuators, B Chem.* **2013**, 186, 380.)

1.3 Graphene quantum dots, gold, and Nafion

Graphene Quantum dots (GQDs), zero-dimensional materials, with a plane size less than 100nm and a thickness of fewer than 10 layers ^[25], have aroused increasing attention because of small size, chemical inertness, stable photoluminescence, low toxicity, and biocompatibility. ^[26] These unique physical and chemical properties lead to several biomedical applications: bio-imaging, optical sensing, effective carriers for drug delivery. ^[26] Moreover, GQDs have unique properties, including high surface area, conductivity, and dispersibility, which enable the promising applications of GQDs in Energy-related applications: batteries, supercapacitors, solar-cells and so on. ^[27]

As a new member of graphene, GQDs have advantageous potentials for electrochemical detection, because these materials have some of the outstanding properties of graphene such as good electron mobility and chemical stability. ^[28] Especially, Pang et al employed GQD as a selective electrochemical detection of dopamine, because GQDs have negative carboxyl groups, which not only offered good stability but also could electrostatically interact with amine groups in dopamine. Furthermore, π - π stacking interaction between GQDs and dopamine makes electron transfer and communication stronger. ^[29]

Gold nanoparticles (AuNPs) are excellent electrocatalytic materials for the electrochemical determination towards various materials due to superior

conductivity, high specific surface area, and great catalytic properties.^[30] They play a pivotal role in enhancing the electron transfer capability^[31] and improving voltammetric detection performance.^[32] The synergistic cooperation of AuNP and GQDs can offer the selective and sensitive environments for the electrochemical sensing of numerous substances.^[31-34] Nafion is a cation exchange polymer, which has been widely used as a membrane on electrode surfaces. The membrane has the ability to attract cations and preclude the approach of anionic species.^[35] Nafion's ion-permeability for cationic species is especially crucial in the selective detection of DA because it can remove the interference effects caused by anionic ascorbic acid (AA) and uric acid (UA).^[36] In addition to this, Nafion was employed as a coating material^[36] to make Au-GQDs nanocomposite firmly attached to the electrode surface, which results in the significantly improved stability and reproducibility.^[29]

In this work, the Au-GQDs composite was produced by simply mixing of GQDs and gold ions (AuCl_4^-) with the sodium citrate as reducing agents. The Au-GQDs-Nafion modified electrode was prepared by pipetting the Au-GQDs composite onto the pretreated GCE surface and dried in air, followed by adding diluted Nafion onto the Au-GQDs modified electrode surface. It was revealed that the Au-GQDs-Nafion/GCE exhibits synergistic cooperation toward the voltammetric sensing of DA, and the modified electrode shows lower

detection limits than the methods reported in the selective detection of DA. Furthermore, it also revealed good stability, reproducibility and potential application in the real sample analysis.

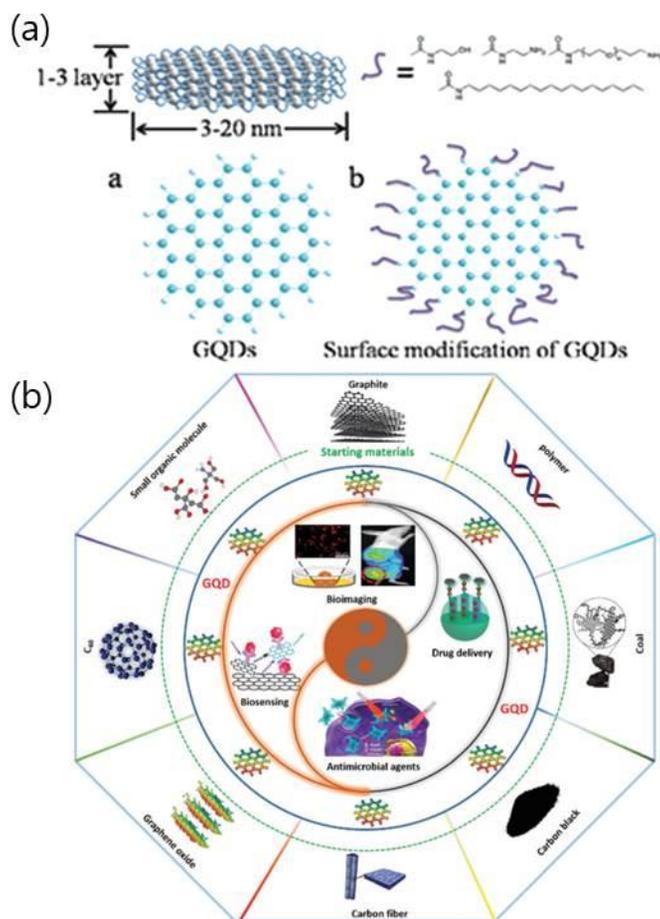


Figure 4. (A) Structural depiction of Graphene Quantum dots. Reprinted with permission from Ref [37] (X. T. Zheng, A. Ananthanarayanan, K. Q. Luo and P. Chen, *Small*, **2015**, 11, 1620–1636) (B) Synthesis and biological applications of GQDs. Reprinted with permission from Ref [26] (K. Li, W. Liu, Y. Ni, D. Li, D. Lin, Z. Su, G. Wei, *J. Mater. Chem.* **2017**, 5, 4811)

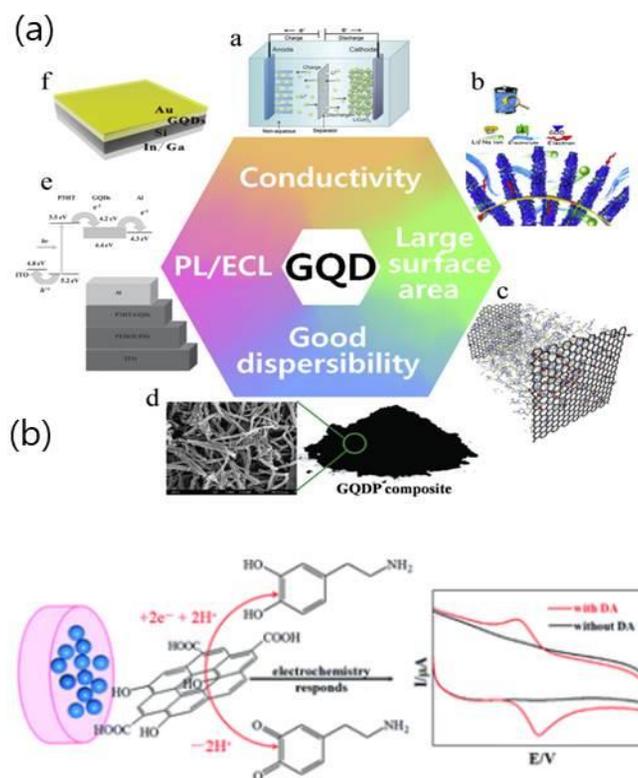


Figure 5. (A) Properties of GQDs with energy-related applications. Reprinted with permission from Ref [27] (S. Bak, D. Kim, H. Lee. *Curr. Appl. Phys.* **2016**, 16, 1192.) (B) GQDs-based electrochemical sensor for the detection of dopamine. Reprinted with permission from Ref [29] (P. Pang, F. Yan, H. Li, H. Li, Y. Zhang, H. Wang, *Anal. Methods.* **2016**, 8, 4912.)

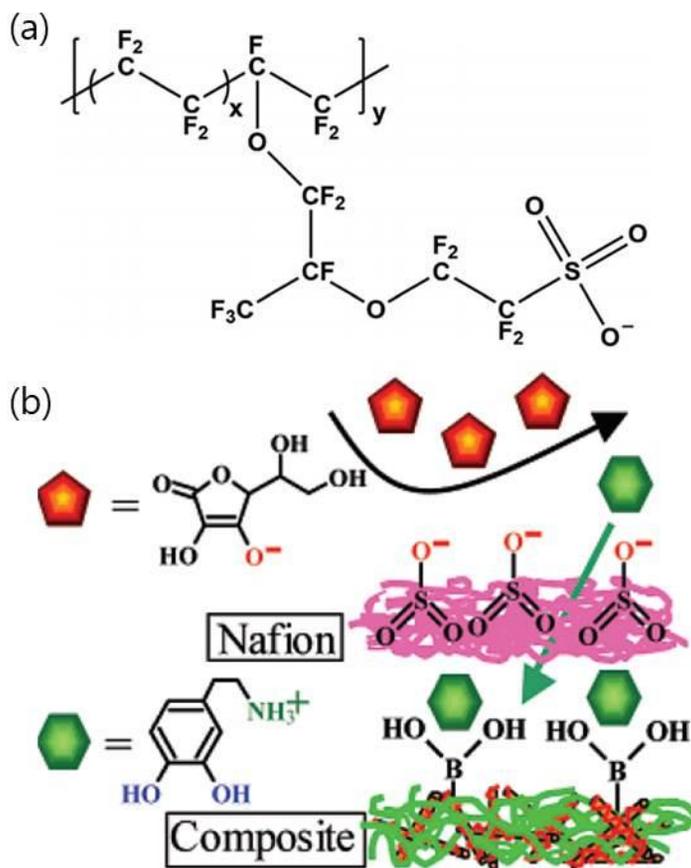


Figure 6. (A) Structure of Nafion. Reprinted with permission from Ref [38] (W. Shi and L. A. Baker, *RSC Adv.*, **2015**, 5, 99284.) (B) The role of Nafion to attract dopamine and repel ascorbic acid. Reprinted with permission from Ref [39] (S. R. Ali, R. R. Parajuli, Y. Balogun, Y. Ma and H. He, *Anal. Chem.*, **2007**, 79, 2583.)

2. Experimental process

2.1 Reagents and apparatus

Vulcan CX-72 carbon black was obtained from Cabot Corporation. Gold (III) chloride trihydrate ($\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$), Dopamine, tri-sodium citrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) and Nafion (5%) were purchased from Sigma-Aldrich. A standard stock solution of dopamine was produced by dissolving dopamine in distilled water and stored in the refrigerator (4°C). The supporting electrolyte was the phosphate buffer solution (PBS 0.1M). All other chemicals were of analytical grade and were used as received without further purification.

The optical absorption spectrum data were collected from a Lambda 35 UV-vis spectrometer (Perkin Elmer, USA). Fluorescence emission spectra were recorded by Fluorescence spectrometer-2 (Scinco, Korea). The morphology was observed by a transmission electron microscopy (TEM, JEOL-2010). The electrochemical measurements were done on a conventional 3-electrode system with the AUTO-LAB potentiostat (Metrohm, USA): Glassy carbon electrode as the working electrode, Ag/AgCl as the reference electrode, and the platinum wire as the counter electrode.

2.2 Synthesis procedure

GQDs were synthesized according to the previous work with slight modification. ^[40] Specifically, 0.2g of dried CX-72 carbon black was put into 50ml of 6mol L⁻¹ HNO₃, followed by refluxing for 24h. The suspension was cooled down to room temperature and then it was centrifuged for 10min. While the sediment was discarded, the obtained supernatant was dialyzed (3500Da, Dialysis bag). After dialysis, the obtained solution (9ml) was transferred into a Teflon-lined autoclave and hydrothermally treated by using the ammonia solution (1ml) at 180°C for 12h with some alteration from the previous research. ^[41] After cooling down to room temperature, the obtained solution was once again dialyzed (3500Da, Dialysis bag).

Preparation of Au-GQDs nanocomposite was based on the previous paper with some modifications. ^[34] Briefly, the prepared GQDs solution (1ml) was added to the 4ml of distilled water. 400µl (25.4mM) of the H₂AuCl₄ solution was put into the 5ml of GQDs solution, and the mixture was heated and vigorously stirred for 15min. 400 µl (0.1M) of trisodium citrate solution was quickly added to the heated solution. The solution was refluxed for 30 min until its color changed into the purplish red. Finally, the synthesized composite was allowed to cool and stay at room temperature.

AuNPs were prepared according to previous research with some modifications. ^[34] Briefly, 400 µl (25.4mM) of the H₂AuCl₄ solution was put into the boiling distilled water (5ml) with the vigorous stirring,

and then 400 μl (0.1M) of trisodium citrate solution was quickly dropped into the heated solution until it became red color. Finally, the obtained AuNPs was allowed to cool and stored at room temperature.

2.3 Fabrication of working electrode and measurement

In the first place, Nafion (5wt %) was diluted to the 1wt % of Nafion with ethanol. Before the modification of electrodes, the bare GCE was polished by 0.3 μ m alumina slurries on a felt pad, cleaned with water and ethanol for then 10 min and then dried under the infrared lamp. The procedure for preparing the modified electrodes was outlined in Fig.7. 5 μ l of Au-GQDs nanocomposite was drop-cast onto the bare GCE and dried by the infrared lamp. After that, 1 μ l of diluted Nafion (1wt %) was added to the Au-GQDs/GCE surface and dried under the infrared lamp to prepare for the voltammetric sensing of dopamine.

A 20ml volume of 0.1M PBS (pH 7.4) and the certain amount of dopamine or sample solution was put into the electrochemical cell, and subsequently, the three-electrode system was arranged into it. Cyclic voltammetry (CV) was carried out in the potential range from 0 to 0.6 V with the scan rate of 100mV s⁻¹. Differential pulse voltammetry (DPV) was conducted in the potential range from 0 to 0.6 V with the following conditions: the pulse amplitude of 4mV and a pulse width of 2s.

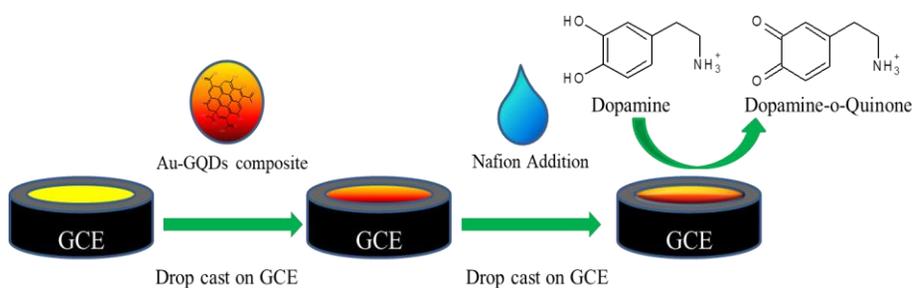


Figure 7. Schematic illustration of the preparation of AuNP-GQDs-Nafion/GCE and the electrochemical determination of dopamine.

3. Results and discussion

3.1 Characterization of nanocomposite

Fig.8A displays the visual images of each material. The optical properties of as-synthesized materials were studied by UV-vis and fluorescence spectroscopy. The UV-vis absorption spectra of each material were shown in the Fig.8B. GQDs have broad absorption spectra below 800nm. The synthesis of AuNPs was verified by the absorption peak around 520nm. ^[34,42] Compared to the pure AuNPs, the absorption peak of Au-GQDs nanocomposite was red-shifted and broadened due to the size increase, ^[34,43] via the neutralization of positively charged gold AuNPs and negatively charged GQDs. ^[34] The fluorescence emission spectra of each material were described in the Fig. 8C. With the excitation at 466nm, GQDs present the strong peak emission intensity, but Au-GQDs nanocomposites have the weak emission intensity at 514.8nm. Y. Liu et al. explained that AuNPs can quench the fluorescent GQDs by making a composite with GQDs and by quenching indirectly at some distance. ^[43] Fig. 8D shows the TEM image of Au-GQDs nanocomposites, which indicates that part of GQDs attached to the AuNPs surface and the rest remained in the solution.

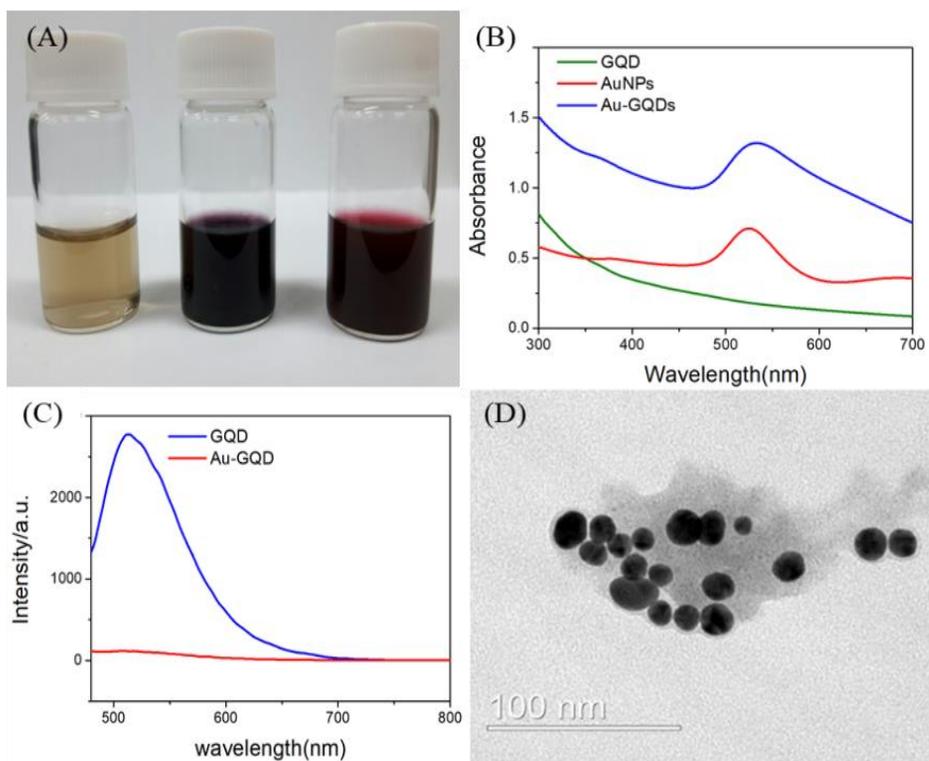


Figure 8. (A) Visual images of GQDs, Au-GQDs nanocomposite, and AuNPs. (B) UV-vis absorption spectra of each material. (C) Fluorescence emission spectra of each material. (D) TEM image of Au-GQDs nanocomposite.

3.2 Cyclic voltammetry (CV) results

3.2.1 Electrochemical characterization

Cyclic Voltammetry (CV) is a useful method to investigate the electron transfer rate and the interaction between different analytes and the electrode surface. ^[44] The CV curves of DA (0.2mM) on different electrodes in 0.1M PBS solution (pH 7.4) are presented in Fig.9. Slow electron transfer and poor redox peaks are observed at the bare GCE; however, Au-GQDs-Nafion/GCE showed a higher oxidation peak current in comparison to GQDs/GCE, AuNP/GCE, and Au-GQDs/GCE. This phenomenon may be ascribed to the synergistic cooperation of three components. Au nanoparticles are electrocatalytic materials, which can improve the electron transfer capability and further enhance the electrochemical performance. Additionally, GQDs have many carboxyl groups, which not only have good stability and but also makes it possible to interact with DA through π - π interaction and electrostatic interaction. ^[45] Nafion is the anchoring agent, which makes Au-GQDs composite firmly attached to the working electrode and accordingly improves the reproducibility and stability. ^[29]

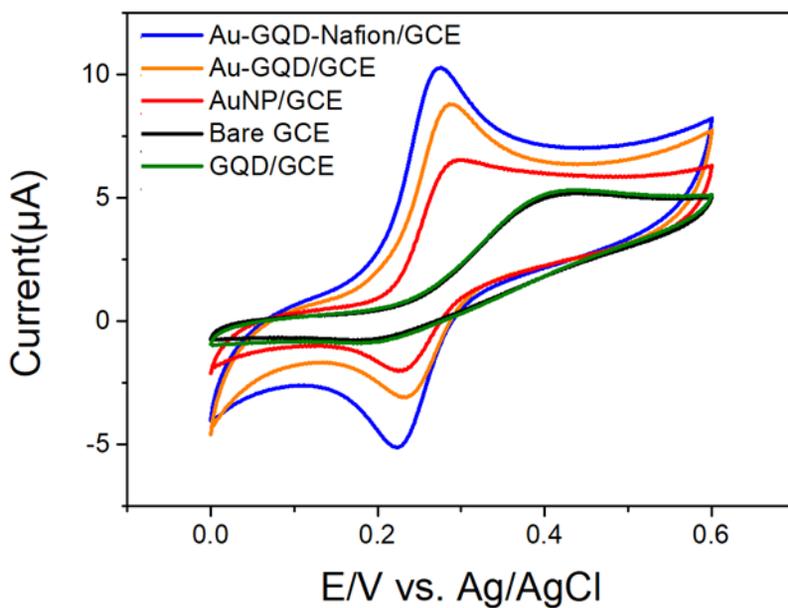


Figure 9. CV responses of 0.2mM dopamine (DA) on the bare GCE, GQD/GCE, AuNP/GCE, Au-GQD/GCE and Au-GQD-Nafion/GCE in 0.1M PBS (pH 7.4) with the Scan rate of 100mV s^{-1} .

3.2.2 Effect of scan rate

Fig. 10 reveals the CV of 0.2mM DA at Au-GQDs-Nafion/GCE with different scan rates from 50 to 350 mV s⁻¹. With the increase of scan rates, redox peak currents increase at the same time. Also, the linear relationship between the redox peak current of DA and scan rate can be obtained, which indicates the typical adsorption-controlled process. [46,47] The linear regression equation is $I_{pa} (\mu A) = 0.04426v (Vs^{-1}) + 2.263 (R^2 = 0.994)$, and $I_{pc} (\mu A) = -0.0456 v (Vs^{-1}) - 0.0467 (R^2 = 0.997)$, respectively. Moreover, the potential gap between E_{pa} and E_{pc} does not change significantly, which indicates the Au-GQDs-Nafion modified electrode has the improved electrochemical performance toward sensing DA.

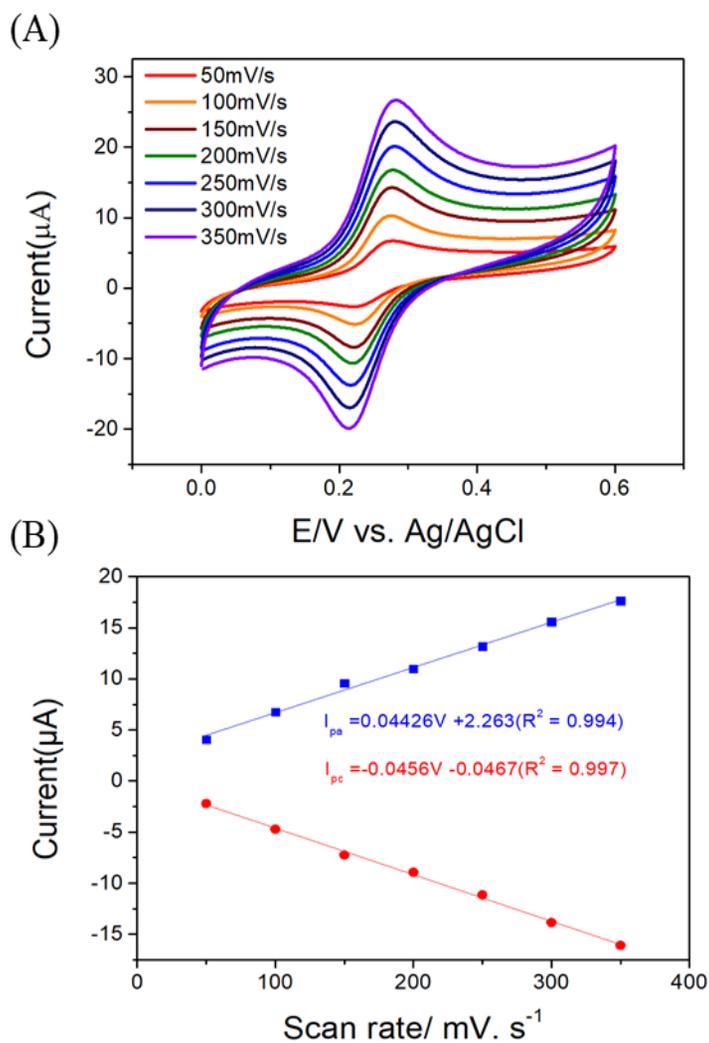


Figure 10. (A) CV responses of the Au-GQDs-Nafion/GCE in 0.1M PBS (pH=7.4) in the presence of 0.2mM DA at different scan rates from 50 to 350mV s⁻¹. (B) The linear relationship between redox currents and scan rates.

3.3 Differential pulse voltammetry (DPV) results

3.3.1 Effect of accumulation time

It is obvious that the accumulation time will influence the sensitivity of the prepared sensor. The accumulation time can multiply the quantity of DA adsorbed on the modified electrode surfaces and subsequently improve the response signal toward DA. ^[45, 48] The influence of accumulation time was studied from the 30s to 3min with DPV. Fig.11 revealed that the response current increased from the 30s to 1min. However, when the accumulation time reached 2 min, the response current was slightly decreased owing to the saturation of DA at the modified electrode surface. Accordingly, 1min was selected as the optimal time.

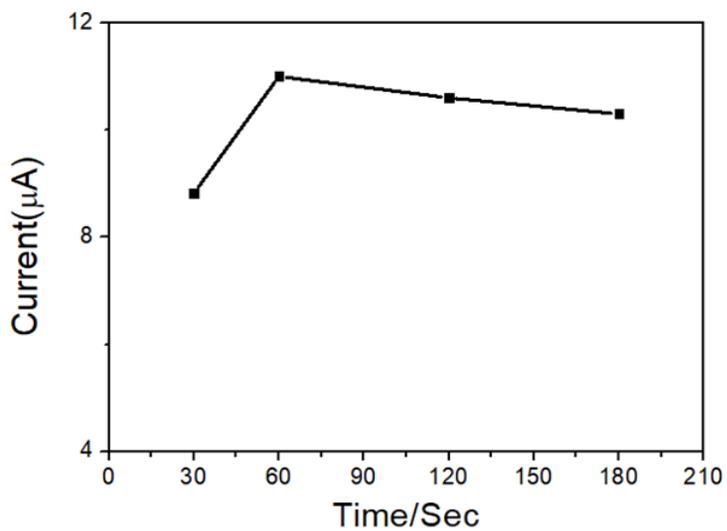


Figure 11. Plots of the peak current of 0.2mM DA *versus* the accumulation time from 30 sec to 3 min at the Au-GQDs-Nafion/GCE by DPV method.

3.3.2 Analytical characteristics and interference test

The differential pulse voltammetry (DPV) method was conducted for the voltammetric sensing of DA because of its more sensitive and quantitative method compared to CV. ^[49,50] Also it can eliminate the contribution of non-faradaic currents. ^[51] Under selected conditions, the oxidation peak current of DA was proportional to its concentration, ranging from 2 μM to 50 μM . The linear regression equation can be obtained as $I_{\text{pa}} (\mu\text{A}) = 0.04745 + 0.06043C (\mu\text{M})$ with the correlation coefficient ($R^2 = 0.998$). The detection limit was 0.84 μM . Furthermore, the electrochemical sensor proposed in this work showed the lower detection limit and better electrochemical detection performance than the other reported methods in table 1.

Fig. 13 shows the influence of 100 μM ascorbic acid (AA), 30 μM uric acid (UA), 50 μM glucose (Glu), 200 μM NaCl and KCl, 100 μM Na_2SO_4 on the detection of 50 μM DA. It can be seen that the DPV signal doesn't change significantly when the above-mentioned interfering substances are added. The reason for the selective determination of DA may be strong π - π stacking interaction between the basal plane of GQD and the phenyl moiety of DA molecules, which enables DA to adsorb on the surface of GQDs, resulting in the specific voltammetric response of DA. ^[29, 52] Moreover,

Nafion membrane has excellent ion-permeable abilities to attract strongly cationic DA and also highly repel anionic AA and UA to reach the electrode, which could lead to the selective voltammetric detection of DA. ^[53]

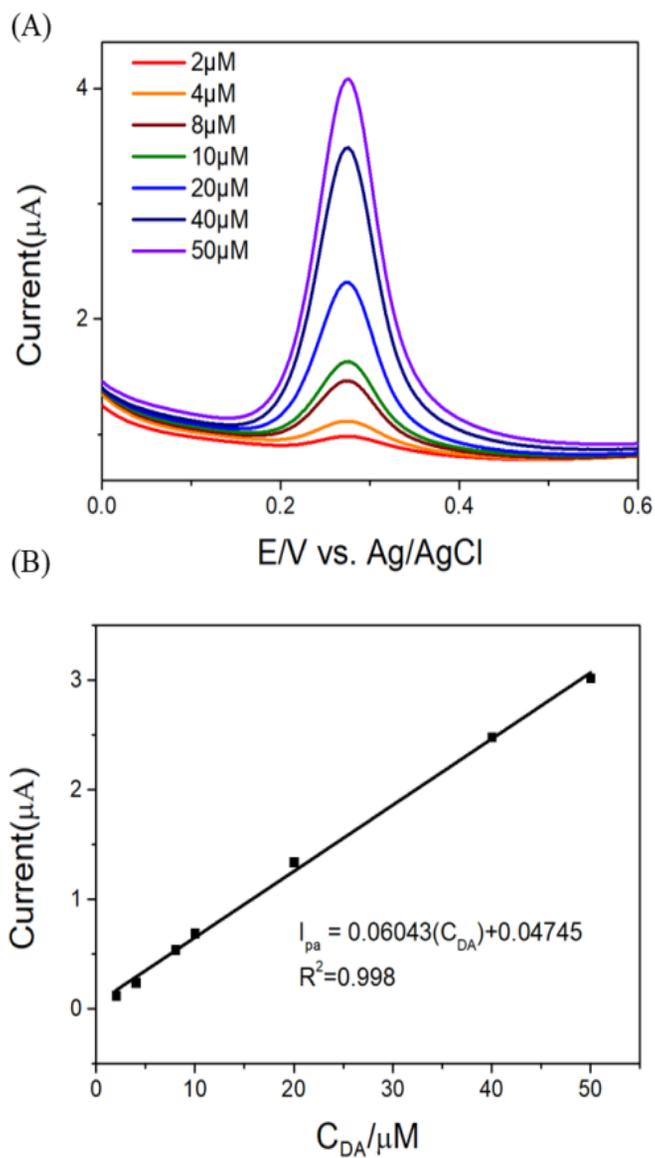


Figure 12. (A) DPV responses of Au-GQDs-Nafion/GCE in 0.1M PBS (pH 7.4) with different DA concentrations from 2 μM to 50 μM . (B) The linear plot of the oxidation peak current (I_{pa}) and concentration of DA.

Modified Electrode (DPV method)	DA		References
	Linear range (μM)	LOD (μM)	
GR/GCE	4 - 100	2.64	[19]
AuNP/GR/GCE	5 - 1000	1.86	[20]
TiO ₂ – GR/GCE	5 - 200	2	[21]
Chit-GR/GCE	1 - 24	1	[22]
MWCNT/CPE	20- 50	1.07	[54]
AuNP/rGO/GCE	6.8 - 41	1.4	[55]
MB/SZP	6 - 100	1.7	[56]
CTAB/GO/MWCNT/GCE	5 - 500	1.5	[57]
N-RGO/MnO/GCE	10 - 180	3	[58]
Au-GQDs-Nafion/GCE	2 - 50	0.84	This work

Table 1. Comparison of different electrochemical sensors proposed for determination of dopamine (DA).

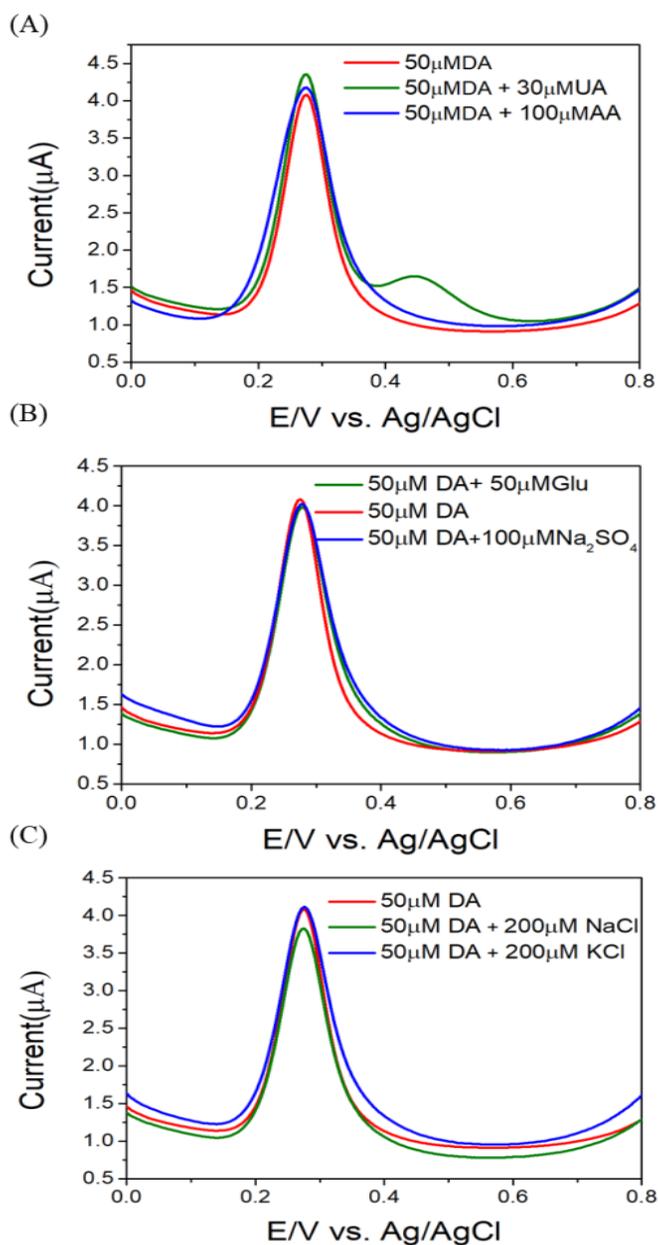


Figure 13. DPV of 50 μM DA with interference materials: (A) 100 μM AA (ascorbic acid) and 30 μM UA (Uric acid), (B) 50 μM Glucose and 100 μM Na_2SO_4 . (C) 200 μM NaCl and KCl.

3.3.3 Reproducibility, stability, and real sample analysis

Reproducibility and stability are essential factors for the electrochemical sensing. ^[59] Reproducibility test was carried out on six modified electrodes by CV method (Fig. 14A), which showed a good reproducibility with a relative standard deviation (RSD) of 2.8%. The stability test was performed over 5 days by DPV method (Fig. 14 B). No conspicuous change was noticed and it maintained 92% of its initial current after storage of 5 days, indicating good stability of the DA sensor.

The Au-GQDs-Nafion nanocomposite was utilized for the detection of DA in human urine samples. The urine samples (40 μ M) were diluted to 20ml with PBS pH 7.4 before the measurements. The results in Table 2 indicated that the recoveries of the spiked samples were in the range from 95% to 98%. Thus, the proposed method may have the potential application for DA sensing in real sample analysis.

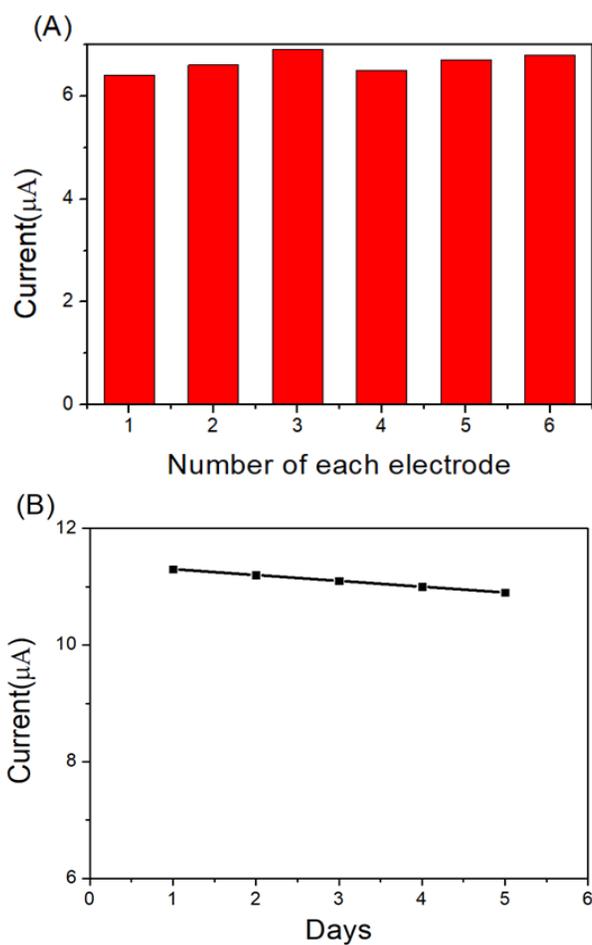


Figure 14. (A) Reproducibility for DA oxidation with six modified electrodes in the solution containing 0.2mM DA, 0.1M PBS (pH=7.4) with the scan rate of 100mV/s (CV method). (B) Stability for DA oxidation with the modified electrode for 5 days after storage (DPV method).

Sample	Species	Added (μM)	Found (μM)	Recovery (%)
Urine	DA	40	39.2	98

Table 2. The detection result of DA in human urine samples by using Au-GQDs-Nafion modified electrode (n=5).

4. Conclusion

In this work, glassy carbon electrode was modified with gold nanoparticle-graphene quantum dots-Nafion (Au-GQDs-Nafion) nanocomposite, which was employed for the voltammetric sensing of dopamine. It showed excellent synergistic cooperation and significantly enhanced peak current toward the electrochemical detection of dopamine (DA) compared with GQD/GCE, AuNP/GCE, and Au-GQD/GCE. Under the selected conditions, the differential pulse voltammetric (DPV) peak current and the concentration of DA displayed a linear range from 2 μM to 50 μM with the detection limit of 0.84 μM . In addition, this proposed sensor presented the selective determination of DA in the presence of some interfering substances. The modified electrode displayed reasonable stability and reproducibility in voltammetric sensing of DA, and also was applied to human urine samples.

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요 약 (국문 초록)

본 연구에서는 금 나노입자, 그래핀 양자점 그리고 나피온 복합체 기반 전극물질을 이용하여 도파민을 전기화학적으로 측정하는 방법을 제시하였다. 만들어진 금 나노입자-그래핀 양자점 복합체의 광학적인 특성은 자외선 및 적외선 흡수 분광분석법과 형광 방출 분광분석법으로 확인하였고, 투과전자현미경을 활용해서 합성된 복합체의 형상을 관찰하였다.

전기화학 측정과정법으로 금 나노입자, 그래핀 양자점 그리고 나피온 복합체 기반 전극물질이 도파민을 측정할 때 나타나는 특징을 살펴보았다. 먼저 순환전압전류법으로 도파민 측정할 때 나타나는 산화 환원 전류 Peak가 상당히 향상되었음을 확인하였다. 순환전압전류법을 통해 알아낸 최적화된 조건을 토대로, 시차펄스 전압전류법에서 수식된 전극은 2 μM 에서 50 μM 까지 전류 Peak 과 선형적인 범위를 나타냈고 기존의 측정방법들 보다 상대적으로 낮은 측정한계치인 0.84 μM 을 나타내었다. 또한 수식된 물질은 선택적인 도파민 탐지능력, 안정성과 재현성, 더 나아가서 Real sample 분석 응용의 가능성을 제시하였다.

주요어 : 그래핀 양자점, 금 나노입자, 나피온, 도파민, 볼타메트리.

학 번 : 2016-26026