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Nanochannel-Confined Graphene Quantum Dots for Ultrasensitive Electrochemical Analysis of Complex Samples

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ABSTRACT: Herein, we present an electrochemical sensing platform based on nanochannel-confined graphene quantum dots (GQDs), which is able to detect a spectrum of small analytes in complex samples with high sensitivity. Vertically-ordered mesoporous silica-nanochannel film (VMSF) is decorated on the supporting electrode, conferring the electrode with excellent anti-fouling and anti-interference properties through steric exclusion and electrostatic repulsion. The synthesized GQDs with different functionalities are confined in the nanochannels of VMSF through electrophoresis, serving as the recognition element and signal amplifier. Without the usual need of tedious pretreatment, ultrasensitive and fast detection of Hg^{2+} , Cu^{2+} and Cd^{2+} (with limit of detection or LOD of 9.8 pM, 8.3 pM and 4.3 nM, respectively) and dopamine (LOD of 120 nM) in complex food (Hg^{2+} -contaminated seafood), environmental (soil leaching solution), and biological (serum) samples are realized as the proof-of-concept demonstrations.

KEYWORDS: *graphene quantum dots • vertically-ordered mesoporous silica-nanochannel • electrochemical detection • heavy metal ion detection • biomarker detection*

Direct and ultrasensitive analysis of complex samples is challenging.^{1,2} Usually sophisticated and time-consuming pre-treatments using bulky equipment (*e.g.*, separation, enrichment) are required, making on-site, real-time, and convenient detection not possible.³⁻⁶ Recently, the electrochemical sensors equipped with vertically-ordered mesoporous silica-nanochannel film (VMSF) have attracted considerable interest for their ability for direct analysis of small analytes in complex samples.⁵⁻⁷ VMSF consists of uniform nanochannels (2-3 nm) perpendicular to the underlying electrode with a high pore density $\sim 40000 \mu\text{m}^{-2}$. Such nanochannels display permselective effects on size, charge and lipophilicity and offer the sensor surface with anti-fouling and anti-interference abilities.⁸⁻¹¹ On the other hand, due to their small size it is difficult to incorporate them with functional nanomaterials for enhanced detection.

Graphene quantum dot (GQD) or 0D graphene, which is an atomically thin and nanometer-wide planar carbon structure, is the most recent addition to the nanocarbon materials family.¹²⁻¹⁷ GQD promises a wide range of applications (*e.g.*, imaging,¹⁸⁻²² sensing,²³⁻²⁸ catalysis,²⁹⁻³² energy storage and conversion³³⁻³⁶) owing to a set of merits including molecular size, highly tunable physicochemical properties, good solubility, high specific surface area, fluorescence properties, and good biocompatibility.³⁷⁻⁴¹ For instance, GQD based fluorescence sensors have been developed for detection of metal ions with high sensitivity.^{25,27} Metal ions act as coordination centers to bridge several GQDs together *via* interaction with the functional groups or dopants on GQDs (*e.g.*, Cu^{2+} or Hg^{2+} with $-\text{OH}$ group on GQD;⁴²⁻⁴⁴ Cd^{2+} with $-\text{NH}_2$ group on GQD;⁴⁵ Fe^{3+} for N-dopant on GQD²⁷), consequently leading to aggregation induced fluorescence quenching.

In this work, we demonstrate an electrochemical analysis platform to detect small analytes in complex samples based on VMSF nanochannel-confined GQDs, which is ultrasensitive, fast, convenient, of low cost and without need of tedious pretreatment (Figure 1). In this platform, VMSF serves as the anti-fouling and anti-interference layer on the supporting electrode while GQD bearing different functional groups serves as the recognition element and signal amplifier through interaction with analytes to attain nanoconfined enrichment and facilitating charge transfer. As the proof-of-concept demonstrations, this technique is employed to detect Hg^{2+} , Cu^{2+} , Cd^{2+} and dopamine in practical samples with ultralow detection limit (9.8 pM, 8.3 pM, 4.3 nM, and 120 nM, respectively).

RESULTS AND DISCUSSION

Wang *et al.*³⁹ have demonstrated a bottom-up synthesis of single-crystalline GQDs (~3.5 nm in diameter, ~1.47 nm thick) based on fusion of 1,3,6-trinitropyrene in alkaline medium under hydrothermal condition. Here, to obtain smaller and thinner GQDs, OH-functionalized GQDs (OH-GQDs) were prepared similarly but with a shorter reaction time (2 h *vs.* 10 h) and a weaker saline condition (0.125 M *vs.* 0.2 M NaOH). As uncovered by transmission electron microscopy (TEM, Figure 2A), OH-GQDs are uniform in size ($1.83 \text{ nm} \pm 0.24 \text{ nm}$, 129 samples) with a lattice spacing of 0.21 nm corresponding to that of graphene (100) planes. Their thickness characterized by atomic force microscope (AFM, Figure 2B) is ~0.8 nm ($\pm 0.13 \text{ nm}$, 107 samples), indicating that the produced GQDs are single layered. Comparing to the 2D counterpart (graphene sheet), GQD's bandgap opens due to quantum confinement and therefore it fluoresces. As shown in Figure 2C, excitation at 485 nm gives the maximum emission at 520 nm. The emission peak remains unchanged with varying excitation wavelength, indicating the good uniformity of GQD size and surface states (Figure 2C). The absolute photoluminescence quantum yield of these green OH-GQDs was measured to be 21.0%. X-ray photoelectron spectroscopy (XPS) confirms the abundant existence of -OH

groups (Figure S1 A-C in SI). Due to ionization of hydroxyl groups, OH-GQDs show negative charges when pH is higher than 2.5 (Figure S1 D in SI). As shown in Figure 2D, the fluorescence of OH-GQDs is obviously quenched by Cu^{2+} and Hg^{2+} (Figure S2 A in SI), suggesting the interaction between GQDs and these positively charged metal ions. The metal ion coordination leads to GQD aggregation and subsequent fluorescence quenching.⁴²⁻⁴⁴ The aggregation of OH-GQDs was confirmed by particle size measurement using dynamic light scattering (Figure S2 B, C in SI). Although Fe^{3+} can also quench OH-GQDs, it is not feasible for electrochemical detection therefore will not interfere.

We also synthesized amine-functionalized GQDs (NH_2 -GQDs) using ammonia and hydrazine hydrate (instead of NaOH) as the alkaline media and nitrogen source. The average diameter and thickness of the NH_2 -GQDs are $1.90 \text{ nm} \pm 0.31 \text{ nm}$ (89 samples) and $\sim 0.7 \text{ nm} \pm 0.12 \text{ nm}$ (133 samples) as shown in Figure S3 A and B in SI. XPS characterization reveals that NH_2 -GQDs bear both amino and hydroxyl groups (Figure S3 C, D in SI). Their isoelectric point is pH 3.5 (Figure S2 E in SI). NH_2 -GQDs are blue fluorescent (maximum emission at $\sim 464 \text{ nm}$ while being excited at 370 nm) (Figure 2E) with the absolute quantum yield of 29.8%. In comparison with OH-GQDs, fluorescence quenching of NH_2 -GQDs caused by Hg^{2+} and Cu^{2+} are less while Cd^{2+} causes strong fluorescence quenching of NH_2 -GQDs due to the coordination between Cd^{2+} and $-\text{NH}_2$ (Figure 2F in SI).⁴⁸ We propose that negatively-charged GQDs bearing different chemical moieties can specifically interact with particular ion species, serving as the recognition and enrichment element.

Vertically-ordered mesoporous silica-nanochannel film (VMSF) attached to the ITO electrode was prepared using Stöber-solution growth approach as previously reported. The cross-section scanning electron microscopy (SEM) image of VMSF/ITO exhibits three layers from top to bottom corresponding to VMSF, ITO and glass, respectively (Figure 3A). VMSF scraped from the ITO surface was further investigated by transmission electron microscopy

(TEM). From the top view, VMSF exhibits uniformly distributed mesopores with a diameter (~ 2.6 nm) slightly larger than a GQD (Figure 3A). The cross-section TEM image of VMSF reveals the densely-aligned and straight silica nanochannels ~ 90 nm long (Figure 3B).

As illustrated in Figure 1, when a positive potential is applied to VMSF/ITO electrode, negatively charged OH-GQDs or NH_2 -GQDs swim into the nanochannels of VMSF *via* electrophoresis. According to the electrochemical window determined by cyclic voltammetry (CV, Figure S4 A,B in SI), +0.8 V and +0.4 V were applied to drive the electrophoresis of OH-GQDs and NH_2 -GQDs respectively to avoid electrochemical oxidation of GQDs while ensuring maximum driving force.

Although SiO_2 nanochannels tend to be melt and roughened under high-energy electron beams (200 kV) (Figure 3C), some crystalline GQDs on the cross-section of OH-GQD@VMSF can be clearly resolved by high-resolution TEM (Figure 3D), indicating the successful deposition of GQDs into the nanochannels. The pore density is $\sim 3.4 \times 10^{12}$ pores/ cm^2 , corresponding to a porosity of 18%. Making use of the fluorescence property of GQDs, laser from optical fiber was applied to illuminate the cross-section of GQD@VMSF/ITO electrode (Figure 3E). As shown in Figure 3F, green OH-GQDs or blue NH_2 -GQDs are embedded within VMSF, further confirming that GQDs are confined within the nanochannels.

The performance of OH-GQD@VMSF/ITO electrode was firstly characterized using the standard electroactive probes $\text{Ru}(\text{NH}_3)_6^{3+}$ and $\text{Fe}(\text{CN})_6^{3-}$. As shown in Figure S4 C (SI), comparing to VMSF/ITO electrode, OH-GQD@VMSF/ITO produces much larger redox peaks of $\text{Ru}(\text{NH}_3)_6^{3+}$ in the CV scan. This suggests that deposited GQDs do not obstruct the mass transport in the nanochannel, instead they promote the enrichment of positively charged analytes. In contrast, the redox peaks of $\text{Fe}(\text{CN})_6^{3-}$ are largely reduced because of the

existence of GQDs, suggesting the negatively charged analytes are electrostatically repelled by GQDs (Figure S4 D in SI).⁷

With the increasing industrialization, heavy metal ion pollution has become a serious global problem. They accumulate in food and water, posing a serious threat to human health.⁴⁹⁻⁵² A low concentration of Hg^{2+} can cause serious damage in central nervous system, kidney failure and birth defects.⁵³ Although Cu^{2+} is a cofactor to some enzymes in human body, excess Cu^{2+} induces gastrointestinal and kidney damages.⁵⁴ Cd^{2+} is extremely toxic and carcinogenic. A small amount results in cardiovascular diseases and damage to liver and kidneys.⁵⁵ These three ion species cause fluorescence quenching of our two types of GQDs, suggesting their specific interaction with the GQDs. However, fluorescence quenching signal is not sensitive enough to detect low existence and require tedious pretreatment of practical samples to avoid interference. Hence, we here use GQDs as the recognition element and enhancer in electrochemical detection. Specifically, the ability of OH-GQD@VMSF/ITO for detection of Hg^{2+} or Cu^{2+} and NH_2 -GQD@VMSF/ITO for detection of Cd^{2+} were investigated.

As illustrated in Figure 1, the electrochemical detection is based on electrodeposition and reduction of metal ions and the following anodic stripping by differential pulse voltammetry (DPV). Different ion species gives stripping current peak at their characteristic potentials. Both OH-GQD@VMSF/ITO (Figure 4 A, B) and NH_2 -GQD@VMSF/ITO (Figure 4 C) electrodes produce significantly enhanced signals compared to VMSF/ITO electrode, indicating significant signal amplification by GQDs owing to their electrostatic attraction and interaction with metal ions, high specific surface area and efficient electron transfer.

Too low a pH value weakens the interaction between GQDs and metal ions whereas too high a pH value converts metal ions into hydroxide. pH values of 4.0, 5.0 and 6.0 are determined to be optimal for Hg^{2+} , Cu^{2+} and Cd^{2+} detection, respectively (Figure S5 in SI).

The stripping signal increases with deposition time until a plateau is reached when the active sites of GQDs are saturated by metal ions. The optimal electrodeposition durations (onset of signal saturation) of 60 s, 30 s and 90 s are determined for Hg^{2+} , Cu^{2+} and Cd^{2+} , respectively.

Figure 4 D-F show the stripping current signals obtained from OH-GQD@VMSF/ITO towards Hg^{2+} , Cu^{2+} and from NH_2 -GQD@VMSF/ITO towards Cd^{2+} at ultra-low concentrations. A good linear correlation is found between the stripping current and the trace concentration of these ions, specifically, 10 pM to 1.0 nM for Hg^{2+} , 10 pM to 1.0 nM for Cu^{2+} , 20.0 nM to 1.0 μM for Cd^{2+} . In addition, a higher concentration range, (1.0 nM-0.5 μM for Hg^{2+} ; 1.0 nM-1.5 μM for Cu^{2+} ; and 1.0 μM -20.0 μM for Cd^{2+}), linear response is also achieved albeit with lower sensitivity (Figure S6 in SI). The limits of detection (LOD) of Hg^{2+} , Cu^{2+} , and Cd^{2+} ions are determined as low as 9.8 pM, 8.3 pM and 4.3 nM ($S/N=3$). These are several orders lower than that from VMSF/ITO electrodes (LOD of 0.3 μM for Hg^{2+} , 32 nM for Cu^{2+} , and 140 nM for Cd^{2+}). Particularly note that the use of OH-GQDs reduces the LOD for Hg^{2+} detection by 5 orders. The signal amplification by OH-GQDs is greater than NH_2 -GQDs, likely due to the higher abundance of $-\text{OH}$ groups (24.6%) than $-\text{NH}_2$ groups (3.3%). Comparison between electrochemical detection of Hg^{2+} , Cu^{2+} and Cd^{2+} using differently modified electrodes is provided in Table S1 (SI). LOD for Hg^{2+} and Cu^{2+} detection by OH-GQD@VMSF/ITO is the lowest among all electrochemical detection methods to the best of our knowledge. LOD for Cd^{2+} detection by NH_2 -GQD@VMSF/ITO is also among the best. Conceivably, increasing the $-\text{NH}_2$ groups on GQDs using a different synthesis route shall further improve Cd^{2+} detection. The highly sensitive detection of our sensors is ascribed to both the high nanochannel density of VMSF (3.4×10^{12} pores/ cm^2) to ensure sufficient mass transport and the facilitating roles of GQDs (selective enrichment of analytes and mediation for charge transfer and transport).

Because the stripping potentials of Hg^{2+} and Cu^{2+} are different, these ions could be simultaneously detected using OH-GQD@VMSF/ITO electrode. To demonstrate, a solution containing 0.25 nM Hg^{2+} and 0.6 nM Cu^{2+} was analyzed at the optimal pH for Hg^{2+} detection (pH 4.0). As seen from Figure S7 (SI), the stripping potentials of both ions are well separated by our sensor and the estimated Hg^{2+} concentration based on the calibration curve obtained at pH 4.0 (Figure 4D) is 0.28 nM which is in a good agreement with the pre-defined concentration. We further demonstrate in Figure S8 (SI) that the detection of Hg^{2+} , Cu^{2+} and Cd^{2+} is not disturbed by the presence of some possible fouling or interfering species including diluted whole blood (100 times dilution), proteins (bovine serum albumin - BSA and hemoglobin - HB), and metal ions may co-exist in environmental or biological samples (Ca^{2+} , Mg^{2+} , Fe^{3+} , Co^{2+} and Cr^{3+}). This is ascribed to four reasons: i) size selectivity because of the narrow opening of the nanochannels; ii) charge selectivity because of negatively charged GQDs and Si-OH groups on the nanochannel surface; iii) specific interaction between analytes and GQDs; and iv) detection recognition based on characteristic peak potential.⁵⁶⁻⁵⁸ Hence, our sensors shall be able to analyze practical complex samples without complicated pretreatment processes.

As Hg^{2+} contamination in seafood is a serious concern, we apply OH-GQD@VMSF/ITO sensor to examine seafood samples. It is worthy pointing out that the detection limit of our sensor (9.8 pM) is much lower than the tolerance level of Hg^{2+} in seafoods (*e.g.*, 139 pM for clams, United States Environmental Protection Agency-USEPA). To evaluate the reliability of our method, inductively coupled plasma-mass spectrometry (ICP-MS) with high sensitivity and low detection limit is used as the golden standard for comparison. As shown in Table 1, the determined Hg^{2+} concentrations by our sensor agree well with those obtained from ICP-MS. Cu^{2+} in human serum sample (11-17 μM in normal human serum) was also determined by OH-GQD@VMSF/ITO sensor. The obtained result ($13.00 \pm 0.33 \mu\text{M}$, $n=3$) is

in accordance with ICP-MS measurement ($12.77 \pm 0.38 \mu\text{M}$, $n=3$). Soil leaching solution (SLS) samples with artificially spiking in a defined amount of Cd^{2+} ions were examined by $\text{NH}_2\text{-GQD@VMSF/ITO}$ sensor whose LOD (4.3 nM) is lower than the tolerance level in soil (22 nM in SLS, Ministry of Environmental Protection of China). Cd^{2+} is not detectable in the original SLS sample. As shown in Table 2, the recovery (agreement between measurements and the pre-set concentrations) of our sensor is satisfactory (between 90.4% to 105.0%). ICP-MS equipment is bulky and expensive, and requires skills and high operating costs. In contrast, our electrochemical sensor is fast (10 min for each analysis), simple, convenient and of low-cost.

As GQDs can intimately interact with various small organic molecules through π - π or electrostatic interaction, we also speculate the potential of OH-GQD@VMSF sensor for detection of electroactive organic molecules. We here choose dopamine (DA), which is a critical neurotransmitter and hormone, as the example for proof-of-concept demonstration. Typically, organic molecules have high oxidation potential on ITO electrode. Therefore we here use Au electrode instead because of its lower overpotential. VMSF is grown on the surface of Au electrode *via* electrochemically assisted self-assembly (EASA) method.^{47,48} As shown in Figure S9 (SI), regular nanochannels (2.3 nm in diameter) are obtained. The pore density is calculated as 9.5×10^{12} pores/ cm^2 , corresponding to a porosity of 39%. Similarly, OH-GQDs are introduced and confined in the nanochannels of VMSF/Au *via* electrophoresis. In comparison with VMSF/Au, improved electrochemical (CV and DPV) signals are observed on OH-GQD@VMSF/Au (Figure 5A and B). The signal amplification is owing to the good charge transfer ability of OH-GQDs and their ability to enrich positively charged dopamine ($\text{pK}_a = 8.9$) through π - π interaction and electrostatic adsorption (Figure. 1). As shown in Figure 5C, the DPV signals resulted from the electrochemical oxidation of dopamine (at 0.16 V) are dose dependent. Good linear correlation is found from 200 nM to 20 μM (sensitivity of

51.2 $\mu\text{A/nM}$) and from 20 to 100 μM (sensitivity of 15.1 $\mu\text{A/nM}$) with a limit of detection of 120 nM ($S/N=3$). As seen, the sensitivity decreases at high concentration range. Such phenomenon is commonly observed in many sensors attributable to decreased active binding sites and mass transfer. The detection of dopamine is not disturbed by the presence of some possible interfering species including amino acids, common ions, protein (concanavalin A-CA) and electroactive molecules including ascorbic acid (AA) and uric acid (UA) even when their concentration is 50 times higher than that of DA (Figure 5D). As AA and UA are usually coexist with dopamine in biological matrixes and have similar oxidation potential as dopamine, the interference from them is usually a serious problem.⁵⁹⁻⁶¹ Our sensor is immune to this problem because of its high non-selectivity toward negatively charged molecules (pK_a of AA = 4.19; pK_a of UA = 5.75).

CONCLUSIONS

In summary, we have developed an electrochemical sensing platform based on nanochannel-confined graphene quantum dots. The nanochannels of vertically-ordered mesoporous silica-nanochannel film (VMSF) decorated on the electrode act as the nano-reactors and selectivity filters to exclude interfering compounds through steric restriction and electrostatic repulsion. The opening of our nanochannels is ~ 2.3 or 2.6 nm which can just snugly accommodate small-sized GQDs (here, < 2 nm). But to meet the requirements for different application purposes, the diameter of nanochannels can be enlarged up to ~ 12 nm *via* biphasic stratification growth approach¹⁰ to accept larger GQDs or macromolecules (*e.g.*, proteins) or macromolecule-functionalized GQDs. The GQDs confined in the nanochannels serve multiple roles to boost the signal, including selectivity enhancer *via* electrostatic repulsion and enrichment, recognition element *via* specific interaction with the analytes, and mediator for charge transfer and transport. GQDs carrying functionalities other than $-\text{OH}$ and $-\text{NH}_2$ could be used to detect other metal ions. GQDs functionalized with

molecular or chemical receptors may be used for specific detection of other biomarkers. In other words, the platform demonstrated here may be extended for detecting a variety of analytes in complex environmental, food, or biological samples. And it is amenable to be miniaturized for portable on-site analysis.

METHODS

Synthesis of OH-GQDs and NH₂-GQDs. As previously reported,³⁹ OH-functionalized GQDs (OH-GQDs) and NH₂-functionalized GQDs (NH₂-GQDs) were synthesized using 1,3,6-trinitropyrene as precursor. OH-GQDs were hydrothermally obtained in NaOH solution (0.125 M) for 2 h at 200 °C. The resulting reddish brown solution containing no solid precipitation was further dialyzed in a dialysis bag (with cut-off molecular weight of 500 Da) for 2 days to remove unreacted small molecules and sodium salt. After being filtered through a 0.22 μm microporous membrane, GQD solution was freeze-dried. The synthetic procedure of NH₂-GQDs was similar except that the mixture of 0.4 M ammonia and 1.5 M hydrazine hydrate was used as the hydrothermal medium.

Synthesis of GQD@VMSF modified electrode. Indium tin oxide (ITO, resistance: <14.5 Ω/square) or Au electrode were used as the supporting electrodes for fabrication of GQD@VMSF electrochemical sensors. VMSF was grown on ITO electrode using Stöber solution-growth approach as previously reported.⁴⁶ Briefly, TEOS (3.50 mM, 99%, Sigma-Aldrich) was hydrolyzed and assembled in presence of CTAB surfactant micelles (SM; 4.39 mM, 99% from Aladdin) in ammonia-ethanol medium on clean ITO surface, followed by 12 h aging at 100 °C. VMSF was deposited on Au electrode using electrochemically assisted self-assembly (EASA) as described by Walcarius *et al.*^{47,48} Specifically, SM@VMSF/Au electrode was obtained by applying a constant current of 80 μA for 5 s in pre-reacted precursor solution (pH 3) consisting of TEOS (0.34 M), CTAB (0.11 M), and NaNO₃ (0.1 M)

in ethanol (40 ml), followed by 12 h aging at 130 °C. After removal of SM by solvent extraction with 0.1 M HCl in ethanol, VMSF/ITO or VMSF/Au electrodes were obtained. GQDs were confined in the nanochannels of VMSF by electrophoresis. Specifically, a positive potential (+0.8 V for OH-GQDs and +0.4 V for NH₂-GQDs) was applied on VMSF/ITO or VMSF/Au for 1 h in GQD solution (0.3 µg/ml).

Characterizations. Transmission electron microscopy (TEM) image of VMSF was obtained from HT7700 (Hitachi, Japan) at operating voltage of 100 kV. TEM, atomic force microscopy (AFM) images, X-ray photoelectron spectroscopy (XPS) and Fluorescence spectra of GQDs were obtained from JEM-2100 (JEOL, Japan) at operating voltage of 200 kV, Bruker Multimode 8 (Bruker, USA) at tapping mode, PHI5300 electron spectrometer with 250 W, 14 kV, Mg K α radiation (PE, USA), and RF-5301PC spectrofluorometer (Shimadzu, Japan), respectively. Absolute photoluminescence quantum yields were measured using FL 3C-11 spectrofluorometer (Hariba Scientific, USA). Scanning electron microscopy (SEM) was conducted on a field-emission scanning electron microscopy (S-4800, Hitachi, Japan) operated at 3 kV. Zeta potential was recorded on Surpass zeta potential system (Anton parr, Austria). The cross-section photographs of GQD@VMSF/ITO while being excited by laser (473 nm for OH-GQD; 405 nm for NH₂-GQD) were taken by a CCD camera mounted on an inverted microscope. Electrochemical measurements were carried out on an Autolab PGSTAT302N electrochemical workstation (Metrohm, Switzerland). A three-electrode system was adopted with modified ITO or Au as working electrode, Ag/AgCl (saturated KCl solution) electrode as reference electrode and Pt-sheet electrode (1 cm $\times$ 1 cm) as counter electrode. Inductively coupled plasma-mass spectrometry (ICP-MS; NexioN 300D, PE, USA) was employed as the current golden standard for heavy metal ion detection.

Detection of Hg^{2+} , Cu^{2+} and Cd^{2+} and dopamine. The standard solutions of Hg^{2+} , Cu^{2+} and Cd^{2+} (1 mM) were purchased from National Standard Materials Center (China). After electrochemical deposition of metal ions (60 s for Cu^{2+} , 30 s for Hg^{2+} and 90 s for Cd^{2+}) in the sample solution (-0.4 V for Cu^{2+} , -0.4 V for Hg^{2+} and -0.95 V for Cd^{2+}), the anodic stripping current of the deposited metal was obtained in the detection buffer using differential pulse voltammetry (DPV). NaAc-HAc (0.1 M; pH 4.0 for Hg^{2+} ; pH 5.0 for Cu^{2+}) or phosphate buffer solution (PBS; 0.1 M, pH 6.0 for Cd^{2+}) was used as the detection buffer. Detection of dopamine was performed in PBS (0.01 M, pH 6.0). Simultaneous detection of Hg^{2+} and Cu^{2+} was performed in NaAc-HAc buffer solution (0.1 M; pH 4.0) and the electrochemical deposition time was 30 s.

Human serum was provided by the affiliated hospital of Zhejiang University (China). For detection of Cu^{2+} in serum, protein-bound Cu^{2+} ions were firstly released by mixing serum (1 mL) with diluted nitric acid (high-purity, 0.7 M, 4 mL) and stirring for 1 min. After pH was adjusted to 5.0 using NaOH (2 M), the obtained mixture was diluted by a factor of 10 using the detection buffer solution. Digested solutions of Hg^{2+} -contaminated seafoods (digested according to GB 5009.17-2014, China) were provided by Center for Disease Control (Hangzhou, China). Before electrochemical detection, the samples were diluted by a factor of 50 using the detection buffer. Soil leaching solution (SLS) was obtained by leaching soil (from an uncontaminated orchard in Chunan Zone, Hangzhou, China) in 100 mL ultrapure water. A defined amount of Cd^{2+} was added into SLS before electrochemical detection.

ASSOCIATED CONTENT

Supporting Information. Nine supplementary figures and one Table. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

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FIGURES

Figure 1. Schematic illustration for the preparation of GQD@VMSF modified electrode through electrophoresis and detection of metal ions (Cu²⁺, Hg²⁺, Cd²⁺) and dopamine from complex samples.

Figure 2. (A) TEM images of OH-GQDs. Insets present high-resolution TEM (HRTEM) image with resolved crystalline lattice (left) and size distribution of 129 OH-GQDs (right). (B) AFM image of OH-GQDs. Inset is the height profile along the indicated red line. (C) Fluorescence (FL) excitation (EX, obtained at the emission wavelength of 520 nm) and emission (EM) spectra of OH-GQDs. Inset presents the photographs of OH-GQD solution under visible (left) or 365 nm UV (right) light. (D) Emission spectrum of OH-GQDs in the absence or presence of Cu²⁺ (0.5 mM) and Hg²⁺ (0.5 mM). (E) EX (obtained at the emission wavelength of 464 nm) and EM spectra of NH₂-GQDs. Inset presents the photographs of

NH₂-GQD solution under visible (left) or 365 nm UV (right) light. (F) EM spectrum of NH₂-GQD solution in the absence or presence of Cd²⁺ (0.5 mM).

Figure 3. (A) Top-view TEM image of VMSF. Insets are the zoom-out image of TEM image (top) and SEM image of VMSF/ITO cross-section (bottom). (B) TEM image of the cross-section of VMSF. (C) TEM image of the cross-section of OH-GQD@VMSF. (D) HRTEM image of the indicated area in (C) with crystalline GQDs highlighted by the circles. (E) Illustration of laser excitation on GQDs confined in the nanochannels of VMSF and (F) the corresponding fluorescence images.

Figure 4. (A-C) DPV curves obtained from VMSF/ITO, OH-GQD@VMSF/ITO and NH₂-GQD@VMSF/ITO electrodes for Hg²⁺ (0.5 μ M), Cu²⁺ (1 μ M) and Cd²⁺ (1 μ M), respectively. (D-E) DPV curves obtained from OH-GQD@VMSF/ITO in response to different concentrations of Hg²⁺ or Cu²⁺. (F) DPV curves obtained from NH₂-GQD@VMSF/ITO in response to different concentrations of Cd²⁺. The insets in D-F show the linear dose response curves in the ultralow concentration range.

Figure 5. (A) CV and (B) DPV curves obtained from VMSF/Au and OH-GQD@VMSF/Au electrodes in dopamine (DA) solution (20 μM in 0.01 M PBS, pH 6.0). (C) DPV curves obtained from OH-GQD@VMSF/Au electrode in response to different concentrations of dopamine. Insets depict the dose response curve (top) and the enlarged view of the DPV curves in the low-concentration region. (D) The relative signal changes (I/I_0) obtained from OH-GQD@VMSF/Au electrode towards DA (20 μM) in the absence (I_0) or presence (I) of different substances (1 mM).

TABLES

Table 1 Determination of Hg^{2+} in Hg^{2+} -contaminated seafood samples.

Sample ^{a)}	Concentration (nM) ^{b)}	
	ICP-MS	OH-GQD@VMSF/ITO
Blood clam	4.99±0.15	4.93±0.21
Macoma clam	15.95±0.64	15.41±0.37
Ruditapes philippinarum	7.98±0.36	7.73±0.26
Loach	6.93±0.35	6.36±0.27
Spiral	3.69±0.15	3.62±0.16

^{a)}The sample was digested solution of each seafood. Digestion was performed according to GB 5009.17-2014 of China.

^{b)}Average of three determinations.

Table 2 Determination of artificially added Cd^{2+} in soil leaching solution (SLS).

Sample	Added (μM)	Determined (μM) ^{a)}	Recovery (%) ^{b)}
	0.020	0.021±0.001	105.0
SLS	0.500	0.452±0.005	90.4
	5.00	5.14±0.16	102.8

^{a)}Average of three determinations.

^{b)} Cd^{2+} in the original SLS is not detected. Recovery=determined concentration/added value×100%.

Table of Contents

An electrochemical sensing platform based on nanochannel-confined graphene quantum dots (GQDs) is designed for ultrasensitive and fast detection of Hg^{2+} , Cu^{2+} , Cd^{2+} and dopamine in complex samples.