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Electrochemiluminescent graphene quantum dots enhanced by MoS_2 as sensing platform: a novel molecularly imprinted electrochemiluminescence sensor for 2-methyl-4-chlorophenoxyacetic acid assay

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ABSTRACT

The ECL properties and application of a novel luminescent material molybdenum disulfide-graphene quantum dots (MoS_2-GQDs) hybrid nanocomposite was reported for the first time. The hybridization of MoS_2 and GQDs endowed nanocomposite with structural and compositional advantages for boosting the ECL performance of GQDs. Impressively, the ECL could be remarkable enhanced using MoS_2-GQDs hybrid nanocomposite, which was ~13, ~185 and ~596-folds larger than the ECL intensity of GQDs, MoS_2 modified electrodes and bare electrode, respectively. Subsequently, as a sensing platform, the MoS_2-GQDs hybrid nanocomposite was applied to fabricate molecularly imprinted electrochemiluminescence sensor for the ultrasensitive and selective determination of 2-methyl-4-chlorophenoxyacetic acid. Under optimal conditions, the detection limit of the prepared sensor was 5.5 pmol L^{-1} (S/N = 3) within a linear concentration range of 10 pmol L^{-1}–0.1 μmol L^{-1}. The developped sensor exhibited high sensitivity, good selectivity, reproducibility and stability, suggesting the potential for detecting pesticides and veterinary drugs at trace levels in food safety and environmental control.

1. Introduction

Molecularly imprinted polymers (MIPs) are synthetic polymers with recognition sites which are spatially and chemically complementary to the template [1–4]. Molecularly imprinted electrochemiluminescence (ECL) sensor (MIECLS) combined the numerous advantages of both ECL analysis and MIPs, demonstrating high sensitivity and selectivity, good controllability, rapidity, simplified optical set-up, low background noise, ease of preparation, reusability and low cost [5]. Since the first MIECLS was reported in 2012 [6], MIECLS have received considerable attentions in analytical fields. Along with the developments of MIECLS, a variety of ECL-emitting species, including ruthenium compounds [7,8], luminol [6,9–11], and nanomaterials [12–14] have been extensively reported. Despite the outstanding developments of MIECLS were achieved, to meet the requirements of rapid expansion, intense research still focused on exploiting the innovative, nontoxic, stable and highly efficient ECL luminescent materials.

Graphene quantum dots (GQDs), carbon fragments derived from graphene with diameters less than 100 nm, are considered as quasi-zero-dimensional material with novel physical and chemical properties [15]. Compared with traditional ECL luminescent materials (ruthenium compounds and luminol) and semiconductor quantum dots, GQDs possesses low toxicity, better biocompatibility, large specific surface area, flexible chemical modification and resistance to photobleaching, making it as highly promising luminescent nanomaterial in establishing ECL sensors [16–18]. Interestingly, it has been reported that GQDs hybridized with other

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nanomaterials exhibit fascinating properties and unexpected characteristics [19–23].

Being a nontoxic, environment-friendly two-dimensional (2D) transition metal disulfides, molybdenum disulfide (MoS_2) have been the focus of fundamental research and technological applications because of their specific 2D layered feature, electronic properties and unique physical and chemical properties [24,25]. Furthermore, the integration of other nanomaterials with this layered material to form hybrid nanocomposite system would be anticipated to obtain superior properties [26–28].

It should be noted that, the GQDs/MoS_2 heterostructure was first investigated about its unique electronic and optical properties in 2015 [29]. And the MoS_2-GQDs hybridization for the use of photodetectors [30], electrochemical biosensor [31] and lithium storage performance [32] were reported very recently. Though the excellent elctronic and optical properties of MoS_2-GQDs hybrid nanocomposite were investigated very recently, its ECL properties owing promising perspect were not fully investigated yet.

Herein, for the first time, a novel ECL luminescent material MoS_2-GQDs hybrid nanocomposite was obtained, which features remarkable enhanced ECL. MoS_2 nanosheets were used as carrier for GQDs with structural and compositional advantages for boosting the ECL performance of GQDs. ECL performance and possible ECL mechanism were investigated and discussed. The MoS_2-GQDs hybrid nanocomposite was subsequently integrated within a MIECLS for the ultrasensitive and selective determination of 2-methyl-4-chlorophenoxyacetic acid (MCPA), which is widely used to control broadleaf weeds in various crop fields. With the increasing usage, residence time of MCPA in the environment and crops become longer, which make it potentially hazardous to human health. The maximum residue limit (MRL) of MCPA in grain and fruits are 0.05 mg/kg and 0.1 mg/kg, respectively in the national food safety standard of China. In 2005, Majzik. et al. tested 55 surface and 110 ground water samples using the established SPE-LC-MS-MS method with a limit of quantitation (LOQ) of 0.01 $\mu g\,L^{-1}$. Detectable phenoxy acid compounds were found in 37 samples and the concentration ranged from 0.01 to 0.35 $\mu g\,L^{-1}$ [33].

2. Experimental

2.1. Instruments and Reagents

All the electrochemical experiments were carried out using an electrochemiluminescence analyzer LK5100 (Tianjin Lanlike Chemical and Electronic High Technology Co., Ltd., China). A conventional three-electrode system was employed, consisting of a bare or modified glassy carbon electrode (GCE, 4 mm diameter) as the working electrode, a saturated calomel electrode (SCE) as the reference electrode and a platinum column electrode as the auxiliary electrode. Transmission electron microscope (TEM, JEM-2010FEF, JEOL, Japan) was employed to observe morphology of the nanoparticles. Fluorescence measurements were performed on a Lumina fluorescence spectrometer (Thermo, USA). ECL detection: the ECL sensors with different concentrations of MCPA were tested in PBS (0.01 $mol\,L^{-1}$, 5 mL, pH = 7.4) containing $K_2S_2O_8$ (100 mmol L^{-1}), scanning from 0 V to −1.4 V with a scan rate of 100 $mV\,s^{-1}$, the voltage of photomultiplier was set at 800 V.

Oxidized graphene quantum dots (GQDs) and MoS_2 nanosheets were purchased from XFNANO Materials Tech Co., Ltd. (Nanjing, China). 2-methyl-4-chlorophenoxyacetic acid (MCPA, 98%) and its structural analogs 2,4-dichlorophenoxyacetic acid (99%), 4-chlorophenoxyacetic acid (99%), phenoxyacetic acid (98%), 2,4-dichlorobenzaldehyde (98%), 2,4-dichlorophenol (99%) and o-phenylenediamine (oPD) (99.5%) were obtained from J&K Scientific Ltd. (Beijing, China). $K_2S_2O_8$ were purchased from Sigma-Aldrich (St. Louis, USA). N,N-dimethylformamide (DMF) were obtained from Alfa Aesar (Tianjin, China). All chemicals were at least analytical grade. Milli-Q purified water was used for all experiments.

2.2. Modification of the electrodes

Prior to modification, bare GCE was polished with 0.3 and 0.05 μm alumina slurry successively followed by rinsing thoroughly with doubly distilled water (DDW) between each polishing step until a mirror-like surface was obtained. The GCE was scanned by cyclic voltammetry (CV) from −0.2 to 0.6 V in aqueous solution consisting of 1 $mmol\,L^{-1}$ $K_3[Fe(CN)_6]$ and 0.1 $mol\,L^{-1}$ KCl until standard cyclic voltammograms of $K_3[Fe(CN)_6]$ appeared. The electrodes were washed with DDW and dried in air before use.

A layer of MoS_2-GQDs hybrid nanocomposite modified GCE (MoS_2-GQDs/GCE) was obtained as follows: MoS_2 (6 mg), GQDs (4 mg) and DMF/H_2O solution (1:1, *v*:*v*, 10 mL) were mixed in a glass bottle with the help of ultrasonic treatment for 3 h to form a homogeneous suspension. Then, the GCE was coated with 10 μL of the resulting MoS_2-GQDs suspension solution and allowed to dry at room temperature. As control, MoS_2 suspension (0.6 $mg\,mL^{-1}$) and GQDs suspension (0.4 $mg\,mL^{-1}$) were prepared to construct MoS_2/GCE and GQDs/GCE respectively.

Simple superposition of MoS_2 and GQDs modified electrodes were obtained as follows: 10.0 μL of 0.4 $mg\,mL^{-1}$ GQDs was coated on the GCE surface firstly. After the GQDs suspension was dried, 10.0 μL of 0.6 $mg\,mL^{-1}$ MoS_2 was coated and allowed to dry at room temperature (MoS_2/GQDs/GCE). GQDs/MoS_2/GCE was modified using the same procedure but changing the modification order of 0.4 $mg\,mL^{-1}$ GQDs and 0.6 $mg\,mL^{-1}$ MoS_2.

The MIPs modified MoS_2-GQDs/GCE was electrochemically synthesized by repetitive CV scans in a deoxygenated acetate buffer solution (pH 5.2) containing 5 $mmol\,L^{-1}$ oPD and 5 $mmol\,L^{-1}$ MCPA at a scan rate of 50 $mV\,s^{-1}$ from 0 to 0.8 V for 5 cycles. Extraction of the template was performed by shaking the electrodes in a methanol/acetic acid (5:1, *v*/*v*) solution for 10 min with magnetically stirring. Similarly, the non-imprinted polymers (NIPs) modified MoS_2-GQDs/GCE was also fabricated under the same conditions in the absence of MCPA.

2.3. Sample preparation

Different sample matrices, enviromental samples including tap water (Tianjin, China), lake water (Tianjin University of Science and Technology) and food sample oat, were sampled nearby or purchased from a local market, and spiking and recovery studies were used to evaluate the application capability of the developed MIECLS. The water samples were filtered with 0.45 μm nylon filter and the food samples were turned into powder using grinder before the extraction process. Each sample (5.00 ± 0.01 mL, 5.00 ± 0.01 g,) was packed into a 100 mL polypropylene centrifuge tube, and spiked with MCPA at three levels: 5.0×10^{-4}, 10.0×10^{-4} and 50.0×10^{-4} $mg\,L^{-1}$ or mg kg^{-1}. After overnight of rest in the dark, ethyl acetate (20.0 mL) with NaCl (1.25 g) was added and the mixture was vortex mixed for 5 min. For liquid samples, the supernatant were transferred into another 100 mL polypropylene centrifuge tube. For solid sample, the supernatant was transferred into another 100 mL polypropylene centrifuge tube after centrifugation at 7,000 rpm for 10 min. The above process was then repeated, and the supernatants were combined. Then the supernatant was dried under nitrogen at 40 °C. Finally, the residue was dissolved with phosphate buffer solution (PBS, 0.01 $mol\,L^{-1}$, pH = 7.4, 5.0 mL) containing 100 $mmol\,L^{-1}$ $K_2S_2O_8$ for the ECL analysis.