Fabricated Electrochemical Sensory Platform Based on the Boron Nitride Ternary Nanocomposite Film Electrode for Paraquat Detection

Jiangyi Zhang, Zhenfeng Lin, Yuan Qin, Yangzi Li, Xin Liu, Qi Li,* and Huayu Huang*®

Shaanxi Key Laboratory of Earth Surface System and Environmental Carrying Capacity, College of Urban and Environmental Science, Northwest University, Xi’an 710127, China

Supporting Information

ABSTRACT: Hexagonal boron nitride (BN), an effective diffusion material for mass transport, was functionalized with molybdenum disulphide (MoS₂) and Au nanoparticles (Au NPs). Then, the working electrodes with developed nanomaterials were applied to construct an electrochemical paraquat sensor. BN was prepared using a solid-state synthesis method combined with solvent-cutting. The electrochemical properties of the BN/MoS₂/Au NP-based glassy carbon electrode (GCE) were investigated using differential pulse voltammetry and cyclic voltammetry. An excellent response signal to paraquat was found from 0.1 to 100 μM with a limit of detection of 0.074 μM, and it had acceptable reproducibility (relative standard deviation = 2.99%, n = 5) and good anti-interference ability. The modified GCE showed superior performance owing to the synergistic effects among all three given nanomaterials. With the proposed method, paraquat in grass samples from an orchard was then investigated. The results of the electrochemical analysis agreed with those of experiments and obtained a 96.28% confidence level via high-performance liquid chromatography, exhibiting relatively high stability. Therefore, the fabricated sensor can be a candidate for the determination of paraquat.

1. INTRODUCTION

With the need to increase food production, pesticides and herbicides have been widely used in agriculture practices. The past few decades have witnessed the issue of herbicide paraquat. Paraquat dichloride is an active composition of one of the dipyridyl compounds. With its nonselectivity and high toxicity, paraquat is usually used against weeds, which has been a threat to our environment, especially in developed countries. Therefore, monitoring paraquat residues in the environment is of great importance. Up until now, several analytical approaches of paraquat determination have been developed, including chromatography/mass spectrometry, colorimetric assay, and surface-enhanced Raman spectroscopy. Nevertheless, these techniques require time-consuming sample pretreatment and are mainly laboratory-based for bulky instruments except for the electrochemical method. In contrast, electrochemical alternatives without any complicated sample pretreatment are easier to operate, have higher sensitivity, and are less expensive for a sensory platform. Nasir developed an electrochemical detection method for paraquat using mesoporous silica thin film modified GCEs. Ye prepared polyvinyl pyrrolidone functionalized graphene and cuprous oxide to fabricate the paraquat electrochemical sensor. Li used polypyrrole-grafted nitrogen-doped graphene to modify the glassy carbon electrode (GCE) to detect paraquat. Thus, electrodes modified with mesoporous and nanostructured materials emerged and have been applied in the field of electroanalysis.

Two-dimensional (2D) nanomaterials have gained an increasing interest in nanoscience and nanotechnology. Boron nitride (BN) nanosheets, with layers of sp² bonded, have become an excellent candidate in optoelectronic materials and sensors owing to the particular optical and electronic properties. The preparation of highly thermally conductive, mechanically stable and thicker BN and its electrochemical application have attracted lots of researchers’ attention. Molybdenum disulphide (MoS₂) consists of layered sheet morphology with S=Mo=S covalent bonding and is stacked vertically with interplanar van der Waals interactions. Owing to...
well-known semiconducting properties, MoS₂ has been applied as one of the modified GCE materials in amperometric- and impedance-based sensors for different analytes.²² With BN and MoS₂ deposited on GCE, the enhanced mobility and carrier conductivity could allow efficient energy transfer. Because of the special properties of 2D materials, these composite materials have been successfully developed and studied in many fields.

In comparison with individual 2D materials, electrical and thermal conductive interfaces and mechanical reinforcement can be improved by the doping 2D materials.²³ In addition, controlling their intrinsic electronic properties is another strategy to optimize the sensing properties of semiconductors.²⁴ Therefore, numerous doping approaches such as defect engineering, molecule physisorption, and chemical doping methods have aimed at changing the materials' charge concentrations.²⁴,²⁵ In particular, with metal nanoparticles (NPs), surface adatoms can be an effective way for the combination of 2D material.²⁵,²⁶

Inspired by the foregoing research, scalable BN was developed by a solid-state reaction combined with the solvent-cutting method. MoS₂ was created by liquid phase exfoliation, offering large surface areas. Au NPs can be easily made, usually as a support for target sensors, and thus, they enhance adsorbance.²⁷ The BN/MoS₂/Au NP nanocomposites were designed to achieve preferable sensing performances. Herein, the self-assembled structures were characterized and discussed. Furthermore, the paraquat electrochemical behavior on the sensor was investigated by voltammetry. Paraquat in grass samples can be detected according to the selected electrochemical measurement.

2. RESULTS AND DISCUSSION

2.1. Characterization of the BN/MoS₂/Au NPs. The crystal structures of BN and MoS₂ were researched using X-ray diffraction (XRD) (Bruker, Germany) to characterize. From Figure 1A (blue), three sharp diffraction peaks (26.4°, 41.8°, and 54.5°) representing the (002), (100), and (004) lattice planes can be observed, indicating the well-crystallized BN colloidal nanocrystals. Figure 1A (red) displays 12 distinct peaks at 14.4°, 29.1°, 32.7°, 33.5°, 35.9°, 39.6°, 44.3°, 49.9°, 56.1°, 58.4°, 50.3°, and 62.9°, respectively, confirming MoS₂ synthesized, as in the literature.²⁸–³⁰ The Raman spectra of BN (blue), MoS₂ (red), and BN/MoS₂/Au NPs (black) have been shown in Figure 1B. It is clear that the characteristic band of BN at 1390 cm⁻¹ corresponds to the E²g phonon mode. Besides one prominent peak of BN, the Raman spectra of the BN/MoS₂/Au NP composites have the other two main peaks at 464 and 570 cm⁻¹, which belong to the in-plane E¹g modes and out-of-plane A₁g modes of MoS₂. The result also confirms that BN and MoS₂ exist in the composites.

To investigate the morphology of BN and MoS₂, scanning electron microscopy (SEM) (ZEISS, Germany) and transmission electron microscopy (TEM) (FEI, Netherlands) analyses were applied. Figure 2 displays the SEM images of BN and MoS₂. TEM mappings of BN, MoS₂, Au NPs, and the hybrid composite were displayed in Figure 3. Figure 2A clearly illustrates the feature of BN with an obvious gap and some voids visualized using SEM. The TEM image of BN (Figure 3A) displays clear lattice fringes, indicating a high degree of crystallinity. The TEM image of MoS₂ (Figure 3B) shows the assembled composite monolayers. Figure 3C shows the assembled composite monolayers.
monolayers with high surface coverage. The growth on top of each other between 2D BN and 2D MoS$_2$ is the result of the van der Waals heterostructures. Thus, MoS$_2$ is decoupled in the lateral locations of the BN monolayer. Furthermore, Au NPs of the hybrids were decorated on the edges of the BN and MoS$_2$, which improves the electronic conductivity of MoS$_2$ and prevents MoS$_2$ aggregation.

2.2. Electrochemical Behaviors of Paraquat. The electrochemical performance of paraquat was investigated with differential-pulse voltammetry (DPV) after the decoration of the BN/MoS$_2$/Au NP GCE (Figure 4). With different GCEs, there are strongly different signal reactions on their charge. The peak current at a bare GCE was lower than the current at other modified GCEs, while the highest currents of peak 1 (P1) and peak 2 (P2) at the BN/MoS$_2$/Au NP electrode were up to 10.9 and 5.1 $\mu$A, respectively. The signal according to the Randles-Sevck relationship can be described as eq 1

$$i_p = 2.69 \times 10^5 n^{3/2} A^{1/2} C_0^{1/2}$$

where $i_p$ is the forward peak current, $n$ is number of electrons exchanged per molecule, $A$ is the electrode active area ($m^2$) ($A = 0.07 \text{ cm}^2$), $D$ is diffusion coefficient ($m^2 \text{ s}^{-1}$), and $C_0$ is the concentration of paraquat (mol L$^{-1}$). Therefore, it is clear that the improved properties of the BN/MoS$_2$/Au NP GCE were considerably contributed to the increasing active area (1.8 cm$^2$). Additionally, peak potentials, which can be seen, are approximately $-0.55$ and $-0.90$ V (Figure 4). The other GCEs’ active areas (BN/GCE, MoS$_2$/GCE, and Au/GCE) are 0.61, 0.31, and 0.27 cm$^2$, respectively. The two peak potentials are attributed to the two successive one-electron transfers. The redox mechanism of paraquat is obviously well-described as given below:

2.3. Cyclic Voltammetric Characterization. To further understand the dynamic performance of paraquat on the BN/MoS$_2$/Au NP composites, cyclic voltammetry (CV) curves of the proposed electrochemical sensor in PB (0.1 M, pH = 8.5) containing paraquat (50 $\mu$M) were recorded at scan rates ranging from 10 to 300 mV s$^{-1}$, as shown in Figure 5A. Figure 5B shows that the redox peak current varied linearly with the increasing of square root of the scan rate ($\sqrt{v}$), suggesting a diffusion-controlled kinetic process on the BN/MoS$_2$/Au NP-based electrode in accordance with other ref 14. The linear regression equations are $I_{p1} = 0.4077\sqrt{v} + 0.2026$ and $I_{p2} = -0.492\sqrt{v} - 0.4002$ with $R^2 = 0.9934$ and 0.9902, respectively.

2.4. Optimization of the Paraquat Signal on the Modified Electrode. To obtain the optimum conditions for paraquat analysis, main factors including the pH value of PB, the volume of the BN/MoS$_2$/Au NP suspension, and accumulation time were found. Figure 6A shows the paraquat responses detected by DPV in PB solution (0.1 M) at a series of pH values. In addition, the P1 current at around $-0.58$ V is detected, and the potential of P1 is unrelated to pH, while the P2 current at approximately $-0.90$ V is detected only in an alkaline environment, and there is a weak shift in P2 in the same condition. These phenomena can be ascribed to proton participation in the redox reaction. In Figure 6B, the peak current grows as the pH value of PB changes from 4.5 to 8.5 and then decreases when the pH value varies from 8.5 to 9.7. Therefore, the paraquat signal is maximal in PB (pH = 8.5), which is similar to the previous research. Consequently, PB, when its pH value was adjusted to 8.5, was used in all subsequent work. Adsorption increases with decreasing acidity because the herbicide paraquat exists in its cationic form in water (pK_a = 11). At lower pH, the BN/MoS$_2$/Au NP GCE surface was saturated with hydronium ions (H$_3$O$^+$); thus, the high competition between these ions and positively charged paraquat decreased the adsorption of paraquat. When the pH value is up to 8.5, the peak current achieves maximum with the adsorption of paraquat being highest. Subsequently, the current response begins to fall down because of the maximum possible coverage of the electrode surface with paraquat.

The behavior on the GCE decorated with different volumes of the BN/MoS$_2$/Au NP suspension was also investigated to determine optimal values for further detection. As presented in Figure 7, the signals of P1 and P2 have nearly the same inclination. As the amount of the BN/MoS$_2$/Au NP composite increases from 2 to 5 $\mu$L, the peak currents also show an increase. The currents decline in the range of 5–8 $\mu$L. Hence, 5 $\mu$L was used as the optimum for subsequent measurements. This is
attributed to the thickness of the BN/MoS2/Au NP film covered successfully on the GCEs. As the volume of BN/MoS2/Au NPs decorated on the GCE increased, the adsorbed paraquat amount also increased. However, the film became too thick with more than 5 μL of BN/MoS2/Au NP suspension-modified GCEs, which blocked the electron transfer between the electrolyte and the electrode. Consequently, the appropriate amount of BN/MoS2/Au NPs is 5 μL. In this way, not only the electron transfer is fastest but also the surface area for the enhancement of paraquat is largest. The sensitivity is thus also improved.

The effects of accumulation time on the DPV response for paraquat under the accumulation potential of −1.4 V can be seen in Figure 8. For the solution containing 50 μM paraquat, the P1 and P2 currents apparently increase with concentration time until 120 s. The results confirm that adsorption equilibrium cannot be obtained instantly. Thus, considering the sensitivity of target analyte detection, 2 min is the best for the lower concentration of the paraquat.

2.5. Analytical Characterization of the BN/MoS2/Au NP-Modified Electrode. The analytical performances of paraquat on the GCE with 5 μL BN/MoS2/Au NP modifying were obtained in PB (0.1 M, pH = 8.5) for 2 min accumulation mentioned above, and it can be shown that the signal of peak currents varies with concentration (Figure 9). As seen in Figure

Figure 5. (A) CVs signals on BN/MoS2/Au NP-modified GCE with 50 μM paraquat in pH 8.5 PB at a scan rate ranging from 10 to 300 mV s⁻¹. (B) Relationship between peak currents and square root of the scan rate.

Figure 6. (A) Paraquat responses detected by DPV in PB solution (0.1 M) at a series of pH values. (B) Effect of pH on the current of paraquat determination (50 μM) in PB (0.1 M, pH = 8.5).

Figure 7. Effects of the BN/MoS2/Au NP coating solution volumes on the peak current of paraquat (50 μM) in PB (0.1 M, pH = 8.5).

Figure 8. Effects of the accumulation time on the peak current of paraquat determination (50 μM) with 5 μL BN/MoS2/Au NPs modifying GCE in PB (0.1 M, pH = 8.5).
9, peak currents at a potential around of ~0.5 V versus Ag/AgCl are used as the calibration data, the black line represents voltammogram for blank concentrations and a stripping response is then observed at concentrations between 0.1 and 100 μM. Fresh sample solutions were used for each individual concentration, and five measurements were made for each data point. Hence, the relative standard deviation (RSD) of P1 is 2.99%. There is a very linear behavior between I and C, which can be shown as the equation $I = -0.4332 + 0.0857C$ ($R^2 = 0.9941$). The limit of detection (LOD) was calculated according to the reported literature. The LOD ($3\sigma$) of P1 is $0.074 \times 10^{-6}$ mol L$^{-1}$. The figures of interest obtained using the BN/MoS$_2$/Au NP-modified electrode and other sensors in the reported figures of interest obtained using the BN/MoS$_2$/Au NP-modified electrode are shown in Figure 9. (A) DPV responses of paraquat in pH 8.5 at the BN/MoS$_2$/Au NP GCE with increasing concentration: 0, 0.1, 0.5, 1, 5, 10, 20, 25, 30, 35, 40, 45, 50, 60, 70, 80, 90, and 100 μM, respectively. (B) Dependence of the DPV peak current on increasing paraquat concentration.

2.6. Reproducibility, Stability, and Interferences. To evaluate the precision of the BN/MoS$_2$/Au NP GCE sensor, a series of repetitive analysis was conducted in PB with 10 μM paraquat using five different modified electrodes under the optimal electrochemical conditions (pH = 8.5, the volume of BN/MoS$_2$/Au NP suspension was 5 μL, and the accumulation time was 120 s). The average RSD of 5 time measurements of the paraquat was around 3% (P1), demonstrating superior repeatability. Furthermore, given the stability of the modified electrode, 10 modified electrodes were stored for a month at room temperature. The peak currents of P1 and P2 retained approximately 90 and 88%, respectively, of the original responses, suggesting a potential for continuous operation. Different analyses were examined considering their interference with the determination of paraquat. Inorganic ions including K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, Fe$^{3+}$, Cl$^-$, SO$_4^{2-}$, and PO$_4^{3-}$ had no influence on the detection of paraquat. Moreover, some organic substances added into the detection solution are listed in Table 2. The electrochemical alternative makes the paraquat recovery between 99.4 and 102.7%, indicating relatively excellent selectivity.

2.7. Real Sample Determination. The fabricated sensor’s analytical utility was estimated by determining paraquat in grass samples obtained from an orchard. The 200 μL sample was diluted in 2 mL PB solution. The same stored samples were detected five times in a parallel comparison to calculate the RSD. The voltammograms for the real sample analysis are presented in Figure S2. All of the real-life samples were also determined by HPLC. According to Table 3, the proposed method demonstrated good accuracy and reliability with a relative error of approximately 4%.

3. CONCLUSIONS

BN was prepared using a solvent-cutting method, and the size of BN required customization dependent on the reaction temperature. With MoS$_2$ decoupled in the lateral locations of the BN monolayer, the active area has been enhanced. With Au NPs, the electronic conductivity has been improved and MoS$_2$.

| electrode | technique | linear range (μM) | detection limit (μM) | references |
|-----------|-----------|-------------------|----------------------|------------|
| mesoporous silica thin films/GCE$^c$ | SWV | 0.01−0.05 | 0.012 | 1 |
| PVP-GN/micro-Cu$_2$/O/GC-RDE$^b$ | DPV | 1−200 | 0.26 | 12 |
| PPY-g-NGE/GCE$^c$ | DPV | 0.05−2 | 0.041 | 14 |
| Au NPs/DNA/GCE$^d$ | DPV | 5−1000 | 1.3 | 38 |
| BN/MoS$_2$/Au NPs/GCE | DPV | 0−100 | 0.074 | this work |

“Mesoporous silica thin film-modified glassy carbon electrode. $^b$Polyvinyl pyrrolidone-graphene/Cu$_2$-modified glassy carbon-rotating disk electrode. $^d$Polyipyrrrole-grafted nitrogen-doped graphene-modified glassy carbon electrode. $^c$Au NPs–DNA-modified gold electrode.

| interferent | interferent concentration (μM) | PQ recovery (%) |
|------------|--------------------------------|-----------------|
| uric acid  | 50                             | 101.2           |
| theophylline | 50                            | 102.5           |
| pyrazinamide | 50                            | 100.2           |
| nitrophenol | 50                            | 102.7           |
| aminophenol | 50                            | 99.5            |
| quercetin  | 50                             | 100.3           |
| metronidazole | 50                           | 99.4            |

| samples | proposed method (DPV)/μM | comparative method (HPLC)/μM | relative error/% |
|---------|--------------------------|------------------------------|------------------|
| sample 1 | 1.23 ± 0.14              | 1.10 ± 0.18                  | −1.56            |
| sample 2 | 1.72 ± 0.06              | 1.68 ± 0.23                  | 1.20             |
| sample 3 | 1.52 ± 0.13              | 1.50 ± 0.11                  | −3.72            |
aggregation has been prevented. The combination of BN, MoS₂, and Au NPs shows a large surface area and facilitates electron transfer, which is used to fabricate an efficient sensory platform for the determination of parquat, expanding the application of BN as an electrochemical sensor material. Therefore, the synergy existing between BN, MoS₂, and Au NPs may facilitate BN as an electrochemical sensor material. Therefore, the

for the determination of paraquat, expanding the application of electron transfer, which is used to fabricate an efficient sensory platform for the determination of parquat, expanding the application of BN as an electrochemical sensor material. Therefore, the synergy existing between BN, MoS₂, and Au NPs may facilitate BN as an electrochemical sensor material. Therefore, the

4. EXPERIMENTAL SECTION

4.1. Chemicals and Apparatus. The chemicals used are the following: some are Nafton-117 and paraquat (98%) (SIGMA-Aldrich, USA); others are boric acid (BA), melamine, cyclohexane, formaldehyde, N-methyl pyrrolidine (NMP), and ethchloroauric acid tetrahydrate (HAuCl₄·4H₂O) (Sino-pharm group, China). Phosphate butter (PB, 0.1 M) with pH values from 4.5 to 9.5 was prepared with Na₂HPO₄ and NaH₂PO₄. The other chemicals used were of analytical grade.

4.2. Preparation of BN. BN colloidal nanocrystals were synthesized following a reported article. Naturally, the mixture of BA and melamine (n₁/n₂ = 1:6) was milled with agate mortar and pestle. The milled sample was then heated in a horizontal tube furnace to 1000 °C (10 °C/min) and kept for 2 h with 5% H₂/N₂ mixed gas. The gained crude samples were then trimmed using ethylene glycol at 40 °C for 2 h. The final obtained powders were dialyzed for 1 week to remove melamine, and then, stable dispersions of the BN sheets were gained.

4.3. Preparation of MoS₂. A procedure for obtaining MoS₂ is as follows. The dispersed MoS₂ nanosheet suspension was prepared with the bulk MoS₂ powders (50 mg) in 10 mL NMP solution by sonication at 25 °C for 6 h. The MoS₂ was prepared by ultrapure water rinsing and dried at 60 °C.

4.4. Preparation of Au NPs. Au NPs were obtained by the following steps in the literature. Solutions of sodium citrate (1% by weight) and HAuCl₄ (0.01% by weight) were prepared. Afterward, the HAuCl₄ solution (0.5 mL) was added in the boiled sodium citrate solution (48.5 mL). The mixture was then heated until the color changed to a brilliant red. The obtained suspension was subsequently centrifuged and concentrated to a volume of 5 mL.

4.5. Preparation of the BN/MoS₂/Au NP Composites. MoS₂ nanosheets (1.5 mg) were dispersed in 1 mL of monodisperse Au suspension by ultrasonic treatment for 1.5 h until a black solution was formed. BN (1.5 mg) was then added into the prepared MoS₂/Au NP suspension by ultrasonication for 1.5 h. After that, these self-assembled structures were added with 20 μL of Nafton-117 (5 wt %) to form a well-dispersed suspension, which was kept at 4 °C.

4.6. Fabrication of BN/MoS₂/Au NP Electrode. The 3 mm GCE was processed with alumina powder (0.05 μm) and washed using 1 M H₂SO₄, deionized water, and ethanol several minutes for sonication until it was cleaned. Subsequently, the dispersions containing BN-based hybrid structures (5 μL) were drop-cast on the GCE surface. For comparison, others were similarly prepared using BN, MoS₂, and Au NP dispersions.

4.7. Analytical Procedure. CV and DPV were performed using CHI 660E Instruments (China). CV and DPV were investigated at the potential ranging from −1.2 to −0.2 V.

The grass samples with sprayed parquat were collected from the orchard after a week in Zhangqiao of Weinan, China. The samples were air dried and mixed uniformly. The as-obtained samples were sieved (0.075 mm) and thoroughly homogenized. Five grams of processed samples and 20 mL of ultrapure water were added into a centrifuge tube. The remaining parquat in the samples was recovered by sonication for 1 h. The supernatant was then obtained through centrifugal separation. Each sample was divided into two portions and kept in labeled polypropylene containers at 5 °C before analysis.

Paraquat was determined by electrochemical analysis and high-performance liquid chromatography (HPLC) (2695, Alliance, USA). The chromatographic separation of the analytes was performed with a 25 cm length ZORBAX Extend C₁₈ column at 30 °C. The mobile phase consisted of sulfonate (3.64 g), phosphoric acid (16 mL), acetonitrile (100 mL), and water (900 mL), and the pH value of the mobile phase was adjusted to 2 with trimethylamine. The flow rate, injection volume, and detection wavelength were 1 mL min⁻¹, 10 μL, and 290 nm, respectively.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.9b02658.

- Energy-dispersive X-ray spectroscopy elemental mapping of elements in the BN/MoS₂/Au NP composites and description of the electrochemical detection of grass samples using the BN/MoS₂/Au NP-modified electrode (PDF)

AUTHOR INFORMATION

Corresponding Authors
*E-mail: qili726@nwu.edu.cn. Phone: +86-29-88308427 (Q.L.).
*E-mail: huanghy@nwu.edu.cn. Phone: +86-29-88308417 (H.H.).

ORCID
Huayu Huang: 0000-0003-1819-5515

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the Program for Key Research and Development Plan in Shaanxi Province (no. 2019SF-243).

REFERENCES

(1) Nasir, T.; Herzog, G.; Hébrant, M.; Despas, C.; Liu, L.; Walcarius, A. Mesoporous silica thin films for improved electrochemical detection of paraquat. ACS Sens. 2018, 3, 484–493.

(2) de Figueiredo-Filho, L. C. S.; Baccarin, M.; Janegitz, B. C.; Fatibello-filho, O. A disposable and inexpensive bismuth film microsensor for a voltammetric determination of diquat and paraquat pesticides in natural water samples. Sens. Actuators, B 2017, 240, 749–756.

(3) Walcarius, A.; Lamberts, L. Square wave voltammetric determination of paraquat and diquat in aqueous solution. J. Electroanal. Chem. 1996, 406, 59–68.

(4) Valera, E.; García-Febreiro, R.; Pividori, I.; Sánchez-Baeza, F.; Marco, M.-P. Coulombimetric immunoassay for paraquat based on electrochemical nanoprobes. Sens. Actuators, B 2014, 194, 353–360.

(5) Pizzutti, I. R.; Vela, G. M. E.; de Kok, A.; Scholten, J. M.; Dias, J. V.; Cardoso, C. D.; Conenço, G.; Vivian, R. Determination of paraquat and diquat: LC-MS method optimization and validation. Food Chem. 2016, 209, 248–255.

18403 DOI: 10.1021/acsomega.9b02658
ACS Omega 2019, 4, 18398–18404
(6) Lamei, N.; Ezoddin, M.; Kakavandi, N. R.; Abdi, K.; Ghazikhansari, M. Ultrasound-Assisted Switchable Solvent in Determination of Quaternary Ammonium Herbicide Parquat in Biological, Environmental Water, and Apple Juice Samples Using Chemical Reduction Process Coupled to GC-MS Detection. *Chromatographia* 2018, 81, 923–930.

(7) Chuntib, P.; Jakmunee, J. Simple flow injection colorimetric system for determination of parquat in natural water. *Talanta* 2015, 144, 432–438.

(8) Siangproh, W.; Somboonsuk, T.; Chaalapulk, O.; Songsirokte, K. Novel colorimetric assay for parquat detection on-silica bead using negatively charged silver nanoparticles. *Talanta* 2017, 174, 448–453.

(9) Fang, H.; Zhang, X.; Zhang, S. J.; Liu, L.; Zhao, Y. M.; Xu, H. J. Ultrasensitive and quantitative detection of parquat on fruits skins via surface-enhanced Raman spectroscopy. *Sens. Actuators, B* 2015, 213, 452–456.

(10) Zen, J.-M.; Jeng, S.-H.; Chen, H.-J. Determination of parquat by square-wave voltammetry at a perfluorosulphonated ionomer/clay-modified electrode. *Anal. Chem.* 1996, 68, 498–502.

(11) Kenne Dedzo, G.; Pégy Nanseu-Njiki, C.; Ngameni, E. Anemometric sensors based on sawdust film modified electrodes: Application to the electroanalysis of parquat. *Talanta* 2012, 99, 478–486.

(12) Ye, X.; Gu, Y.; Wang, C. Fabrication of the CuO/polyvinyl pyrrolidone-graphene modified glassy carbon-rotating disk electrode and its application for sensitive detection of herbicide parquat. *Sens. Actuators, B* 2012, 173, 530–539.

(13) Kalinke, C.; Mangrich, A. S.; Marcolino-Junior, L. H.; Bergamini, M. F. Carbon paste electrode modified with biochar for sensitive electrochemical determination of parquat. *Electroanalysis* 2016, 28, 764–769.

(14) Li, J.; Lei, W.; Xu, Y.; Zhang, Y.; Xia, M.; Wang, F. Fabrication of polypropylene-grown nitrogen-doped graphene and its application for electrochemical detection of parquat. *Electrochim. Acta* 2015, 174, 464–471.

(15) Zhang, R.; Wang, J.; Han, P. Highly efficient photocatalysts of Pt/NdCs designed by using the Pt as the electron acceptor and the BN as the holes transfer for H₂ production. *J. Alloys Compd.* 2015, 637, 483–488.

(16) Yang, D.-T.; Shi, Y.; Peng, T.; Wang, S. BN-Heterocycles Bearing Two BN Units: Influence of the Linker and the Location of BN Units on Electronic Properties and Photoreactivity. *Organolettica* 2017, 36, 2654–2660.

(17) Wu, Y.; Xue, Y.; Qin, S.; Liu, D.; Wang, X.; Hu, X.; Li, J.; Wang, X.; Bando, Y.; Golberg, D.; Chen, Y.; Gogotsi, Y.; Lei, W. BN nanosheet/polymer films with highly anisotropic thermal conductivity for thermal management applications. *ACS Appl. Mater. Interfaces* 2017, 9, 43163–43170.

(18) Hu, J.; Huang, Y.; Yao, Y.; Pan, G.; Sun, J.; Zeng, X.; Sun, R.; Xu, J.-B.; Song, B.; Wong, C.-P. Polymer composite with improved thermal conductivity by constructing a hierarchically ordered three-dimensional interconnected network of BN. *ACS Appl. Mater. Interfaces* 2017, 9, 13544–13553.

(19) Griffin, A.; Harvey, A.; Cunningham, B.; Scullion, D.; Tian, T.; Shih, C.-J.; Gruening, M.; Donegan, J. F.; Santos, E. J. G.; Backes, C.; Coleman, J. N. Spectroscopic Size and Thickness Metrics for Liquid-Exfoliated-BN. *Chem. Mater.* 2018, 30, 1998–2005.

(20) Khan, A. F.; Brownson, D. A. C.; Randviir, E. P.; Smith, G. C.; Banks, C. E. 2D Hexagonal boron nitride (2D-hBN) explored for the electrochemical sensing of dopamine. *Anal. Chem.* 2016, 88, 9729–9737.

(21) Li, Q.; Huo, C.; Yi, K.; Zhou, L.; Su, L.; Hou, X. Preparation of flake hexagonal BN and its application in electrochemical detection of ascorbic acid, dopamine and uric acid. *Sens. Actuators, B* 2018, 260, 346–356.

(22) Barua, S.; Dutta, H. S.; Gogoi, S.; Devi, R.; Khan, R. Nanostructured MoS₂-Based Advanced Biosensors: A Review. *ACS Appl. Nano Mater.* 2018, 1, 2–25.

(23) Davletshin, A. R.; Ustiuzhanina, S. V.; Kistanov, A. A.; Saadatmand, D.; Dmitriev, S. V.; Zhou, K.; Korznikova, E. A. Electronic structure of graphene- and BN-supported phosphorene. *Phys. B* 2018, 534, 63–67.

(24) Zhang, Y.-H.; Chen, Y.-B.; Zhou, K.-G.; Liu, C.-H.; Zeng, J.; Zhang, H.-L.; Peng, Y. Improving gas sensing properties of graphene by introducing dopants and defects: a first-principles study. *Nano-technology* 2009, 20, 185504.

(25) Li, W.; Xu, H.; Zhai, T.; Yu, H.; Chen, Z.; Qiu, Z.; Song, X.; Wang, J.; Cao, B. Enhanced triethylamine sensing properties by designing Au@SnO₂/MoS₂ nanostructure directly on alumina tubes. *Sens. Actuators, B* 2017, 253, 97–107.

(26) Zhang, Y.-H.; Li, Y.-L.; Gong, F.-L.; Xie, K.-F.; Zhang, H.-L.; Fang, S.-M. Double-platelet Pd@ZnO microcrystals for NO₂ chemical sensors: a facile synthesis and DFT investigation. *Phys. Chem. Chem. Phys.* 2019, 21, 22039–22047.

(27) Jin, K.; Xie, L.; Tian, Y.; Liu, D. Au-Modified Monolayer MoS₂ Sensor for DNA Detection. *J. Phys. Chem. C* 2016, 120, 11204–11209.

(28) Zou, H. L.; Li, B. L.; Luo, H. Q.; Li, N. B. 0D-2D heterostructures of Au nanoparticles and layered MoS₂ for simultaneous detections of dopamine, ascorbic acid, uric acid, and nitrite. *Sens. Actuators, B* 2017, 253, 352–360.

(29) FRENS, G. Controlled nucleation for the regulation of the particle size in monodisperse gold suspensions. *Nat. Phys. Sci.* 1973, 241, 20–22.

(30) Darsara, S. A.; Seifi, M.; Askari, M. B. One-step hydrothermal synthesis of MoS₂/CdS nanocomposite and study of structural, photocatalytic, and optical properties of this nanocomposite. *Optik* 2018, 169, 249–256.

(31) Geim, A. K.; Grigorieva, I. V. Van der Waals heterostructures. *Nature* 2013, 499, 419–425.

(32) Lu, N.; Guo, H.; Wang, L.; Wu, X.; Zeng, X. C. van der Waals trilayers and superlattices: modification of electronic structures of MoS₂ by intercalation. *Nanoscale* 2014, 6, 4566–4571.

(33) Zhang, Y.; Chen, M.; Li, H.; Yan, F.; Pang, P.; Wang, H.; Wu, Z.; Yang, W. A molybdenum disilicide/gold nanorod composite-based electrochemical immunosensor for sensitive and quantitative detection of microcystin-LR in environmental samples. *Sens. Actuators, B* 2017, 244, 606–615.

(34) Bird, C. L.; Kuhn, A. T. Electrochemistry of the viologens. *Chem. Soc. Rev.* 1981, 10, 49.

(35) El Kasmi, S.; Lahrich, S.; Farahi, A.; Zrioull, M.; Ahmamou, M.; Bakasse, M.; El Hammedi, M. A. Electrochemical determination of parquat in potato, lemon, orange and natural water samples using sensitive-rich clay carbon electrode. *J. Taiwan Inst. Chem. Eng.* 2016, 58, 165–172.

(36) Laviron, E. Adsorption, autoinhibition and autocatalysis in polarography and in linear potential sweep voltammetry. *J. Electroanal. Chem. Interfacial Electrochem.* 1974, 52, 355–393.

(37) Desimoni, E.; Brunetti, B. Presenting analytical performances of electrochemical sensors. Some Suggestions. *Electroanalysis* 2013, 25, 1645–1651.

(38) Ribeiro, J. A.; Carreira, C. A.; Lee, H. J.; Silva, F.; Martins, A.; Pereira, C. M. Voltammetric determination of parquat at DNA-gold nanoparticle composite electrodes. *Electrochem. Acta* 2010, 55, 7892–7896.

(39) Yang, X.; Qin, L.; Wang, L.; Ding, R.; Shi, L.; Lv, B. Scalable synthesis of quasi-monodispersd BN colloidal nanocrystals by “solvent cutting” and their anti-electrochemical corrosion coating. *Chem. Eng. J.* 2018, 333, 191–199.