Sonoelectrochemical fabrication of Pd-graphene nanocomposite and its application in the determination of chlorophenols

Jian-Jun Shi\textsuperscript{a,b}, Jun-Jie Zhu\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a} Key Laboratory of Analytical Chemistry for Life Science (MOE), School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, China
\textsuperscript{b} School of Chemical Engineering, Anhui University of Science and Technology, Huainan 232001, China

\section*{Abstract}
A novel electrochemical sensor for chlorophenols was fabricated by using the Pd-graphene nanocomposite and ions liquid. The Pd-graphene nanocomposite was prepared via a sonoelectrochemical route, and the possible formation mechanism was proposed. Transmission electron microscopy, scanning electron microscopy, X-ray diffraction and Raman spectrum were used for the characterization of structure and morphology of the nanocomposite. The experimental results showed that Pd nanospheres comprised of small Pd nanoparticles were uniformly attached on graphene sheets. The electrocatalytic properties were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV), which indicated that the Pd-graphene nanocomposite had high activity for chlorophenol oxidation. Herein, 2-chlorophenol was selected as the model molecules. The results showed that graphene played an important role in the fabrication of the chlorophenols sensor. The nanocomposite with large electrochemical active surface led to the excellent electrocatalytic activity, and ionic liquid further enhanced the catalytic activity of Pd-graphene for chlorophenols.

\textsuperscript{*} Corresponding author. Tel.: +86 25 8359 7204; fax: +86 25 8359 7204.
\textit{E-mail address: jjzhu@nju.edu.cn (J.-J. Zhu).}

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tion of graphene can be summarized as follows: (1) exfoliating the graphite into discrete graphene sheets; (2) comparing with mechanical stirring with ultrasonic irradiation, the aggregation is effectively suppressed in the process of the reduction of graphite oxide (GO); (3) promoting the crystallization of NPs by the ultrasonic cavitations [27]. Sonoelectrochemical technique [28,29] has been successfully employed to synthesize metal, semiconductor nanoparticles [30,31] and nanocomposites [32], which is promising to meet the two above-mentioned requirements for the construction of graphene-based nanocomposites.

Herein, we report a one-pot route for the fabrication of Pd-graphene nanocomposite via sonoelectrochemical method. Transmission electron microscopy (TEM), scanning electron microscopy (SEM), X-ray diffraction (XRD), and Raman spectrum were used for the characterization of nanocomposite structure. The electrocatalytic properties were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) by using 2-chlorophenol (2-CP) as model molecules. The as-prepared Pd-graphene nanocomposite was found to have excellent electrocatalytic activity for the oxidation of CPs in the determination of phenolic pollutants. In the fabrication of the sensor, ions liquid (IL) was chosen as a linker to show an enhanced effect on the electrocatalysis.

2. Materials and methods

2.1. Reagents

Graphite powder (99.95%, 325 mesh), palladium chloride (PdCl₂), potassium nitrate (KNO₃), and sodium hydroxide (NaOH) were purchased from Chinese Shanghai Regent Co. Nanion solution (5% in isopropanol and water), polydiallyldimethylammonium chloride (PDDA, 20 wt.% in H₂O) was purchased from Sigma-Aldrich. 2-Chlorophenol (2-CP), hydrate hydrate, disodium hydrogen phosphate, sodium dihydrogen phosphate, concentrated H₂SO₄, K₂S₂O₈, P₂O₅ and H₂O₂ were obtained from Nanjing Chemical Reagents Factory (Nanjing, China). 1-Butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF₄]) ion liquid (IL, purity >99%) was purchased from Lanzhou Greenchem. ILS, ILCP, CAS, China. All the chemicals were used as received without further purification. All solutions were prepared with Millipore water.

2.2. Apparatus

A sonoelectrochemical device was employed to prepare the Pd-graphene nanocomposite. In brief, a titanium horn (ultrasonic liquid processor VC-750, 20 kHz, Sonics & Materials) acts both as the cathode and the ultrasound emitter. The electroactive part of the sonoelectrode is the planar circular surface with an area of 1.23 cm² at the bottom of the horn. The immersed cylindrical part was covered by an isolating plastic jacket. This sonoelectrode produced a sonic pulse that was triggered immediately following a current pulse. A CHI 660B electrochemical workstation (CH Instruments Co., USA) was operated in the pulse current regime (without using a reference electrode). A platinum sheet (1.0 cm × 1.0 cm) was used as a counter electrode. The pulse on time of the current was 0.5 s, the pulse off time of the current was 0.5 s, and the duration of the ultrasonic pulse was 0.5 s. Electrochemical measurements were performed with a CHI 660D electrochemical workstation (CH Instruments Co., USA). A conventional three-electrode system comprised of a platinum wire auxiliary electrode, glassy carbon working electrode and a saturated calomel reference electrode. Characterizations were performed via high resolution transmission electron microscopy (HRTEM, JEOL 2100, with a 200 kV accelerating voltage) and X-ray powder diffraction (XRD, Shimadzu XD-3A, with Cu Kα radiation, λ = 0.15418 nm). Raman spectra were measured by using a Renishaw-in-Via Raman microscope equipped with a 50× objective using an excitation wavelength of 514.5 nm on 1800-line grating. All samples were deposited on slide glass in powder form without using any solvent.

2.3. Synthesis of Pd-graphene nanocomposite

PDDA-functionalized graphene was prepared according to the procedure reported previously [33]. Firstly, GO was prepared from graphite powder by a modified chemical oxidation method of Hummers and Offeman [34]. Subsequently, the homogeneous GO aqueous dispersion (50 mL) was mixed with 0.25 mM PDDA solution and stirred for 30 min. The resulting mixture was further treated with 0.25 mL hydrazine hydrate for 24 h at 90 °C. Finally, the black PDDA-functionalized graphene was collected by filtration and further washed with deionized water. Pd-graphene nanocomposite was prepared via sonoelectrochemical route [35]. Briefly, 2 mL of H₂PdCl₄ (56.5 mmol L⁻¹ solution, 7 mL of KNO₃ (1 mol L⁻¹) solution and 1 mL of graphene (0.5 g L⁻¹) solution were added into 50 mL of PDDA (7.5 g L⁻¹) under stirring. Then, the pH was adjusted to 6.5 with NaOH solution (0.1 mol L⁻¹). The nanocomposite was produced in a sonoreactor with a current density of 25 mA cm⁻², an ultrasonic intensity of approximately 20 W and a reaction time of about 70 min. Pd NPs was synthesized under the same condition for comparison.

2.4. Preparation of IL-Pd-graphene modified GCE

A bare glassy carbon electrode (GCE) with a 3 mm diameter was polished with 1.0, 0.3 and 0.05 μm α-Al₂O₃ successively, ultrasonically cleaned in ethanol and water bath twice for 5 min and dried under nitrogen stream. IL was used as a linker due to its excellent electro-conductivity and chemical inertness, which have been available in the fabrication of metal-carbon hybrid nanomaterials [36], as well as modified electrode [37]. For the preparation of Nanion/IL-Pd-graphene modified GCE, 200 μL of 5.5 g L⁻¹ Pd-graphene was first mixed with 2 μL of IL and sonicated for 1 h to form a homogenous mixture. Then, 5 μL of the suspension mixture was dropped to the GCE and dried in a desiccator overnight at room temperature. 5 μL of 0.1% Nanion was dropped on the GCE surface to increase the stability of the electrode, and the solvent was evaporated at room temperature.

2.5. Electrochemical experiments

Buffers were purged with highly purified nitrogen for 15 min prior to experiments. A nitrogen environment was kept during the whole experiment. CVs were recorded in the solution with 0.5 mol L⁻¹ NaOH to determine the adsorption of atom H at the Pd and Pd-graphene modified electrodes, deposited by casting in equal weights at a glassy carbon electrode. The electrochemical behavior at the IL-Pd-graphene modified GCE was investigated in the phosphate buffer (pH 7.4) with 80 μmol L⁻¹ 2-CP. DPV measurements were performed from 0.2 to 1.0 V with pulse amplitude of 0.05 V and pulse width of 0.05 s.

3. Results and discussion

3.1. Characterization of the Pd-graphene nanocomposite

In Fig. 1A and B, the SEM and TEM images of the Pd-graphene show that the spherical Pd NPs with average size of 30−40 nm were successfully combined with the graphene sheets. The further magnification indicates that the 3D Pd NPs are composed of small Pd nanoparticles with several nanometers as shown in Fig. 1C. The
clearly marked interplanar \( d \) spacing is 0.23 nm, which corresponds to that of the \( \{111\} \) lattice planes of fcc Pd. In Fig. 1B, it can be observed that all the Pd NPs are well separated, which indicates that they are firmly attached to graphene sheets. Fig. 1D shows the XRD patterns of graphite oxide, PDDA functionalized graphene and Pd-graphene nanocomposite, respectively. The peak at 25° in the graphene corresponds to the interspacing distance between the different graphene layers [13]. The pattern of the Pd-graphene exhibits three diffraction peaks that can be indexed to diffraction from the \( \{111\} \), \( \{200\} \), and \( \{220\} \) of the fcc that corresponds to Pd. As shown in the XRD pattern of graphite oxide, the disappearance of the native graphite peak at about 26.4° (JCPDS No. 41-1487) and the appearance of the peak in 10.4° corresponding to interlayer spacing of 0.85 nm reveal the oxidation and exfoliation of the starting graphite, while restacked in the XRD sample preparation by drying process. In contrast to the XRD pattern of graphite oxide, the disappearance of the peak at about 10.4° indicates the restacking of the reduced graphene oxide and Pd-graphene were successfully prevented.

As shown in Fig. 2, the Raman spectrum of various samples consists of four bands at 1350, 1584, 2690 and 2932 cm\(^{-1}\), which can be designated as D, G, 2D and 2G bands, respectively. It is found that the frequencies of the D and G bands in the graphene (b) and Pd-graphene (c) are similar to what observed in the graphite oxide (a), and the D/G intensity ratio does not change obviously, suggesting that the sonoelectrochemical process does not reduce the size of in-plane sp\(^2\) domains greatly, which is favorable to the electrical conductivity of graphene nanosheets [38]. Moreover, the second order resonant Raman processes are usually addressed as the 2D and 2G bands. The typical fingerprint of graphene is the 2D peak at about 2700 cm\(^{-1}\). The shape, position and intensity of the 2D peak depend markedly on the number of layers [39]. As seen in Fig. 2(c), 2D-band of the Pd-graphene is centered at 2690 cm\(^{-1}\) with the broader peak compared with that of graphene and graphite oxide, which indicates the presence of loosely stacked graphene layers with the intercalation of metal NPs [40], resulting in the increase of the distance between the graphene sheets [41], which is consistent with the XRD results.

3.2. Mechanism for the formation of Pd-graphene nanocomposite

Scheme 1 illustrates a four-step evolution driven under electric and ultrasonic fields, which can be explained as follows: firstly, Pd complex ions diffused towards the surface of the sonoelectrode; then, Pd complex ions were reduced by a controlled electric pulse to form the Pd primary particles at the electrode; the primary particles were vibrated from the electrode surface by the pulse ultrasonic jet streams with the concomitant effects on the dispersion of graphene.
sheets. When the amount of primary Pd particles reached a certain value, they could spontaneously aggregate into larger Pd NPs clusters, and eventually lead to the formation of 3D spherical Pd NPs. Simultaneously, both the Pd NPs and the residual primary Pd particles, which were dispersed under the ultrasonic field, were directly captured by graphene sheets through ultrasonic assembling process [42] coupled with Van der Waals interactions [43] between the PDDA-functionalized graphene and PDDA-capped Pd NPs. Finally, a well dispersed aqueous solution with Pd-graphene nanocomposite could be obtained by repeating the above procedures.

3.3. Electrochemical behaviors of Pd-graphene nanocomposite

The electrochemically active surface area (ECSA) for the Pd-graphene nanocomposite modified electrode could be estimated by using the formula ECSA = Qd/Qd,H from the average charge transfer (Qd) based on integrated values of hydrogen adsorption/desorption in the range −0.7 to −1.1 V [44]. Assuming the charge per real area of catalyst with monolayer adsorption of hydrogen is Qd,H = 210 μC cm⁻² to cover the Pd surface totally [45], according to the CV curves in Fig. 3, the estimated electrochemically active special surface area (ECSA) is 23.14 cm² cm⁻² for Pd modified electrode, 58.86 cm² cm⁻² for Pd-graphene modified electrode, respectively (see Table 1). This suggests that the Pd-graphene modified electrode has the higher value of ECSA, which is consistent with the improved adhesion, accessibility, and the dispersion of the Pd active sites in the 3D Pd nanostructure, which displays the good performance in electrocatalysis.

Furthermore, the electrochemical properties of 2-CP at graphene, Pd and Pd-graphene modified electrode were investigated. As seen in Fig. 4 insert, a visible oxidation of 2-CP on graphene was observed, which is similar to the previous report for the oxidation of CPs on CNT modified electrode [46]. The DPV peaks in Fig. 4 at 0.60 V, 0.65 V and 0.72 V correspond to the oxidation of 2-CP on the Pd-graphene nanocomposite (a), Pd (b) and graphene (c) modified GCE, respectively. The peak current of 2-CP on Pd-graphene increased greatly in comparison to Pd and graphene. This enhanced effect could be attributed to the excellent conductivity of graphene and more catalytic active sites.

The enhanced effect of IL was also studied by CVs. As shown in Fig. 5, a well-defined and sensitive oxidation peak of 2-CP appears at 0.63 V during the first anodic potential sweep from 0.0 to 1.0 V in the presence of IL. On the reverse scan, no corresponding reduction peak was observed, revealing that the electrode process of 2-CP was totally irreversible. The insert in Fig. 5 also shows that the oxidation current gradually decreases and the peak potential shifts positively with the increase of the number of sweep. The decreases of peak current and positive shift of oxidation peak potential can be ascribed to the adsorption of 2-CP or its oxidative product at the IL-Pd-graphene modified GCE surface. Therefore the oxidation current was recorded in the first anodic sweep in order to get higher sensitivity and better reproducibility.

In order to investigate the rate-determining step of chlorophenol oxidation, the effect of scan rate on the CV peak current was discussed. It is well-known that the typical characteristics in the polarization process are defined as charge transfer, mixed and mass transfer control region [47]. If the adsorbed species are electrochemically active and adsorption-controlled, the peak current can increase linearly with the scan rate. As shown in Fig. 6, the peak current is directly proportional to the scan rate from 25 to 200 mV s⁻¹, indicating that the electrochemical reaction of 2-CP at the electrode is an adsorption-control process. In the experiment, 50 mV s⁻¹ was
chosen as the scan rate. It was also observed that the oxidation current depended on the accumulation time employing adsorptive stripping DPV method. Before the accumulation time increased to 5 min, the oxidation peak current changed linearly. However, with further increase of accumulation time, the peak current reached the certain value, which indicated that the limiting amount of 2-CP adsorbed on the electrode has been achieved. Therefore, an accumulation time of 5 min was selected. Here, both the graphene and IL linker played the important roles in the electrocatalytic oxidation of 2-CP.

### 3.4. Determination of 2-chlorophenol

Fig. 7 shows the changes in the peak current of 2-CP for its increasing concentration. The linearity from 4 to 800 μmol L⁻¹ indicates first order kinetics with respect to the bulk concentration of 2-CP, with a regression equation of \( i_p = 0.0246c + 0.4866 \) (n = 6), \( R = 0.9985, c \) in μmol L⁻¹, \( i_p \) in μA. The detection limit was 1.5 μmol L⁻¹. The reproducibility of the IL-Pd-graphene modified GCE was also examined by repetitive measurement in 80 μmol L⁻¹ of 2-CP. After determination, the electrode was treated as described in the experimental method. For three successive measurements, the relative standard deviation (RSD) is 0.78%, suggesting that the modified GCE has excellent reproducibility. The storage stability of the developed sensor was also studied. The DPV response of the sensor stored at room temperature over 4 weeks was not significantly changed.

Several phenol derivatives, such as 4-chlorophenol (4-CP), hydroquinone, 2-aminophenol and 4-nitrophenol, were employed to investigate the selectivity by cyclic voltammetric method. It was found that these derivatives were oxidized at different potentials and did not interfere with the determination of 2-CP. Conversely,

### Table 1

The calculated results of ECSA and ECSSA from CV in Fig. 3.

| Electrode   | Loading (mg cm⁻²) | \( Q_a \) (μC cm⁻²) | \( S_{ECSA} \) (cm² mg⁻¹) | \( S_{ECSSA} \) (cm² cm⁻²) |
|------------|----------------||-----------------|-----------------|-----------------|
| Pd         | 0.238          | 4.86            | 97.24           | 23.14           |
| Pd-graphene| 0.250          | 11.31           | 215.43          | 58.86           |

### Table 2

Determination of 2-CP in water samples using the method of standard additions.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2-CP added (μmol L⁻¹)</th>
<th>2-CP calculated (μmol L⁻¹)</th>
<th>2-CP determined (μmol L⁻¹)</th>
<th>Recovery (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.0</td>
<td></td>
<td>0.0</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>0.0</td>
<td>4.0</td>
<td>3.8</td>
<td>102.5</td>
</tr>
<tr>
<td>3</td>
<td>0.0</td>
<td>40.0</td>
<td>45.2</td>
<td>103.2</td>
</tr>
<tr>
<td>4</td>
<td>0.0</td>
<td>400.0</td>
<td>404.0</td>
<td>100.4</td>
</tr>
</tbody>
</table>
the characteristic CV patterns of 4-CP was similar to that of the 2-CP, strongly interfering with 2-CP determination. This behavior suggests that the Pd-graphene nanocomposite is more appropriate for the voltammetric determination of total chlorophenols.

The concentration of 2-CP in several secondary effluent samples from a wastewater treatment plant (Nantong, China) was determined using the method of standard additions. Prior superfiltration (3 kDa) to remove the suspended solid particles was necessary. The value of the determined 2-CP was extrapolated from the calibration curves, and the results are shown in Table 2. The recoveries were in the range of 100.4–103.2%, suggesting the proposed method has good accuracy. The positive effect on the recovery might be caused by the electroactive species coexisting in the water sample, such as 4-CP.

The proposed electrochemical technique is facile and rapid-response for the determination of CPs in contrast to the conventional chromatographic methods. Especially, it exhibited better stability and reproducibility than the electrochemical sensor previously reported [48].

4. Conclusions

In summary, a novel nanocomposite with three-dimensional Pd nanoparticles on the graphene surface was fabricated via a sonoelectrochemical route, which exhibited high electrocatalytic activity for chlorophenol oxidation. The possible formation process driven by the electric and ultrasonic pulses was proposed. An electrochemical sensor for chlorophenols was constructed based on the nanocomposite. The as-prepared IL-Pd-graphene nanocomposite exhibited remarkable current enhancement and good stability in the determination of CPs. The peak current is linear with the concentration of phenol in the range from 4 to 800 μmol L⁻¹, and the detection limit is 1.5 μmol L⁻¹. This method can also be extended to prepare other graphene-based nanocomposites and fabricate catalysistype electrochemical sensor for more target molecules.

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