The Comparing on 4-chlorophenyl Sulfoxide Modified the Reduced Graphene Oxide Composite for the Adsorption/Desorption of Pd (II) and Pt (IV) Ions

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Research Article

Keywords: reduced graphene oxide composite, Pd ( ), Pt ( ), adsorption/desorption, separation, enrichment

Posted Date: April 6th, 2023

DOI: https://doi.org/10.21203/rs.3.rs-2753061/v1

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Version of Record: A version of this preprint was published at Chemical Papers on July 27th, 2023. See the published version at https://doi.org/10.1007/s11696-023-02964-4.
Abstract

The reduced graphene oxide aerogel modified by 4-chlorophenyl sulfoxide was obtained by a simple self-assemble process under the basic reduction-oxide condition, then freeze-dried for future using. The prepared aerogel was shortly named 4CS-rGO, which was characterized by fourier transform infrared spectroscopy, Raman spectroscopy, scanning electron microscope, et al. 1 mg of 4CS-rGO composite was used as an adsorbent to adsorb Pd (II) and Pt (IV) in 1.0 mL 4 mM Britton-Robinson buffer solution with various pH. The adsorption efficiency of Pd (II) increased with the increase of pH, whereas the hydrolysis of Pd (II) happened at pH 13, and the maximum adsorption efficiency of Pd (II) was 91.82% at pH 12, which was mainly driven by electrostatic attraction. Besides, the adsorption behavior of the 4CS-rGO composite for Pt (IV) was explored to evaluate the possibility to isolate Pd (II) and Pt (IV) ions by using aerogel. We found that, quite interestingly, hydrogen bond, hydrophobic interaction and van der Waals force can strongly conquer electrostatic repulsion driven Pt (IV) ions adsorption behaviour at pH 5, and Pt (IV) ions displaced by cationic surfactant. Moreover, a tighter Pt (IV) ions adsorption behaviour than Pd (II) ions was observed while we used with/without 4-chlorophenyl sulfoxide modified the graphene to adsorb them respectively. While branched TBAB was easier and more effectively replaced the adsorbed Pt (IV) ions than strained CTAB.

Introduction

Graphene oxide (GO) is a rising carbon materials in recent years, which attracting many researchers’ interests from material science, biological chemistry, analytical chemistry, environmental and electrochemistry et al, due to its extraordinary properties. GO is precursor to prepare three-dimensional graphene-based composite because of enrichment of oxide-contain groups. Porous graphene-based materials have extensive attention for applications in catalysis, gas adsorption and separation, energy storage and conversion and environmental protection, due to their tunable porosity, high biocompatibility, low mass density, high specific surface area, high electrical conductivity and high chemical stability. Especially, porous materials with extremely high ratio of surface area to mass or volume allows intimate interaction with diverse organic or inorganic species to adsorb on the surface and in the interior porous space. Therefore, three-dimensional porous graphene-based composite have a big potential to be an excellent solid-extraction material through modification by chemical way for applications in separation/enrichment fields.

Noble metal resources are very scarce and precious in earth, and their extraordinary chemical and physical properties made them more valuable and irreplaceable. For example, both platinum and palladium showed an excellent catalytic activity for $\text{H}_2\text{O}_2$, $\text{CH}_4$, $\text{CO}$, $\text{CO}_2$ reduction et al. In the metallurgical chemistry, liquid-liquid extraction is a common way to separation/enrichment of Pt, Pd, Rh, Ir from the aqueous solution. Palladium and platinum are widely employed in the manufacture of the advanced materials with their special functions and properties. However, the separation of Pt (IV) and Pd (II) by solvent extraction is difficult due to their similar extraction behaviors.
and weak selectivity of solvent extractants. Therefore, extensive research has been done to find extraction systems by which either Pt (IV) or Pd (II) is selectively extracted from the hydrochloric acid solution and cyaniding solution. Compared with liquid-liquid, solid extraction can enrich targets in a low concentration, with less environment pollution and avoid large usage of organic agent. Solid extraction materials could be more selectively specific by functionalization and modification.

Only a few papers reported about palladium and platinum separation by using graphene-based materials as adsorbents. In this work, using Pt ( ) and Pd ( ) hydrochloride acid solution as model, we prepared 4CS-rGO composite for exploring surface adsorption between the composite and Pt ( ) / Pd ( ) ions, respectively, for the sake of further understanding adsorption mechanism and exploiting a new method to meet palladium and platinum circular use, recycle and reuse in low concentration.

Materials And Methods

Materials and reagents

Graphite powder, ethylenediamine (EDA), hexadecyl trimethyl ammonium bromide (CTAB), choline chloride (CC), tetrabutylammonium bromide (TBAB) and 4-chlorophenyl sulfoxide (4-CS) were purchased from Aladdin Chemistry Co., Ltd. (Shanghai, China). Palladium (II) chloride (Bide Chemical reagent Co., Ltd., Shanghai, China) was used as received. The other reagents were purchased from Guoyao Chemical reagent Co., Ltd. (Shanghai, China). Britton-Robinson (B-R) buffer was prepared by mixing 0.04 M phosphoric acid, boric acid and acetic acid, and pH was adjusted by using 0.2 mol L^{-1} NaOH. All the reagents employed were at least of analytical reagent grade if not stated otherwise. Deionized water was used in all the experiment.

Preparation of the 4CS-rGO composite

GO was synthesized mainly according to Hummers’ method by Chen, 5 mg mL^{-1} of GO aqueous suspension was obtained by sonication for 10 h. 5 mg 4-chlorophenyl sulfoxide was added into 200 µL ethylenediamine to dissolution by sonication for 5 mins. Then, the mixer was added into 10 mL GO dispersion immediately. The mixture was sealed and put into a water bath without stirring at 95°C for 8 h under the atmosphere temperature. After the black rGO hydrogel was formed, it was taken out and washed by deionized water for a few times to remove the residue, and then freeze-dried into an aerogel under vacuum for 48 h for further use.

Characterization of the 4CS-rGO composite

X-ray photoelectron spectroscopy (XPS) scanning curves of the 4CS-rGO composite were recorded on an ESCALAB 250 spectrometer (Thermo Fisher, Waltham, MA, USA). The surface morphologies of the 4CS-rGO composite were characterized under an Ultra Plus scanning electron microscope (SEM, Zeiss, Jena, Thuringia, Germany), in which Schottky field emission electron sources were used. Raman spectra of the 4CS-rGO composite were recorded by a Laser Raman spectroscopy (LabRAM XploRA, Paris, France)
using a 638 nm excitation laser. Fourier transform infrared (FT-IR) spectra of the 4CS-rGO composites and GO were recorded by using an IR Prestige-21 spectrometer (Shimadzu, Japan). The surface charge property of the 4CS-rGO composite was measured by a Nano-ZS90 Zetasizer (Malvern, UK), in which B-R buffer aqueous solution varied from pH 4 to 12.

**Pt (I) /Pd (II) ions adsorption and desorption with the 4CS-rGO composite**

In this work, 1.0 mg of the 4CS-rGO composite was added into 1.0 mL of Pd (II) or Pt (II) chloride acid solution (the original concentrations were all 80.0 µg mL\(^{-1}\)), which then were added into a 1.5 mL centrifuge tube. Afterwards, the centrifuge tube was mixed for a while, then kept static for a while. Finally, the phase separation was performed via centrifugation for 5 mins at 5000 rpm. Thereafter, the supernatant was collected to determine the concentration of the residual Pt (II)/Pd (II) ions using atomic absorption spectrometer (AAS) AA-6300 (Shimadzu, Japan). The recovery of Pt (II)/Pd (II) ions retained on the 4CS-rGO composite was performed by using surfactant, urea and B-R buffer as eluent reagents.

**Results And Discussion**

**Preparation and characterization of the 4CS-rGO composite**

The FT-IR spectra of 4CS-rGO composite and GO as shown in Fig. 1. Compared with GO, the adsorption band of -C=O stretching vibration at 1700.34 cm\(^{-1}\) of the 4CS-rGO composite appeared instead of the adsorption band at 1665.86 cm\(^{-1}\) of the GO (Fig. 1b), which illustrated that part of -COOH groups of GO was reduced and -C=O were partly retained although reduction reaction happened. The adsorption band at 2972.05 cm\(^{-1}\) and 2888.25 cm\(^{-1}\) of the 4CS-rGO composite (Fig. 1a) were ascribed to C-H stretching vibration from benzene ring skeleton of graphene-based materials. Besides, the new adsorption bands of N-H bending vibration at 1597.71 cm\(^{-1}\), N-H stretching vibration from -NH\(_2\) group at 3400.29 cm\(^{-1}\) and S=O stretching vibration at 1053.26 cm\(^{-1}\) appeared. It is proved that sulfoxide was partly reduced and the amino groups from EDA were modified on the composite.

The Raman spectrum of the feature peaks of graphene have two intense D band and G band Raman features, the 4CS-rGO composite had the two similar feature peaks as shown in Fig. 2. The D/G intensity ratio of the 4CS-rGO composite was 1.073, while the corresponding ratio of the GO was 0.938. It was consistent with previous papers\(^{37-39}\) and the results of FT-IR spectra, illustrating that GO was reduced successfully.

The XPS spectrum of the 4CS-rGO composite was determined as illustrated in Fig. 3, which showed that the variation of elemental and functional groups of the 4CS-rGO composite. The peaks at 166.15 eV attributed to sulphur, 401.55 eV attributed to nitrogen, 531.9 eV attributed to oxygen and 532.5 eV attributed to carbon respectively. The peaks of the sulphur and nitrogen were appeared respectively. Narrow scan of S 2p was inserted in a top of left corner, which were the peaks at 164.75 eV and 159.45
eV respectively assigned to S 2p\textsubscript{1/2} and S 2p\textsubscript{3/2}. These results clearly revealed the elemental state of sulphur existing in the structure of the 4CS-rGO composite after reduced self-assembly. It was consistent with the results of FT-IR spectrum of 4CS-rGO composite.

The surface topographies of the GO and 4CS-rGO composite were characterized by the scanning electron microscope. The wrinkle surface of GO resulted in the single GO sheet stacking or adhere together by van der Waals force or conjugate interaction, however, electronic repulsion force or hydrogen bonds between the GO sheets. Compared with the SEM image of GO (Fig. 4a), the prepared graphene-based composite exhibited inter-connected 3D architecture with uniformly dispersed pores in micrometers size (Fig. 4b), and its the surface area was enlarged obviously. In a summary, the porous and 4-chlorophenyl sulfoxide modified aerogel was prepared successfully.

**Pt (□)/Pd (□) ions adsorption behavior onto the 4CS-rGO composite**

The adsorption behavior of Pd (□) on the 4CS-rGO aerogel was investigated in 4 mM B-R buffer with pH ranging from 4 to 12 within 30 min, as shown in Fig. 5a. The adsorption efficiency of Pd (□) was increasing as the increase of the pH, giving a rise to an adsorption efficiency of 84.92% at pH 12. Compared with the lighter yellow Pd (□) solution at pH 4–12, solution became white suspension at pH 13 due to Pd (□) hydrolyzed in alkali environment, which showed in the inserted picture (Fig. 5a). The first stage hydrolysis of palladium divalent ion expressed as $\text{Pd}^{2+} + \text{H}_2\text{O} = \text{Pd(OH)}^+ + \text{H}^+$, causing the solution becoming white. Therefore, the adsorption process of Pd (□) on the 4CS-rGO aerogel was not further investigated in pH >12. Based on background, Pt (□) was used as model to investigate the adsorption behavior of Pt (□) on the surface of 4CS-rGO aerogel as shown in Fig. 5b. The maximum adsorption efficiency of Pt (□) happened at pH 5 and it descended with the increasing of pH, within ~20% adsorption efficiency at pH 11. The composite was negatively charged at pH 12 as shown in Fig. 5c, the electrostatic attractive force mainly drove the Pd (□) adsorb onto the composite. The composite was charged positively at pH 5 while it was closed to 0 mV, the electrostatic repulsion made less contribution to preventing adsorbing between Pt (□) and the aerogel. It is interesting that below ~20% Pt (□) adsorbed onto the composite even electrostatic attractive force existed in pH 11. It illustrates that electrostatic interaction had little effects on the Pt (□) adsorption process, while played an important role in the Pd (□) adsorption.

To investigate the effect of adsorption time on the adsorption behavior, the time was varied within 5-120 mins. As shown in Fig. 6a, the adsorption efficiency of Pd (□) onto the 4CS-rGO composite was ~80% above in the whole time, and adsorption efficiency reached 83.13% in 5 mins. Adsorption efficiency of Pd (□) increased as the adsorption time increased while the adsorption efficiency decreased lightly after 60 mins. Compared with clear solution at 5 mins, solution became turbid at 120 mins (Fig. 6a). It is possible that the hydrolysis of palladium divalent ions happened after incubating long time at basic condition. To confirm the adsorption stability, the effect of pH increased from 4–12 within 60 mins on adsorption efficiencies was performed as Fig. 6b showed, adsorption efficiency increased as the pH adding, giving a
rise of adsorption efficiency was 91.82% at pH 12. The electric charge of the 4CS-rGO composite increased from pH 4–12 (as illustrated in Fig. 5c) meant that the electrostatic interaction between Pd ( ) ion and the 4CS-rGO composite enhanced. It illustrated that adsorption balance between Pd ( ) and the composite can reach in a short time, which was driven by electrostatic attractive force under alkaline condition. In other side, the adsorption efficiency of Pt ( ) onto the 4CS-rGO composite increased as time increased, then tended to balance (Fig. 6c). As shown in Fig. 6d, maximum adsorption efficiency of Pt ( ) was 91.3% at pH 5 even electrostatic repulsion existed, then adsorption efficiency declined as the pH rose, and 20.8% adsorption efficiency was found at pH 11 with 50 mins. From the results of Fig. 5, electrostatic interaction had few influences on the Pt ( ) adsorbed onto the surface of the 4CS-rGO composite. It was likely that the other covalent bond interaction intensively drove Pt ( ) adsorption behavior. Although the composite charged positively, however, it was very closed to zero at pH 5, therefore electrostatic repulsion between the Pt ( ) and the composite was weak, and it was easily conquered by other acting forces. It was possible that strong hydrophobic interaction, hydrogen bond and van der Waals force were the driving forces for the adsorption process. For more details about adsorption mechanism, we discussed in desorption process.

The adsorption capacity of the 4CS-rGO composite for Pt ( ) and Pd ( ) were investigated at room temperature with various concentration in 4 mM B-R buffer as shown in Fig. 7. The adsorption capacity increased at the increase of concentration of PdCl$_4^{2-}$ solution, then almost no change happened while the concentration of Pd ( ) > 100 µg mL$^{-1}$. Finally, the adsorption capacity of the composite for Pd ( ) was ~ 69 µg mg$^{-1}$. The similar tendency was found in platinum adsorption process, the adsorption capacity of Pt ( ) on the composite was ~ 120 µg mg$^{-1}$. In the whole, the 4CS-rGO composite showed a better adsorption capacity to Pt ( ) than Pd ( ).

The abovementioned adsorption experiments measured the kinetics and capacity of Pt ( ) / Pd ( ) adsorption. The obtained information, however, just indicated that part of the adsorption affinity and mechanism. To further understand and get more information, we then performed Pt ( ) / Pd ( ) desorption experiments respectively. Urea, CTAB, TBAB, SDS, choline chloride and B-R buffer were used to recycle the adsorbed Pt ( ) / Pd ( ) ions. As Fig. 8a showed, Pd ( ) was recovered by 0.5% CTAB, giving a rise of a recovery was 81.84%. CTAB is cationic surfactant, can compete adsorption and displace Pd ( ) from the composite. Besides, we changed the surface charges of the 4CS-rGO composite by adding B-R buffer with pH 2–7, and below ~ 46% Pd ( ) was recovered from the surface of 4CS-rGO composite. Only 29.24% Pd ( ) could be obtained by using 2% CC as an eluent. It proved that electrostatic attractive mainly contribute to the Pd ( ) adsorption onto the surface of 4CS-rGO composite. Hydrogen bonding was probed by using urea in the experiment. $^{40-41}$ Urea can disrupt the hydrogen bonding, ~ 80% Pt ( ) was desorbed when the concentration of urea was 1.5% (Fig. 8c), which illustrated hydrogen bonding existing and mainly driving the Pt ( ) adsorption process.

On the other side, for further exploring desorption process, urea, the anionic and cationic surfactants were used to recovery of Pt ( ) ions. Pt ( ) were effectively eluted by various concentration of CTAB, TBAB, SDS
and urea, giving a rising of the recovery were 59.37% Pt ( ) with 0.5% TBAB, 48.59% with 1.20% CTAB, 12.09% with 1% SDS and 88.25% with 1% urea, respectively (As Fig. 9). It is interesting that cationic surfactant performed a better recovery than anionic surfactant, moreover, branched chain cationic surfactant had a better desorption efficiency than linear chain. This suggested that the surfactant likely interacted with composite via its hydrophobic tail and using van der Waals force to displace the Pt ( ). Branched chain TBAB can be more easily taken up on the surface of the composite in terms of spatial structure, thereby only 0.5% TBAB can eluted much more Pt ( ) than CTAB. Moreover, the composite was negatively charged at neutral, it existed stronger electrostatic repulsion force between SDS and the composite, thereby only a few Pt ( ) can recover by using SDS as an eluent. As Fig. 9d showed, the obtained Pt ( ) was desorbed by adding urea to break hydrogen bond.

The comparison of the adsorption and recovery of Pt ( ) than Pd ( ) onto the two composites, which with or without modification by 4-chlorophenyl sulfoxide were performed to further understand adsorption process on the composites. Compared with the composite without modification, the graphene-based composite modified by 4-chlorophenyl sulfoxide exhibited a better adsorption behavior for Pd ( ), and the adsorption efficiency of Pd ( ) were improved from 35.67–91.82% (Fig. 10a). And absorbed Pd ( ) can be effectively eluted by CTAB with > 64% desorption rate. Two composites showed good adsorption on Pt ( ), giving a rise of an adsorption efficiency of 80% above (Fig. 10b). However, the composite without being modified by 4-chlorophenyl sulfoxide had much higher adsorption affinity to Pt ( ), which resulted in the difficulty to recover. Finally, absorbed Pt ( ) were much more easily eluted by branched chain cationic surfactant from the surface of the 4CS-rGO composite. In a conclusion, the composite modified 4-chlorophenyl sulfoxide had a better adsorption for Pd ( ) at pH 12 and showed a strong affinity on Pt ( ) at pH 5 driven by different acting force. Two of them can be recovered by CTAB effectively with different mechanism.

**Conclusions**

In this work, the 4CS-rGO composite were prepared by modifying with 4-chlorophenyl sulfoxide via a simple way in low temperature and characterized. It was used to adsorb Pd ( ) and Pt ( ) respectively for exploring new separation method and understanding the adsorption mechanism. Hydrogen bond interaction exhibited a vital role in the adsorption behaviour no matter Pd ( ) or Pt ( ). It is striking that electrostatic interaction almost showed no contribution to Pt ( ) adsorption process while electrostatic attribution force mainly driving Pd ( ) adsorb/desorb onto the surface of the composite. Therefore, hydrogen bond, hydrophobic interaction and van der Waals force were stronger than charge repulsion, making Pt ( ) adsorb stably in acidic condition, branched TBAB can elute the obtained Pt ( ) effectively. The obtained Pd ( ) were eluted by CTAB easily due to the electrostatic interaction at pH 12, however, over basic condition caused Pt ( ) hydrolyzed. This research provides a reference for preparing a novel graphene-based composite and related surface interaction. It also provided a potential and effective method for enrichment/isolation of Pd ( ) and Pt ( ) through changing pH.
Declarations

Conflict of Interests

The authors declare no conflict of interest.

Acknowledgements

This work was financially supported by the Fundamental Research Funds of Yunnan Province for Youth (No. 202001AU070134, No. 202001AU070112) and China University Innovation Fund, Beichuan Teaching Assistant Project (2021BCA02006).

References

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**Figures**
Figure 1

FT-IR spectra of 4CS-rGO composite (a) and GO (b).
Figure 2

Raman spectra of 4CS-rGO composite (a) and GO (b).
Figure 3

XPS spectrum of the 4CS-rGO composite. Insert: narrow scan of sulphur element.
Figure 4

SEM images of GO (a) and 4CS-rGO composite (b).

Figure 5

pH-Dependent adsorption efficiencies of Pd (a) and Pt (b) onto the 4CS-rGO composite; ζ potential of the 4CS-rGO composite dispensed in 40 mM B-R buffer from pH 4-12 (c). Concentration/volume of each solution, 80 μg mL⁻¹/1.0 mL; adsorbent, 1.0 mg; adsorption time, 30 mins.
Figure 6

Effects of time on adsorption efficiencies of Pd ( ) onto the 4CS-rGO composite at pH 12 (a) and Pt ( ) onto the 4CS-rGO composite at pH 5 (c); and effects of pH on adsorption efficiencies of Pd ( ) within 60 mins (b) and Pt ( ) within 50 mins (d), respectively. Concentration/volume of each solution, 80 μg mL$^{-1}$/1.0 mL; adsorbent, 1.0 mg.
Figure 7

The adsorption capacity of Pd ( ) (a) and Pt ( ) (b) on the 4CS-rGO composite.

Figure 8

The effect of the amount of CTAB (a), B-R buffer with different pH and 2% CC (b) and urea (c) on the recovery of Pd ( ). Adsorption: 1.0 mL of 80 μg mL\(^{-1}\) Pd ( ) solution in 4 mM B-R buffer; elution: 1.0 mL of CTAB and urea with various concentration, B-R buffer and 2% CC; the time for adsorption and elution: 60 mins for each.
Figure 9

The effect of the amount of CTAB (a), TBAB (b), SDS (c) and urea (d) on the recovery of Pt ( ).
Adsorption: 1.0 mL of 80 μg mL⁻¹ Pt ( ) solution in 4 mM B-R buffer; elution: 1.0 mL of CTAB, SDS, TBAB and urea with various concentration; the time for adsorption and elution: 50 mins for each.
Figure 10

The comparison of the adsorption and recovery of Pd ( ) (a) and Pt ( ) (b) onto the two composites (with/without modified by 4-chlorophenyl sulfoxide). Adsorption: 1.0 mL of 80 μg mL$^{-1}$ PdCl$_4^{2-}$ or PtCl$_6^{2-}$ solution in 4 mM B-R buffer; elution: 1.0 mL.