Supporting Information on

Spectroscopic and theoretical study on the counterion effect of Cu(II) ions and graphene oxide interaction with titanium dioxide

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Synthesis of graphene oxide (GO). The GO was synthesized by chemical oxidation of expanded graphite using modified Hummers method. Typically, 2.0 g of flake graphite (48 µm, 99.95% purity) and 1.5 g NaNO$_3$ (as co-solvent) were added into 250 mL round bottom flask, then 150 mL concentrated H$_2$SO$_4$ was added under stirring and ice-water bath conditions. Then 9.0 g of the oxidizing agent (KMnO$_4$) was slowly added into the suspension more than 2 h, the suspension was continually stirred for 5 d at room temperature. Then 280 mL of 5 wt % H$_2$SO$_4$ was added and the temperature was kept at 98 °C for 2 h. 12 mL of H$_2$O$_2$ (30 wt %) was added in the suspension when the temperature was reduced to 60 °C. After reactions, the mixture was centrifuged and washed with 10 wt % H$_2$SO$_4$ solution to remove residual metal ions. The precipitate was then washed with distilled water and centrifuged repeatedly until the solution became neutral. The GO was obtained by centrifuging at 18000 rpm for 60 min after ultrasonic treatment at 400 W for 30 min.

Characterization. The TiO$_2$ was further characterized by using X-ray diffraction (XRD) and size distribution. The GO was characterized by using transmission electron microscopy (TEM), Fourier-transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy and size distribution. The XRD pattern was recorded on a MAC Science Co. M18XHF diffractometer by using CuKα radiation (λ = 0.154 nm). The TEM image was obtained by a transmission electron microscope (JEM-1011, Japan). FTIR spectrum was performed by a Bruker
Tensor 27 FTIR spectrophotometer in the range of 4000 - 400 cm\(^{-1}\) using the KBr disc technique. XPS data was acquired with a Thermo Escalab 250 XPS with Al Kα radiation at 150 W. Raman spectroscopy was carried out on the InVia Reflex Raman spectrometer (Renishaw) at 532 nm.

The characterization results of TEM, FTIR, XPS and Raman of the prepared GO are given in Figure S2. The TEM image (Figure S2A) shows that GO nanosheets are closely agglomerated together by thin and randomly aggregated nanosheets. According to the FTIR spectrum (Figure S2B), the characteristic bands at 1060 cm\(^{-1}\) (C-O bond), 1228 cm\(^{-1}\) (C-O-C bond), 1400 cm\(^{-1}\) (C-OH vibration), 1622 cm\(^{-1}\) (stretching of benzene ring) and 1728 cm\(^{-1}\) (C=O stretching vibration) are found, which indicates that large amounts of oxygen-containing functional groups (hydroxyl, carboxyl, carbonyl and epoxy groups) are present on the surface of GO.\(^2\) The degree of oxidation with different functional groups is further demonstrated by XPS. The C\(_1\)s XPS spectrum of GO (Figure S2C) shows a dominant peak of sp\(^2\) C=C at 284.7 eV, which is attributed to the graphitic structure. Several small peaks of C-O at 286.1 eV and C=O at 288.7 eV are assigned to carbon atoms attached to different oxygen-containing moieties.\(^3\),\(^4\) Furthermore, the ratio of C-C/C-O/C=O calculated from the ratio of C-C/C-O/C=O XPS peak area is 10 : 3 : 1. The main features in the Raman spectrum are the so-called “G” and “D” peaks, which lie at around 1580 and 1350 cm\(^{-1}\), respectively, for visible excitation (Figure S2D). The “G” peak is assigned to the bond stretching mode for all pairs of sp\(^2\) atoms in both rings and chains. The “D” peak
is from the vibration of sp³ carbon atoms of defects and disorder. The weak and broad 2D peak at $\sim 2700 \text{ cm}^{-1}$ is another indication of disorder as the result of an out-of-plane vibration mode. The size diameter distribution of GO under different pH is shown in Figure S3. As the pH decreases from 3.0 to 1.0, the size diameter increases from 240 to 6700 nm, indicating large aggregation is formed which is consistent with the findings in the literatures.

In the XRD pattern of TiO$_2$ (Figure S4A), the peaks at 25.4°, 37.7°, 48.1°, 53.9°, 55.1° and 62.6° are indexed to the typical representations of the anatase phase of (101), (004), (200), (105), (211) and (204) reflections (JCPDS card No. 21-1272), respectively. The size diameter distribution of TiO$_2$ under different pH is shown in Figure S4B. The size of the TiO$_2$ is approximately 90 nm at the whole pH, indicating that TiO$_2$ is chemically stable in aquatic solution.

Computational Details.

The graphene model is built by the unit cell parameters of graphite: $a = b = 2.460 \text{ Å}$, $c = 6.800 \text{ Å}; \alpha = \beta = 90°, \gamma = 120°$ (Figure S5A). For the TiO$_2$, since the peaks in the XRD patterns of TiO$_2$ (Figure S4A) are well indexed to the structure of anatase (JCPDS card NO. 21-1272), we took the unit cell parameters of the anatase TiO$_2$ as $a = b = 3.776 \text{ Å}, c = 9.486 \text{ Å}; \alpha = \beta = \gamma = 90°$ (Figure S5B). A four-layer slab is used with the atoms in the bottom two layers are fixed to their bulk positions with a vacuum layer of 2.5 nm. In order to model the interaction between the GO and the TiO$_2$ surface, a rectangular supercell of graphene ($a' = 5b - 5a, b' = 3a + 3b$) is built.
to fit the 2 × 2 supercell of TiO$_2$ (101) surface, and the final lattice parameters of the graphene supercell are $a' = 21.304$ Å, $b' = 7.38$ Å. The GO is constructed randomly by oxygen atoms at the bridge site with a C : O ratio of 5 : 1. The optimized structures of GO and TiO$_2$ are shown in Figure S6A and S6B, respectively.

**Sorption Isotherms.** The sorption isotherms of GO and Cu(II) on TiO$_2$ at 293, 308 and 323 K are shown in Figure S7. The highest sorption isotherm is found at 323K and the lowest isotherm is found at 293K, suggesting that higher temperature is more conducive to GO and Cu(II) sorption on TiO$_2$. To quantify the sorption data and to gain a better understanding of the sorption mechanism, the Langmuir and Freundlich models are applied to simulate the experimental data. The Langmuir isotherm model usually describes the monolayer sorption process that takes place on a homogeneous surface. It can be expressed by the following equation:

$$q_e = \frac{bq_{max}C_e}{1 + bC_e}$$

(1)

where $q_{max}$ (mg/g) is the maximum sorption capacity, $b$ (L/mol) is a binding constant that relates to the heat of sorption. The Freundlich expression is an exponential equation that represents properly the sorption data at low and intermediate concentrations on heterogeneous surfaces. Its form can be expressed as:

$$q_e = K_F C_e^n$$

(2)

where $K_F$ (mg$^{1-n}$/L$^n$/g) represents the sorption capacity when the equilibrium concentration of GO and Cu(II) equals to 1, and $n$ represents the degree of dependence of sorption with equilibrium concentration. As shown in Table S1, GO
and Cu(II) sorption on TiO₂ can be satisfactorily fitted by Langmuir model ($R^2 > 0.9$) as compared to Freundlich model ($R^2 < 0.9$), indicating the monolayer sorption of GO and Cu(II) on TiO₂. The maximum sorption capacities ($q_{\text{max}}$) of GO and Cu(II) on TiO₂ calculated from Langmuir model are 60.0 and 32.3 mg/g at 293 K, respectively (Table S1). Furthermore, the sorption isotherm of Cu(II) on GO at 293 K is shown in Figure 1G and the $q_{\text{max}}$ value of Cu(II) on GO is calculated to be 45.2 mg/g. Comparing the sorption properties of Cu(II) on different materials (Table S3), one can see that the GO has higher sorption capacity due to its abundant functional groups such as hydroxyl, carboxyl and epoxy groups (Figure S2), which can form strong surface complexes with heavy metal ions.⁴,¹¹,¹² Thus, when Cu(II) coexist with GO in the aqueous solutions, they may influence each other.

The amounts of GO retained by TiO₂ for different addition sequences are shown in Figure 1E. The $q_{\text{max}}$ values of GO adsorbed on TiO₂ are in the order of (TiO₂-GO)-Cu > (GO-Cu)-TiO₂ > (TiO₂-Cu)-GO > TiO₂-GO. In the system of (TiO₂-Cu)-GO, the sorption of Cu(II) to TiO₂ particles increases the TiO₂ surface charge and enhances the sorption of negatively charged GO molecular to TiO₂-Cu. Therefore, the $q_{\text{max}}$ value of GO in (TiO₂-Cu)-GO system is higher than TiO₂-GO system. But, the surface-bound Cu(II) may block parts of active sites on TiO₂ surface and prevents GO from reaching them when added later due to the steric effects, hindering GO uptake. Although the firstly adsorbed Cu(II) ions occupy some sorption sites on GO, many oxygen containing groups on GO can still interact with terminal -OH on TiO₂ through
hydrogen bond. In addition, the GO in aqueous solutions can also interact with the unoccupied surface functional groups of TiO$_2$ and further improves the removal of GO, so the sorption capacity of GO in (GO-Cu)-TiO$_2$ system is higher than (TiO$_2$-Cu)-GO system. TiO$_2$ has stronger complexation ability with GO through electrostatic attraction and hydrogen bond than Cu(II) and the pre-adsorbed Cu(II) can lower the negative surface charge of GO, so the removal of GO is in the order of (TiO$_2$-GO)-Cu > (GO-Cu)-TiO$_2$.

From the sorption isotherms of Cu(II) on coexisting TiO$_2$ systems at different addition sequences (Figure 1F), the $q_{\text{max}}$ values of Cu(II) are calculated to be 56.0 mg/g for (TiO$_2$-GO)-Cu, 45.1 mg/g for (GO-Cu)-TiO$_2$, 42.8 for (TiO$_2$-Cu)-GO and 32.3 mg/g for TiO$_2$-Cu. In (TiO$_2$-Cu)-GO system, the Cu(II) ions are firstly adsorbed on TiO$_2$ through surface complexation, then the TiO$_2$-Cu complexes interact with GO through electrostatic attraction and hydrogen bond, and the remaining Cu(II) in the aqueous solutions can also interact with the oxygen-containing functional groups of GO. So, the $q_{\text{max}}$ value of Cu(II) in (TiO$_2$-Cu)-GO system is higher than single-adsorbate system. The sorption of Cu(II) in (GO-Cu)-TiO$_2$ system is similar to that of (TiO$_2$-Cu)-GO system. But due to its negatively charged surface and abundant oxygen-containing functional groups (e.g. OH and COO$^-$), GO can interact with more Cu(II) ions by electrostatic attraction and surface complexation as compared with TiO$_2$. Therefore, the $q_{\text{max}}$ value of Cu(II) on (GO-Cu)-TiO$_2$ is slightly higher than that of Cu(II) on (TiO$_2$-Cu)-GO. In the system of (TiO$_2$-GO)-Cu, the sorption of GO
molecules to TiO$_2$ particles decreases the TiO$_2$ surface charge and enhances the sorption of positively charged Cu(II) ions to TiO$_2$-GO. The surface adsorbed GO can also provide more functional groups and available sites to bind Cu(II) ions through the formation of surface complexes, and thereby results in more Cu(II) ions' sorption. The results indicate that GO plays an important role in the enhanced retention of Cu(II) on TiO$_2$ through the formation of strong surface complexes.

**Figure S1.** The UV-vis absorption curve of GO.
Figure S2. The characterization of GO: (A) TEM image; (B) FTIR spectrum; (C) C 1s XPS survey spectrum and (D) Raman spectrum.

Figure S3. Size diameter under different pH values.
**Figure S4.** The characterization of TiO$_2$: (A) XRD pattern; (B) Size diameter under different pH values.

**Figure S5.** The unit cell parameters of the GO (A) and TiO$_2$ (B).
Figure S6. The optimized structures for GO (A) and TiO$_2$ (B) from the top view and side view.

Figure S7. Sorption isotherms of Cu(II) (A) and GO (B) on TiO$_2$. pH = 5.0 ± 0.1, $I = 0.01$ mol/L NaNO$_3$, $m/V = 1$ g/L. The solid lines represent the Langmuir model. The dashed lines represent the Freundlich model.
Figure S8. Ti 2p XPS spectra of TiO₂, TiO₂+Cu, TiO₂+GO and TiO₂+GO+Cu.

Table S1. Parameters for the Langmuir and Freundlich isotherm models at different temperatures.

<table>
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<tr>
<th>Adsorbate</th>
<th>T (K)</th>
<th>q_{max} (mg/g)</th>
<th>b (L/mol)</th>
<th>R^2</th>
<th>K_F (mg^{1-n} L^n/g)</th>
<th>n</th>
<th>R^2</th>
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<tr>
<td>Cu(II)</td>
<td>293</td>
<td>32.3</td>
<td>0.07</td>
<td>0.954</td>
<td>5.1</td>
<td>0.41</td>
<td>0.825</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>35.1</td>
<td>0.12</td>
<td>0.920</td>
<td>7.7</td>
<td>0.34</td>
<td>0.738</td>
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<tr>
<td></td>
<td>323</td>
<td>37.9</td>
<td>0.19</td>
<td>0.932</td>
<td>10.9</td>
<td>0.30</td>
<td>0.716</td>
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<tr>
<td>GO</td>
<td>293</td>
<td>60.0</td>
<td>0.06</td>
<td>0.961</td>
<td>6.6</td>
<td>0.50</td>
<td>0.884</td>
</tr>
<tr>
<td></td>
<td>308</td>
<td>68.5</td>
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<td>0.960</td>
<td>8.5</td>
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<td>0.865</td>
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<tr>
<td></td>
<td>323</td>
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<td>0.10</td>
<td>0.965</td>
<td>11.6</td>
<td>0.46</td>
<td>0.868</td>
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Table S2. Binding energies (E_b) of elements in TiO₂ before and after removal of Cu(II) and GO.

<table>
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<tr>
<th>Sample</th>
<th>Ti2p</th>
<th>O1s</th>
<th>C1s</th>
<th>Cu2p</th>
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<tr>
<td>TiO₂</td>
<td>457.47</td>
<td>531.96</td>
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<tr>
<td>TiO₂+Cu</td>
<td>459.54</td>
<td>534.28</td>
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<td>TiO₂+GO</td>
<td>463.66</td>
<td>535.12</td>
<td>293.04</td>
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</tr>
<tr>
<td>Adsorbents</td>
<td>Experimental conditions</td>
<td>$q_{\text{max}}$ (mg/g)</td>
<td>References</td>
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<td>-----------------------------</td>
<td>-------------------------</td>
<td>--------------------------</td>
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<tr>
<td>TEPA modified carbon sphere</td>
<td>pH 5.0, T 298 K, m/V 10</td>
<td>33.33</td>
<td>[13]</td>
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<tr>
<td>LDH-Cl</td>
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<td>38.77</td>
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<td>montmorillonite</td>
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<td>14.87</td>
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<tr>
<td>Fe$_3$O$_4$</td>
<td>pH 5.0, T 293 K, m/V 0.4</td>
<td>11.89</td>
<td>[11]</td>
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<td>GO/Fe$_3$O$_4$</td>
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<td>18.26</td>
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<tr>
<td>TiO$_2$</td>
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<td>This study</td>
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<td>45.2</td>
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Table S3. Comparison of Cu(II) sorption capacities on different adsorbents.

References


