Single-step One-pot Synthesis of Graphene Foam/TiO$_2$ Nanosheet Hybrids for Effective Water Treatment

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Millions of tons of wastewater containing both inorganic and organic pollutants are generated every day, leading to significant social, environmental, and economic issues. Herein, we designed a graphene foam/TiO$_2$ nanosheet hybrid, which is able to effectively remove both chromium (VI) cations and organic pollutants simultaneously. This graphene foam/TiO$_2$ nanosheet hybrid was synthesized via a facile single-step one-pot hydrothermal method. The structure of the hybrid was characterized by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The hybrid was evaluated for both chromium (VI) and organic pollutants (using methyl blue (MB) as an example) removal, and the removal mechanism was also investigated. During water treatment, graphene and TiO$_2$ nanosheets function complimentarily, leading to a significant synergy. The hybrid exhibited outstanding chromium (VI) and MB removal capacity, much superior to the performance of the individual pure TiO$_2$ sheets or pure graphene foam. The hybrid could also be easily separated after water treatment, and exhibited excellent recycle stability. Considering the very facile synthesis of this graphene foam/TiO$_2$ nanosheet hybrid, and its excellent water treatment performance and recycle stability, such a hybrid is promising for large scale production for practical applications where both chromium (VI) cations and organic dyes are the main pollutants.
a much higher chromium (VI) removal efficiency can be achieved if the adsorbent can reduce the chromium (VI) to chromium (III). In this way, the adsorbent would never be saturated with chromium (VI) and can remove chromium (VI) continuously. Titanium dioxide, one of the most widely used photo-catalysts, has the ability to reduce chromium (VI) to chromium (III) under UV radiation. Moreover, TiO$_2$ is desirable because of its high efficiency, low cost, nontoxicity, and high stability. Nanoscale TiO$_2$ with a high specific surface area would be a particularly ideal choice for chromium (VI) removal.

Waste water also contains various of organic pollutants, including pesticides, herbicides, phenols, and dyes. Those pollutants could be removed by oxidation, ion exchange, electro-dialysis, electrolysis, adsorption, etc. Adsorption is considered one of the best methods to remove organic pollutants, because of its universality, as well as low cost and ease of operation. Carbon based materials (such as activated carbon, carbon nanotubes, etc.) have been used broadly as adsorbents owing to their high specific surface area. Graphene is a single atomic layer of graphite, which is composed of $sp^2$-hybridized carbon atoms. Graphene has gained significant attention due to its incredibly high specific surface area (theoretical value: 2620 m$^2$g$^{-1}$), high thermal conductivity, and outstanding electrical conductivity. Most of the pollutants are aromatic, which contain benzene rings and can be easily adsorbed on graphene surface due to π−π stacking effect. Graphene that adsorbed aromatic pollutants efficiently can help degrade many kinds of organics under UV light. Degradation reaction would happen after organic pollutants are adsorbed on graphene if TiO$_2$ is attached on graphene.

Since wastewater contains both inorganic and organic pollutants, it is ideal if they can be removed through a single process. To achieve this goal, herein we designed a nanostructured hybrid, graphene foam attached with TiO$_2$ nanosheets (graphene foam/TiO$_2$ nanosheet hybrid, abbreviated as G/TiO$_2$ hybrid) via a single-step one-pot hydrothermal method. For chromium (VI) removal, TiO$_2$ nanosheets can reduce hexavalent chromium to trivalent chromium. During this process, graphene can promote the electron mobility and render the light excited electron-hole pairs on TiO$_2$ nanosheets to separate more efficiently. As such, graphene foam and TiO$_2$ hybrid can improve electron transfer rate and thus expedite the degradation process. In addition to serving as a platform to help collect organic pollutants, graphene foams can improve electron transfer rate and thus expedite the degradation process. As such, graphene foam and TiO$_2$ nanosheets are complimentary to each other during both organic and inorganic pollutants removal. Furthermore, by designing a foam based structure, the hybrid can maintain a high removal efficiency owing to the high transport nature of the porous foam structure, as well as being easily separated from wastewater after treatment, leading to a facile and effective recycling process.

**Experimental Materials.** Graphite (Grafguard 160–50N) was obtained from GrafTech. Sulfuric acid (95.0–98.0%), phosphorus pentoxide (>98%), potassium persulfate (>99%), potassium permanganate (>99.0%), titanium n-butoxide (>99%), hydriodic acid (48–51%), and potassium dichromate (>99.0%) were purchased from Alfa Aesar and used as received without further purification.

**Synthesis of graphene foam.** A sample of 100 mg GO (made by the modified Hummers’ method) was charged into a beaker with 20 mL DI water. After ultrasonication, a stable GO suspension was obtained. Then the GO suspension was transferred into a 50 mL Teflon® lined autoclave and heated at 180 °C for 24 hours. After hydrothermal treatment, the suspension was filtrated and washed with DI water for 3 times, then dried under vacuum at room temperature for 24 hours.

**Synthesis of TiO$_2$ nanosheets.** A sample of 1.6 mL titanium n-butoxide was added into a Teflon® beaker together with 0.2 mL HF acid (48–51%). After stirring for 3 minutes, the solution was transferred into a Teflon® lined autoclave and hydrothermally treated for 24 hours at 180 °C. After the hydrothermal treatment, the dispersion was filtrated and washed with DI water for 3 times, then dried under vacuum at room temperature for 24 hours.

**Synthesis of G/TiO$_2$ hybrid.** A sample of 100 mg GO was charged into a Teflon® beaker with 20 mL DI water. After ultrasonication, the solution was transferred into a Teflon® lined autoclave and hydrothermally treated for 24 hours at 180 °C. After the hydrothermal treatment, the dispersion was filtrated and washed with DI water for 3 times, then dried under vacuum at room temperature for 24 hours.

**Characterization.** The morphology and structure of the samples were characterized by scanning electron microscopy (SEM, JEOL JSM-6335F FESMs with an accelerating voltage of 10 kV) and transmission electron microscopy (TEM, FEI Tecnai T12 with an accelerating voltage of 120 kV).

**Evaluation of chromium (VI) removal ability.** In this work, we choose fluorescent light as the light source for sample treatment out of the consideration of future practical applications. The ultraviolet radiation in fluorescent light is able to initiate the photocatalytic reaction for the removal of pollutants. A sample of 30 mg G/TiO$_2$ hybrid was added into 25.0 mL (400μg/L) potassium dichromate solution. After 4 hours of vigorous shaking under fluorescent light (SYLVANIA T5 fluorescent lamp, 28 W, 2 meters distance between the sample and lamp), 10.0 mL solution was collected and mixed with 0.2 mL phosphoric acid (85 wt%) and 0.5 mL coloring agent (1,5-diphenylcarbazide, DPC, 2.0 g/L). The obtained solution was analyzed by a UV-Vis spectrophotometer (Varian Cary 5000 UV-Vis NIR) by recording the absorbance. The absorbance of the characteristic peak at 540 nm
is proportional to the concentration of chromium (VI) ion according to the Lambert-Beer’s Law. After the first cycle of evaluation, the G/TiO₂ hybrid was collected by 2 minutes of gravity settling and subsequently washed by DI water for 3 times and dried in an oven. The dried G/TiO₂ hybrid was used for the next cycle of evaluation through the same procedures.

**Evaluation of MB removal ability.** A sample of 30 mg G/TiO₂ hybrid was mixed with 25.0 mL (10 mg/L) methyl blue (MB) solution. After 4 hours of vigorous shaking under fluorescent light, 5.0 mL solution was collected and subsequently diluted by 10.0 mL DI water. The obtained solution was analyzed by a UV-Vis spectrometer (Varian Cary 5000 UV-Vis NIR) by recording the absorbance. The absorbance of characteristic peak at 664 nm is proportional to the concentration of MB according to the Lambert-Beer’s Law. After the first cycle of evaluation, the G/TiO₂ hybrid was collected by gravity settling and subsequently washed by DI water for 3 times and dried in an oven. The dried G/TiO₂ hybrid was used for the next cycle of evaluation through the same procedures.

**Results and Discussion**

**Structure and morphology of G/TiO₂ hybrid.** Graphene can be synthesized as a form of foam via hydrothermal treatment of graphene oxide suspension. G/TiO₂ hybrid was synthesized via a similar approach by incorporating TiO₂ nanosheets. The morphology and structure of the G/TiO₂ hybrid was characterized by SEM and TEM. As presented in Fig. 1a and b, the G/TiO₂ hybrid shows a rough surface and a porous structure. After the hydrothermal reaction, the graphene oxide and TiO₂ nanosheets were condensed to a small cylinder-shaped foam, as shown in the inset of Fig. 1a. Under TEM, square-shaped TiO₂ nanosheets were uniformly dispersed on the surface of large graphene sheets, as shown in Fig. 1b. Graphene sheets also exhibited folds and wrinkles. The exact amount of graphene and TiO₂ in the synthesized hybrid was determined by thermogravimetric analysis to be 23.6 and 6.4 mg, respectively.

**Hexavalent chromium removal ability of G/TiO₂ hybrid.** Figure 2 shows the chromium (VI) removal evaluation results by the G/TiO₂ hybrid. Pure graphene foam and pure TiO₂ nanosheets were also synthesized and evaluated as controls. The results show that G/TiO₂ hybrid can remove chromium (VI) ions much more effectively compared to the two control samples. Pure graphene foam has virtually no adsorption ability, which is
expected. This also indicates that TiO$_2$ is the key component in the G/TiO$_2$ hybrid for chromium (VI) removal. Meanwhile, the results clearly show that the performance of the pure TiO$_2$ nanosheets is much inferior to that of the graphene/TiO$_2$ foam that contains the same amount of TiO$_2$ nanosheets, which is exactly as designed. This series of results show that the G/TiO$_2$ hybrid exhibited the designed synergy between the graphene foam and TiO$_2$ nanosheets. Graphene is a single layer of graphite composed of sp$^2$-hybridized carbon atoms, which possesses superior electron conductivity\textsuperscript{31}. Since the entire removal process is basically a photocatalytic reduction of chromium (VI) ions, the existence of graphene can expedite the separation rate of electron-hole pairs by rapidly conducting the light-excited electrons\textsuperscript{37}. In this way, the photocatalytic efficiency is improved significantly, thus G/TiO$_2$ hybrid demonstrates a much higher chromium (VI) removal rate than the pure TiO$_2$ sheets.

To further validate the efficiency of the G/TiO$_2$ hybrid for chromium (VI) removal, it was also evaluated with the same mass amount of TiO$_2$ nanosheets. As shown in Fig. 2, the chromium (VI) removal ability of 30 mg of G/TiO$_2$ hybrid (containing 23.6 g TiO$_2$ nanosheets) was even higher than that of 30 mg of pure TiO$_2$ nanosheets. This result further suggests that the existence of graphene can effectively speed up the reduction of chromium (VI) ions, thus increasing the practical capacity of TiO$_2$ nanosheets for chromium (VI) removal.

As discussed above, TiO$_2$ nanosheets can barely adsorb chromium (VI) ions physically; the main mechanism for chromium (VI) removal by TiO$_2$ nanosheets is photo-catalyzed reduction of hexavalent chromium to trivalent chromium under UV radiation\textsuperscript{21,22}. As such, we further evaluated the chromium (VI) removal efficiency of the TiO$_2$ sheets under both fluorescent light and dark. The TiO$_2$ nanosheets only removed a small amount of chromium (VI) ions under the dark condition, while it exhibited a much higher adsorption under the fluorescent light, as shown in Fig. 3. This result is expected and is consistent with our initial hypothesis. Figure 3 also shows the chromium (VI) removal capacity of the G/TiO$_2$ hybrid under fluorescent light and dark. The 30 mg G/TiO$_2$ hybrid removed less chromium (VI) ions under the dark compared to the 30 mg of pure TiO$_2$ nanosheets under the same conditions, which is probably because of the fact that there is only ca. 23.6 mg of TiO$_2$ nanosheets in the hybrid, and such TiO$_2$ nanosheets are less exposed to light, and meanwhile graphene cannot adsorb chromium (VI) ions. After applying room light, the removal capacity of the G/TiO$_2$ hybrid (containing ca. 23.6 mg of TiO$_2$ nanosheets) increased dramatically, even higher than that of the 30 mg of pure TiO$_2$ nanosheets. This result further shows the promoting effect of graphene on TiO$_2$ nanosheets for chromium (VI) ions removal, in which graphene can increase the electron mobility\textsuperscript{37}. As such, graphene can improve the photocatalytic efficiency of TiO$_2$ nanosheets and therefore chromium (VI) removal rate can be significantly enhanced.

The recycle evaluation result in Fig. 4 shows that the G/TiO$_2$ hybrid has an excellent recycle stability for chromium (VI) removal. The removal capacity in terms of percentage of chromium (VI) ions removed changed little after 5 cycles of operation. Since the adsorption mainly due to the photocatalytic degradation of chromium (VI) and limited physical adsorption of chromium (VI) ions on the G/TiO$_2$ hybrid, it is able to maintain excellent recycle stability.

**Methyl blue removal ability of G/TiO$_2$ hybrid.** Methyl blue (MB) was selected as a representative organic component to evaluate the organic pollutant removal capacity of the G/TiO$_2$ hybrid. The MB removal capability of 30 mg of G/TiO$_2$ hybrid (containing ca. 6.4 mg of graphene foam and 23.6 mg of TiO$_2$ nanosheets) was proved to be much higher compared to 6.4 mg of pure graphene foam only or 23.6 mg of pure TiO$_2$ nanosheets only, as shown in Fig. 5. Moreover, 30 mg of G/TiO$_2$ hybrid removed more MB than 30 mg of pure graphene foam only or 30 mg of pure TiO$_2$ sheets only, clearly showing the synergy between the two components.

Graphene foam is composed of graphene sheets. Since graphene sheets can adsorb organics, especially the ones with benzene rings due to π–π stacking effect, MB could be physically adsorbed by graphene foams. TiO$_2$ nanosheets can remove MB by photocatalytic degradation. This photocatalytic reaction requires photons to excite the electrons and further react with MB. The rate of the photocatalytic reaction could not meet the rate of physical adsorption of graphene. This explains why the pure graphene foam can remove more MB from solution compared
to the pure TiO<sub>2</sub> nanosheets (as shown in Fig. 5). The G/TiO<sub>2</sub> hybrid contains TiO<sub>2</sub> nanosheets attached on the surface of graphene. Under such a structure, graphene foam can adsorb MB to the surface and facilitate TiO<sub>2</sub> nanosheets to be in contact with MB. As a result, photocatalytic reaction occurred and the adsorbed MB was degraded, which opens space for additional MB molecules to be adsorbed by graphene foam and subsequently degraded by TiO<sub>2</sub> sheets. In addition, graphene can also help speed up the electron transfer rate in the photo-catalysis process<sup>37</sup>. Such coherent synergy between the physical adsorption by graphene sheets and the photo-catalyzed reduction by TiO<sub>2</sub> nanosheets lead to very effective MB removal by the G/TiO<sub>2</sub> hybrid.

To further investigate the photo-catalyzed degradation, the MB removal reaction was conducted under both fluorescent light and dark. The results showed that TiO<sub>2</sub> nanosheets can remove a small amount of MB even at dark (Fig. 6), which suggests that TiO<sub>2</sub> nanosheets can remove MB by physical adsorption as well. However, the overall MB removal capacity is relatively low. The result of MB removal capacity of the G/TiO<sub>2</sub> hybrid under room light and dark shows that a large percentage of MB molecules were removed by physical adsorption of both TiO<sub>2</sub> nanosheets and graphene foam while not applying the light. This is mainly contributed by the high physical adsorption capacity of graphene foam. However, nearly all MB molecules were removed when applying light. This result again confirms that the MB removal by G/TiO<sub>2</sub> hybrid is a combination of physical adsorption and photocatalytic degradation. TiO<sub>2</sub> can degrade MB while graphene can physically adsorb MB to its surface until saturated. For graphene/TiO<sub>2</sub> foam, the MB adsorbed on graphene foam can be degraded by TiO<sub>2</sub> nanosheets. Thus, graphene surface would not be saturated and thus can adsorb MB continuously. Meanwhile, TiO<sub>2</sub> nanosheets can degrade MB more rapidly with the help of graphene, since graphene can help improve electron transfer rate. As a result, there is an ideal synergistic effect between TiO<sub>2</sub> and graphene, leading to highly effective removal of MB.
Recycling is essential for adsorbents. It would be ideal if adsorbents can be used for many times while the efficiency remains high. The G/TiO$_2$ hybrid was designed to be used for multiple cycles because of its removal mechanism. Its overall foam structure also makes it easy to be separated from the water being treated. The recycle testing result (Fig. 7) shows that the G/TiO$_2$ hybrid has a very good recycle stability, while graphene foam lost part of adsorption ability after each cycle. This result is expected and can be explained by the different adsorption mechanisms of these two foams. Pure graphene foam can only physically adsorb MB to its surface, thus eventually will be saturated during the treatment. As a result, it will lose some MB removal ability after each cycle. For the G/TiO$_2$ hybrid, it is never the case. TiO$_2$ nanosheets can degrade the MB molecules adsorbed by graphene foam. In this way, graphene surface would always have open room for MB molecules, thus the adsorption process goes on and on.

Hexavalent chromium ions & methyl blue mixture removal ability of G/TiO$_2$ hybrid. As most wastewater contains both inorganic and organic pollutants, the synthesized G/TiO$_2$ hybrid was also evaluated for simultaneous removal of chromium (VI) ions and MB. Figure 8 displays the mixed adsorption of both pollutants by the G/TiO$_2$ hybrid. The results show that the G/TiO$_2$ hybrid can effectively remove both chromium (VI) ions and MB simultaneously and effectively. This results suggests that the G/TiO$_2$ hybrid are promising for practical applications where both chromium (VI) ions and organic pollutants present.

Conclusions
In this work, a G/TiO$_2$ hybrid was designed and synthesized through a single-step one-pot hydrothermal method. The hybrid exhibited excellent chromium (VI) and methyl blue (MB) removal ability compared to pure TiO$_2$ sheets or pure graphene foam. During water treatment, graphene foam and TiO$_2$ nanosheets function...
complimentarily, leading to a significant synergy. The hybrid could also be easily separated after water treatment, and exhibited excellent recycle stability. Considering the very facile synthesis of this G/TiO2 hybrid, and its excellent water treatment performance and recycle stability, such a hybrid is promising for large scale production for practical applications where both chromium (VI) cations and organic dyes are the main pollutants.

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Author Contributions
W.W., Z.Z., and L.S. conceived the idea and designed the research. Z.W. participated in the project design. W.W. conducted the experiments. J.L. conducted microscopy imaging of the samples. W.W. and L.S. wrote the first draft of the manuscript, and all authors contributed to revise the manuscript.

Additional Information
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