Photocatalytic Antifouling Graphene Oxide-Mediated Hierarchical Filtration Membranes with Potential Applications on Water Purification

Chao Xu,* Yuelian Xu, and Jiaoli Zhu

Research Institute of Photocatalysis, State Key Laboratory of Photocatalysis on Energy and Environment, Fuzhou University, Fuzhou 350002, P. R. China

Ⓢ *Supporting Information*

ABSTRACT: Graphene oxide-based filtration membranes with photocatalytic antifouling function have been successfully synthesized by a two-step method for the first time. First, graphene oxide particles composite sheets are prepared by decorating graphene oxide sheets with appropriate amount of TiO_2 nanoparticles, which can be assembled into filtration membranes with suitable permeation and retention rates. Then, an additional TiO_2 particle layer (P25) with strong photo-catalysis activity is coated on these films by filtration, forming hierarchical structure membranes. The filtration properties of the as-obtained films are investigated by treating dye solution, and the results demonstrate that these membranes possess favorable photocatalytic antifouling function under UV light irradiation, which can maintain the clean films and their filtration properties, broadening the horizon for the vast use of these graphene-involved films in water purification.

KEYWORDS: graphene oxide, TiO_2, filtration membrane, photocatalysis, antifouling,
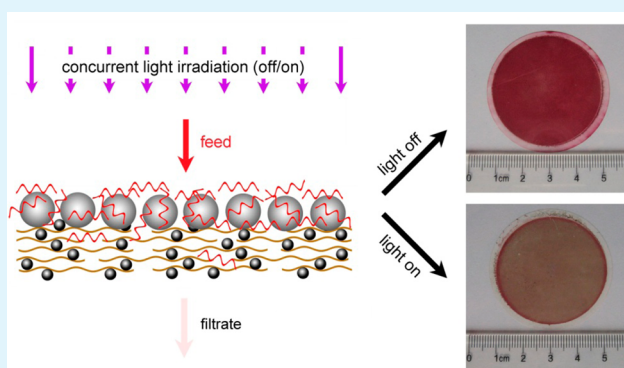
■ INTRODUCTION

Graphene-based films, which are obtained by assembling graphene-based sheets, are now drawing more and more attention in fields like optics, electricity, energy, sensors, and so forth.[1−4] Due to the ability to form unique two-dimensional nanochannels between these restacked sheets, graphene-based films have recently been considered as a kind of alternative separation membrane.[5−7] Commonly, these as-formed special channels, arising from the interactions between neighboring graphene-based sheets, are very fastidious with poor permeability, which limits their potential use as filtration membranes in water treatments.[8−10] By appropriate modification, the in-plane nanochannels between these carbon sheets can be adjusted to improve the percolation performances, which make the assembled filtration membranes more robust for the uses in separating ions, organic molecules, and nanoparticles from water.[11−14] For example, by using pure graphene sheets with special structure (such as wrinkle or pores) as starting materials, the as-formed channels in the films can be adjusted to be adaptable in filtration.[11,12] Additionally, organic molecules or nanoparticles are also utilized to modify these carbon sheets in order to broaden the interlayer spacing and improve water permeation performances of these assembled films.[13,14] Thus, graphene-based membranes with appropriate nanochannels have shown great potential applications as filtration membranes in environmental areas, especially for water treatment.

Despite of these advances, these graphene-based membranes also face a big obstacle in broadening their uses similar to traditional filtration films, that is, the membrane fouling caused by the accumulation of filtered contaminants (especially the organics), which is one of the main drawbacks for both research and industry in the field of membrane-based water treatments.[15−18] Such membrane fouling will reduce the filtration properties and durability of films if not cleaned. Therefore, how to remove the fouling in a timely and effective manner becomes a key point to keep the efficiency of the graphene-based filtration films in water purification.[19−21] Several approaches including chemical and physical methods have been adopted to clean traditional filtration membranes, whereas recovery of these fouled membranes will consume additional agents (for example, water or chemical agents) and time, which greatly affect the utilization efficiency of these films. Among a series of cleaning methods, photocatalysis technology seems to be an effective way utilized in decomposing organic contaminant, which can overcome those drawbacks mentioned above in cleaning the fouling membranes.[22−26] By endowing these films with photocatalysis properties, these intercepted substances can be decomposed quickly under light irradiation during the

filtration process, which can keep the membranes clean and improve their water treatment capacity.

As known, graphene-based membranes usually perform superior separation functions due to the circuitous nanochannels in these films. When using these membranes to filter wastewater, most of the contaminants could be effectively intercepted on their surfaces. It is reasonable to imagine that if an additional layer of photocatalysts existed on the surface of these graphene-based films, the intercepted fouling would be decomposed quickly by these catalysts under light irradiation, making these filtration membranes possess self-cleaning function. In fact, coating an additional layer on the surface has already been adopted to endow membranes with such character.[27−31] Therefore, it is feasible that graphene-based filtration membranes with an antifouling function could also be obtained by combining such surface photocatalysis technology.

Herein, we have prepared hierarchical graphene-based filtration membranes with photocatalytic antifouling function and investigated their potential uses in water purification. First, we prepared graphene-based filtration films with improved permeability by inserting appropriate nanoparticles between the restacking graphene oxide sheets. Then, additional photocatalysts with potent activity (P25) are further coated on the surface of these films by simple filtration, resulting in the formation of hierarchical filtration membranes. The filtration performances of these films are investigated by filter organic dyes (Direct Red 80 and Direct Blue 15). Results indicate that these as-prepared filtration membranes possess excellent photocatalytic antifouling function under UV light irradiation, which can effectively remove the intercepted dyes and maintain clean films and improve their filtration performance, showing their great potential applications in water purification.

■ EXPERIMENTAL SECTION

Graphene oxide (GO) sheets were prepared from purified natural graphite (Alfa-Aesar Co.) with mean particle size of 44 μm according to the method reported by Hummers and Offeman.[32]

GO-TiO$_2$ (GOT) composite sheets were prepared according to our previous work.[33] Typically, 30 mg of Ti(SO$_4$)$_2$ (Sinopharm Chemical Reagent Co.) were dispersed in 20 mL of GO dispersion (1 mg/mL), and the mixture was heated at 60 °C for 24 h. The products were centrifuged and washed with distilled water to remove any impurities. After that, the as-obtained samples were redispersed in water and the ammonia was added to the solution to increase the pH value to around 10, forming stable dispersions.

GOT filtration membranes were prepared by vacuum filtration of the as-prepared GOT dispersion (samples containing 0.2 mg of GO in 30 mL water were used as typical ones) through polycarbonate filter membranes (47 mm in diameter, 0.2 μm pore size, Millipore). The hierarchical filtration membranes were prepared by further vacuum filtration of TiO$_2$ suspension (1.5 mg of P25 nanoparticles in 10 mL of water) through the as-obtained GOT films, resulting in the formation of GOT/P25 hierarchical filtration membranes.

The filtration properties of our membranes were evaluated by filtering dye solution. Dye solution (Direct Red 80 or Direct Blue 15, 10 μmol/L, Sigma-Aldrich Co.) was poured on the top of the as-formed membranes, which was then subjected to continuous vacuum suction (with a pressure of around 1 bar) to allow the solution to flow through the membranes. The volume of filtrate was recorded to calculate of flux for filtration membranes, and the filtrate was examined by UV−vis spectroscopy to confirm the retention rate ($R\% = (1 − C_{filtrate}/C_{feed}) \times 100\%$).

The antifouling function of GOT/P25 films was evaluated by concurrent UV light irradiation on their surface (254 nm, the light intensity is about 10 mW/cm^2) during the aforementioned filtration process, and the analysis of flux and retention rate was similar to aforementioned ones.

Characterization. Powder X-ray diffraction (XRD) analyses were performed on a Bruker D8 Advance diffractometer with Cu Kα radiation. The diffraction data were recorded for 2θ angles between 5° and 80°. Thermogravimetric (TG) analyses were performed on NETZSCH thermogravimetric analyzer from 25 to 800 °C at a heating rate of 5 °C/min in air flow. The ultraviolet−visible (UV−vis) absorption spectra were carried out by Varian Cary 50 spectrophotometer. Specific surface areas were calculated from nitrogen adsorption and desorption isotherms conducted at 77 K in an ASAP 2020 M analyzer. Morphology analyses of samples were carried out on Tecnai G2 F20 S-TWIN Transmission Electron Microscope (TEM) and the Hitachi S8010 Field Emission Scanning Electron Microscope (FESEM). A TOC-VCPH analyzer (Shimadzu Co.) was used to analyze the total organic carbon of the degradation.

■ RESULTS AND DISCUSSION

Recent research has demonstrated that graphene-based films, especially GO films, have shown excellent separation properties due to the formation of two-dimensional nanochannels. However, these channels caused by the restacking of carbon sheets are so compact, which instead becomes an obstacle for the use of these films in filtration areas. Since flux properties are a key issue for the use of filtration membranes,[34−36] several efforts have been carried out to broaden the interlayer spacing of GO films in order to improve their percolation performance, for example, inserting organic molecules or nanoparticles between layers in GO.[13,14] The permeability of these membranes can be improved by the foreign support, while the separation ability will turn poor because of the damage of such unique two-dimensional channels. Generally, introduction of additional particles on the surface of GO sheets usually forbids these carbon sheets from being assembled into membranes, let alone the formation of these in-plane nanochannels.[37−40] As the schematic diagram shows in Figure 1, we assumed that if these GO sheets are decorated by
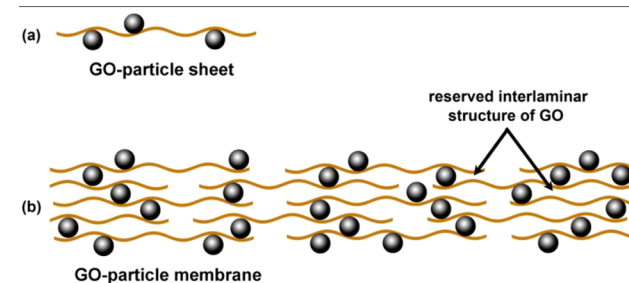

Figure 1. Schematic diagram of GO-particle sheet (a) and membrane (b) structure in our system.

relatively fewer particles, some parts of the interlaminar spacing of assembled films can be propped up by these particles, which will be beneficial for fluid permeation. Meanwhile, some parts of the in-plane nanochannels are reserved, which may contribute to separation effects.

Figure 2 shows TEM images of the as-prepared GO-TiO$_2$ (labeled as GOT) composite sheets. It can be seen that GO sheets are decorated sporadically by TiO$_2$ nanoparticles. Due to the low usage of Ti salt, the loading amount of TiO$_2$ on the surface of GO is also low (the usage weight ratio of GO to TiO$_2$ is about 1:0.5, which can be confirmed by the TG analysis through calculating the remaining mass after calcination under air condition (Figure 3a, and Figure S1, Supporting
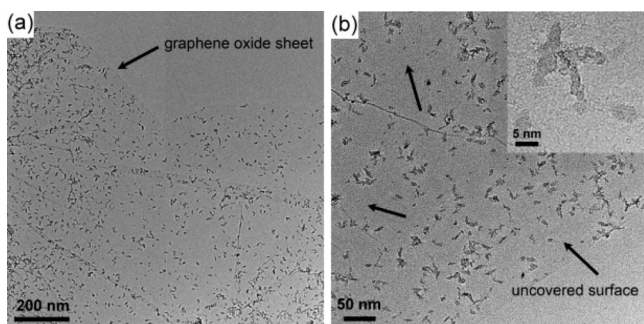
16118

dx.doi.org/10.1021/am5040945 | ACS Appl. Mater. Interfaces 2014, 6, 16117−16123

Figure 2. (a) and (b) display the TEM images of GOT composite sheets. Inset in (b) is the high-resolution TEM image of GOT.

Information (SI)). By magnifying these images, it is clearly seen that these attached nanoparticles are distant from each other, leaving some of the GO sheet surfaces unoccupied (as arrows shown in Figure 2b). Thus, when these composite sheets are assembled into films, such uncovered surfaces may restack with each other, forming the characteristic layer structure of GO again, as the arrows shown in Figure 1. Such structure indeed exists in these as-obtained GOT films, which can be confirmed by XRD analysis.[41,42] Figure 3b shows XRD patterns of GO and GOT films. By comparison, we can find that apart from the signals of TiO_2 (as labeled in Figure 3b), the characteristic layer structure of GO films (001 peak) still appeared in GOT films. Meanwhile, the intensity of this peak becomes relatively weak, which is probably due to these inserted particles disturbing the orderly restacking of GO sheets to some extent. (The low intensity of TiO_2 diffraction peaks is probably due to their poor crystallinity and low content.) Actually, the amount of the attached particles can be adjusted facilely by simply changing the usage of GO and Ti salt, which could also be used to control the layer structure in such films. For instance, the characteristic peak of GO films becomes weaker along with the increasing usage of TiO_2 (SI Figure S2), indicating total collapse of the two-dimensional channels left by loading more particles.

After inserting nanoparticles between the interlayer, the two-dimensional nanochannels are disrupted, which could directly affect the filtration performance of these particle-involved GOT films. On one hand, the compact interlayer of GO sheets is propped up partly by these inserted particles and the spacing between them is widened, which could improve the solvent penetrability of GOT films.[12–14] By filtering pure water, we

simply tested the permeability of the GOT films, and the results show the occurrence of enhanced flux of our films, which increases from about 27 $L \cdot h^{-1} \cdot m^{-2}$ of pure GO membranes to 78 $L \cdot h^{-1} \cdot m^{-2}$ of GOT membranes (the usage of GO sheets is about 0.2 mg). Thus, the water treatment capacity of these filtration membranes could be enhanced by the improvement of penetrability. We utilized direct red 80 (DR) solution as original feed to evaluate the filtration performance of these films, and the results are listed in Table 1. It can be found from

Table 1. Filtration Performance of GO and GOT Films Using DR Dye Solution As Feed for 30 min

entry	sample	usage of GO (mg)	DR solution (10 μmol/L, 35 mL)	
			flux ($L \cdot h^{-1} \cdot m^{-2}$)	retention rate (%)
1	GO	0.1	14.4 ± 0.2	79.1 ± 0.3
2	GO	0.2	10.8 ± 0.2	87.2 ± 1.2
3	GO	0.5	7.9 ± 0.1	98.8 ± 0.1
4	$GO-TiO_2$	0.1	48.8 ± 0.2	48.5 ± 0.7
5	$GO-TiO_2$	0.2	35.4 ± 0.1	58.1 ± 0.2
6	$GO-TiO_2$	0.5	28.2 ± 0.1	76.7 ± 0.2

Table 1 that when using the same amount of GO sheets, GOT films displayed higher permeate flux compared with that of pure GO films, which is attributed to the structural change of these nanochannels. For example, as entries 2 and 5 show, the flux of GOT membranes is about 35 $L \cdot h^{-1} \cdot m^{-2}$, which is about 3 times higher than that of pure GO membranes. On the other hand, the separation ability of films is kept by the reserved two-dimensional channels to certain extent. However, due to the damage to some channels, dye molecules can pass through films more easily, decreasing the retention rates of dye as shown in Table 1. Certainly, the usage of GOT composite sheets have certain influences on both the permeate flux and retention of the dye solution: the greater the amount used, the lower flux and the higher retention rates it exhibits. Such a tendency demonstrates that the filtration properties are controllable through the usage of our GOT films. It is noted that such filtration results are obtained by using a very low amount of sheets (containing 0.1−0.5 mg of GO), and the as-obtained GOT film (entry 5 sample in Table 1) is almost transparent even on a polycarbonate membrane as shown in Figure 4a. Thus, such thin filtration membranes with good separation performance may have their potential utilization in water treatment fields.[43–46]
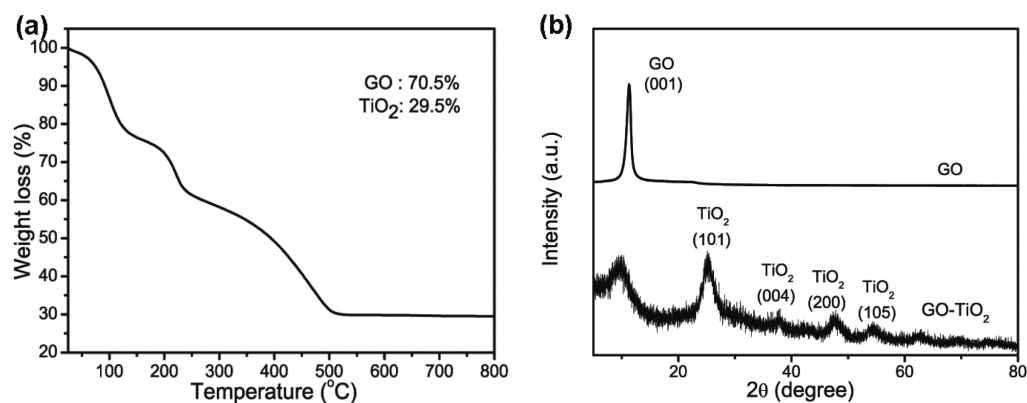

Figure 3. (a) TG analysis of GOT sample; (b) XRD patterns of GO and GOT films.
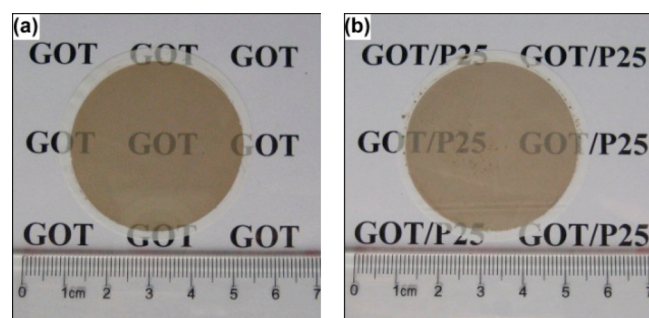
Figure 4. Digital photos of GOT (a) and GOT/P25 (b) membranes, and the usage of GO sheets in these samples is about 0.2 mg.

Though these GOT filtration membranes are promising in potential applications for water purification, they still present a problem in expanding their use, which is the membrane fouling causing by the deposition of organic pollutants on the membrane surface and/or the adsorption into the membranes. Both chemical and physical methods are tried to purify these films. Among these approaches, photocatalysis technology is considered to be an effective and promising way, for it could preserve membrane properties while moving away those organic contaminants at the same time. By combining photocatalysis technology, filtration membranes with self-cleaning functions are prepared, which can quickly remove the intercepted fouling and improve their water treatment ability.[22−24,26] Introduction of photocatalysis technology into these graphene-involved filtration membranes could admirably endow them with antifouling character[30] and improve their filtration performance.

Given that there are TiO_2 nanoparticles in our GOT membranes, we take Entry 5 samples in Table 1 as a model to investigate their filtration properties under concurrent UV light irradiation.[21,47,48] However, as the results in Table 2 (Entries 1

Table 2. Filtration Performance of GOT and GOT/P25 Membranes Using DR Dye Solution As Feed for 30 min with/without UV Light Irradiation

entry	sample[a]	light[b]	DR solution (10 μmol/L, 35 mL)	
			flux (L·h^{-1}·m^{-2})	retention rate (%)
1	GO-TiO$_2$	Off	35.4 ± 0.1	58.1 ± 0.2
2	GO-TiO$_2$	On	35.4 ± 0.7	58.2 ± 2.3
3	GO-TiO$_2$/P25	Off	31.8 ± 0.2	84.9 ± 1.1
4	GO-TiO$_2$/P25	On	28.2 ± 0.6	93.0 ± 2.3

[a]Usage of GO sheets in these samples is about 0.2 mg. [b]Light intensity is about 10 mW/cm^2, 254 nm.

and 2) show, the retention rates toward DR solution of GOT films are not increased obviously even under UV light irradiation, which is probably due to the low amount and poor crystallization of these TiO_2 particles (Figure 3b). Accordingly, it is speculated that these TiO_2 nanoparticles inserted into GOT films function mainly as supports, but not appropriate photocatalysts. As demonstrated, the usage of GO-based sheets in our experiments is very low (0.3 mg containing about 0.2 mg of GO); thus, the adsorption amount of dye by these films can be ignored, and as a result, most of the intercepted dyes are left on the surface of GOT films.[49−52] It is imaginable that addition of a photocatalytic layer on the surface

of such a membrane would be very helpful in removing these intercepted substances by using photocatalysis technology.[27−30]

It has already been demonstrated that graphene-based filtration membranes can intercept nanoparticles on their surface.[11] So it is feasible to apply the same filtration method to coat an additional particle layer on the surface of these films. By filtering dispersions containing nanoparticles (1.5 mg in 10 mL of water), we loaded conventional TiO_2 photocatalysts (Degussa, P25) on the surface of the as-obtained GOT films, forming unique hierarchical structure membranes (labeled as GOT/P25). Such hierarchical structure is confirmed by our morphology analysis. Figure 5 displays the FESEM images of
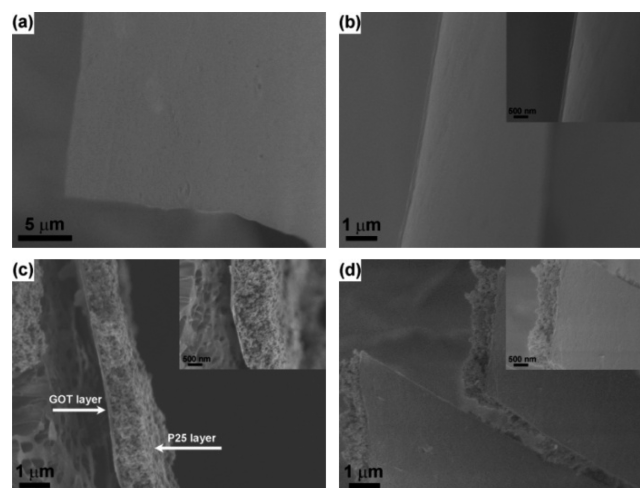

Figure 5. FESEM images of membranes (a) and (b) GOT, and (c) and (d) GOT/P25.

GOT and GOT/P25 films. Due to the low usage (0.2 mg of GO sheets) of GOT films, the thickness of the as-prepared GOT films is very thin (about 150 nm, as shown in Figure 5a,b), which is consistent with digital photos (Figure 4a). Figure 5c,d displays the typical GOT/P25 membranes. From Figure 5c, it can obviously be seen that apart from the GOT films, additional nanoparticle layers (about 1 μm thick) are formed on the surface of these GOT films, indicating the formation of GOT/P25 membranes with hierarchical structure. Furthermore, from the reverse side of such films (Figure 5d), it is found that P25 nanoparticles hardly pass through GOT films, which shows that these GOT filtration membranes can exclude these particles effectively on their surface (the pore size of GOT is about 3.5 nm; SI Figure S3). So, the control of coating thickness is rather easy just by simply adjusting the usage of the nanoparticles. Though coated by another layer, the as-obtained GOT/P25 membranes are thin enough, as transparent as GOT films (Figure 4b).

The filtration performance of GOT/P25 membranes is also investigated by filtering DR dye solutions (as control experiments, the filtration data of GO/P25 are listed in Supporting Information, Table S1). After loading P25, the flux of GOT/P25 films declined slightly, while the retention ratio increased obviously compared with that of GOT membranes (Entries 1 and 3 in Table 2). As shown in Figure 5c,d, these P25 nanoparticles assembled on the surface of GOT, forming an additional layer. Such a nanoparticle layer itself can both absorb some dyes (about 11.6%) and function as filter layer, which influences the filtration properties to some degree. Since the top layer possesses strong photocatalysis activity, the

intercepted molecular dye could be removed under light irradiation. We carried out the same filtration experiments of GOT/P25 membranes under concurrent UV light irradiation (Entry 4 in Table 2). We found that when filtering DR solution for 30 min, the retention rate further increased, indicating that photocatalytic degradation of the intercepted fouling works (P25 photocatalysts can generate reactive oxygen species such as photogenerated hole and superoxide radical under UV light irradiation; organic matter like these dyes can be decomposed effectively by these oxygen species.).[53,54] This is exactly beneficial for maintaining the clean film and its filtration properties.

In fact, due to the accumulation of filtered contaminants, membrane fouling will become aggravated gradually as the filtration time increases. In order to further reveal the photocatalytic antifouling functions of GOT/P25 filtration membranes, we carried out concurrent filtration and light irradiation during a relatively long process (we treated 150 mL of dye solution for 3.5 h).[23−25] Figure 6 displays typical digital
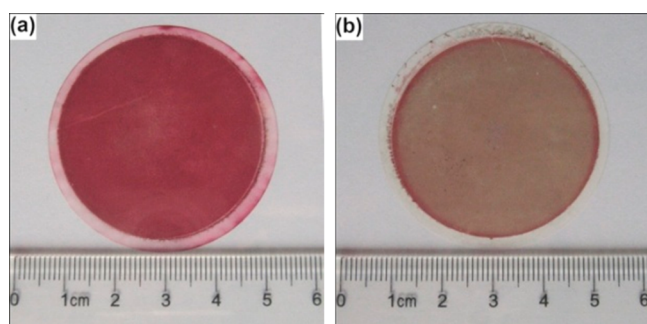

Figure 6. Typical digital photos of GOT/P25 films after filtration DR solution for 3.5 h without (a) and with (b) UV light irradiation.

photos of GOT/P25 membranes after filtering dye solution for 3.5 h with and without concurrent light irradiation. It is clearly seen that the traditional filtration process lead to obvious accumulation of contaminants on the membranes (Figure 6a), which is usually considered the biggest obstacle of using membrane filtration technology. However, with the assistance of photocatalysis, these films are kept relatively clean by effective removal of intercepted fouling (Figure 6b), successfully forming photocatalytic antifouling graphene oxide-mediated filtration membranes. Owning such antifouling function, these GOT/P25 films will perform well in water treatments. As the results show in Figure 7 (solid circle), when

we only use these GOT/P25 membranes to filter the dye solution, the flux and the retention rate gradually become lower along with the increase of filtration time. However, when introducing concurrent UV light irradiation, the filtration performance of these GOT/P25 membranes is quite different from the ones without light irradiation. From Figure 7 (solid square), we can see that both water penetrability and retention rates of GOT/P25 membranes decline but flatten later. Especially, the retention rate almost maintains a high level (around 85%). Such phenomena are probably due to gradual removal of the accumulated fouling on films by P25 photocatalysts under UV light irradiation, maintaining their filtration performance to a certain extent. By comparing the filtrate in SI Figure S4, it is found that the filtrate obtained under light irradiation is very clear, and the total organic carbon (TOC) analyses show that the filter liquor is also clean (SI Table S2).

Additionally, the independent photocatalysis property test of GOT/P25 membranes is also carried out under ordinary pressure as control experiment (without suction filtration). After irradiating for 3.5 h, the retention rate of DR dye in the solution is about 45%, which is much lower than the ones that combined with light irradiation (85%, Figure 6b). Such results demonstrate that the synergistic effects of filtration and photocatalysis contribute to high effeciency for water treatment using these GOT/P25 films in our experiments.[55−58] Furthermore, similar phenomena, especially the retention rate, are also found when using Direct Blue 15 dye solution as feed solutions (little difference is probably caused by the smaller molecular weight of blue dye), as shown in SI Figure S5, indicating promising applications for using these filtration membranes in wastewater purification.

Our results exhibit that by combining with photocatalysis, graphene-based filtration membranes exhibit antifouling function and enhanced wastewater treatment capacity, expanding the use of these graphene-based films. Furthermore, it can be imagined that by appropriate modification (for example, adjusting the properties of inserted nanoparticles and hierarchical layers, carbon sheets etc.), we could endow these graphene-involved filtration membranes with more flexible functions, such as visible light response, solvent resistance, antibacterial property, etc., making them promising multifunctional separation membranes. Accordingly, it is probable to develop many new and useful high-performance graphene-involved membranes, opening up enormous opportunities for the use of them in water treatment areas.[59,60]
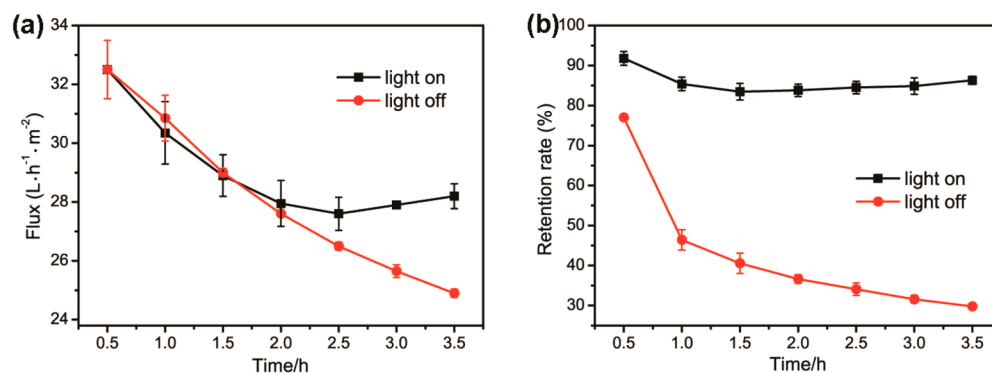

Figure 7. Flux (a) and retention rate (b) of GOT/P25 filtration membranes with and without UV light irradiation using DR 80 as feed.

CONCLUSION

In summary, graphene oxide-involved hierarchical filtration membranes with photocatalytic antifouling function have been prepared successfully. First, GOT membranes with appropriate penetrability and retention rate are prepared by using TiO_2 nanoparticle decorated GO sheets as building blocks. Then, an additional photocatalytic particle layer is loaded on the surface of these GOT membranes by filtering TiO_2 (P25) suspension, resulting in the formation of GOT/P25 filtration membranes. The filtration properties of GOT/P25 films are evaluated by filtering dye solution (Direct Red and Blue), and the results indicate that after integrating with photocatalysis, these GOT/P25 filtration membranes possess a photocatalytic antifouling function under concurrent UV light irradiation, which can effectively reduce the impacts of accumulated fouling to these filtration membranes and obviously enhance their water treatment ability.

This work demonstrates that it is feasible to endow graphene-involved filtration membranes with useful functions, such as antifouling character. It is assumed that a strategy of combination of filtration with photocatalysis technologies into graphene-involved films can be extended to prepare some other multifunctional membranes, qualifying them as the next-generation membrane for water separation applications.

ASSOCIATED CONTENT

Ⓢ Supporting Information

TG analysis of GO and GOT/P25, XRD patterns of GOT composite films with different weight ratios of GO and TiO_2, nitrogen adsorption−desorption isotherms and pore size distribution curve of GOT, filtration performance of GO/P25 films, digital photos and TOC values of the filtrate after DR dye solution passing through GOT/P25 filtration membranes, the flux and retention rate of GOT/P25 filtration membranes with and without UV light irradiation using Direct Blue15 as feed solution. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: cxu@fzu.edu.cn.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

REFERENCES

(1) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Ahn, J. H.; Kim, P.; Choi, J. Y.; Hong, B. H. Large-Scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes. *Nature* **2009**, *457*, 706−710.

(2) Dikin, D. A.; Stankovich, S.; Zimney, E. J.; Piner, R. D.; Dommett, G. H. B.; Evmenenko, G.; Nguyen, S. T.; Ruoff, R. S. Preparation and Characterization of Graphene Oxide Paper. *Nature* **2007**, *448*, 457−460.

(3) Hu, W.; Peng, C.; Luo, W.; Lv, M.; Li, X.; Li, D.; Huang, Q.; Fan, C. Graphene-Based Antibacterial Paper. *ACS Nano* **2010**, *4*, 4317−4323.

(4) Guo, S.; Dong, S. Graphene Nanosheet: Synthesis, Molecular Engineering, Thin Film, Hybrids, and Energy and Analytical Applications. *Chem. Soc. Rev.* **2011**, *40*, 2644−2672.

(5) Nair, R. R.; Wu, H. A.; Jayaram, P. N.; Grigorieva, I. V.; Geim, A. K. Unimpeded Permeation of Water through Helium-Leak-Tight Graphene-Based Membranes. *Science* **2012**, *335*, 442−444.

(6) Li, H.; Song, Z.; Zhang, X.; Huang, Y.; Li, S.; Mao, Y.; Ploehn, H. J.; Bao, Y.; Yu, M. Ultrathin, Molecular-Sieving Graphene Oxide Membranes for Selective Hydrogen Separation. *Science* **2013**, *342*, 95−98.

(7) Kim, H. W.; Yoon, H. W.; Yoon, S.-M.; Yoo, B. M.; Ahn, B. K.; Cho, Y. H.; Shin, H. J.; Yang, H.; Paik, U.; Kwon, S.; Choi, J.-Y.; Park, H. B. Selective Gas Transport through Few-Layered Graphene and Graphene Oxide Membranes. *Science* **2013**, *342*, 91−95.

(8) Kim, H.; Miura, Y.; Macosko, C. W. Graphene/Polyurethane Nanocomposites for Improved Gas Barrier and Electrical Conductivity. *Chem. Mater.* **2010**, *22*, 3441−3450.

(9) Guo, F.; Silverberg, G.; Bowers, S.; Kim, S.-P.; Datta, D.; Shenoy, V.; Hurt, R. H. Graphene-Based Environmental Barriers. *Environ. Sci. Technol.* **2012**, *46*, 7717−7724.

(10) Yang, Y.-H.; Bolling, L.; Priolo, M. A.; Grunlan, J. C. Super Gas Barrier and Selectivity of Graphene Oxide-Polymer Multilayer Thin Films. *Adv. Mater.* **2013**, *25*, 503−508.

(11) Qiu, L.; Zhang, X.; Yang, W.; Wang, Y.; Simon, G. P.; Li, D. Controllable Corrugation of Chemically Converted Graphene Sheets in Water and Potential Application for Nanofiltration. *Chem. Commun.* **2011**, *47*, 5810−5812.

(12) Han, Y.; Xu, Z.; Gao, C. Ultrathin Graphene Nanofiltration Membrane for Water Purification. *Adv. Funct. Mater.* **2013**, *23*, 3693−3700.

(13) Hu, M.; Mi, B. Enabling Graphene Oxide Nanosheets as Water Separation Membranes. *Environ. Sci. Technol.* **2013**, *47*, 3715−3723.

(14) Xu, C.; Cui, A.; Xu, Y.; Fu, X. Graphene Oxide-TiO_2 Composite Filtration Membranes and Their Potential Application for Water Purification. *Carbon* **2013**, *62*, 465−471.

(15) Van der Bruggen, B.; Mänttäri, M.; Nyström, M. Drawbacks of Applying Nanofiltration and How to Avoid Them: A Review. *Sep. Purif. Technol.* **2008**, *63*, 251−263.

(16) Rana, D.; Matsuura, T. Surface Modifications for Antifouling Membranes. *Chem. Rev.* **2010**, *110*, 2448−2471.

(17) Vatanpour, V.; Madaeni, S. S.; Moradian, R.; Zinadini, S.; Astinchap, B. Fabrication and Characterization of Novel Antifouling Nanofiltration Membrane Prepared from Oxidized Multiwalled Carbon Nanotube/Polyethersulfone Nanocomposite. *J. Membr. Sci.* **2011**, *375*, 284−294.

(18) Yu, L.; Zhang, Y.; Zhang, B.; Liu, J.; Zhang, H.; Song, C. Preparation and Characterization of Hpei-Go/Pes Ultrafiltration Membrane with Antifouling and Antibacterial Properties. *J. Membr. Sci.* **2013**, *447*, 452−462.

(19) Zhao, H.; Wu, L.; Zhou, Z.; Zhang, L.; Chen, H. Improving the Antifouling Property of Polysulfone Ultrafiltration Membrane by Incorporation of Isocyanate-Treated Graphene Oxide. *Phys. Chem. Chem. Phys.* **2013**, *15*, 9084−9092.

(20) Zinadini, S.; Zinatizadeh, A. A.; Rahimi, M.; Vatanpour, V.; Zangeneh, H. Preparation of a Novel Antifouling Mixed Matrix Pes Membrane by Embedding Graphene Oxide Nanoplates. *J. Membr. Sci.* **2014**, *453*, 292−301.

(21) Zhu, J.; Cao, Y.; He, J. Facile Fabrication of Transparent, Broadband Photoresponse, Self-Cleaning Multifunctional Graphene-TiO_2 Hybrid Films. *J. Colloid Interface Sci.* **2014**, *420*, 119−126.

(22) Xi, B.; Verma, L. K.; Li, J.; Bhatia, C. S.; Danner, A. J.; Yang, H.; Zeng, H. C. TiO_2 Thin Films Prepared Via Adsorptive Self-Assembly for Self-Cleaning Applications. *ACS Appl. Mater. Interfaces* **2012**, *4*, 1093−1102.

(23) Zhang, T.; Wang, Y. J.; Ng, J. W.; Sun, D. D. A Free-Standing, Hybrid TiO_2/K-Oms-2 Hierarchical Nanofibrous Membrane with High Photocatalytic Activity for Concurrent Membrane Filtration Applications. *RSC Adv.* **2012**, *2*, 3638−3641.

16122

dx.doi.org/10.1021/am5040945 | *ACS Appl. Mater. Interfaces* 2014, 6, 16117−16123

(24) Liu, L.; Liu, Z. Y.; Bai, H. W.; Sun, D. D. Concurrent Filtration and Solar Photocatalytic Disinfection/Degradation Using High-Performance Ag/TiO_2 Nanofiber Membrane. *Water Res.* 2012, 46, 1101−1112.

(25) Zhang, X. W.; Du, A. J.; Lee, P. F.; Sun, D. D.; Leckie, J. O. TiO_2 Nanowire Membrane for Concurrent Filtration and Photocatalytic Oxidation of Humic Acid in Water. *J. Membr. Sci.* 2008, 313, 44−51.

(26) Zhu, L.; Gu, L.; Zhou, Y.; Cao, S.; Cao, X. Direct Production of a Free-Standing Titanate and Titania Nanofiber Membrane with Selective Permeability and Cleaning Performance. *J. Mater. Chem.* 2011, 21, 12503−12510.

(27) Ganesh, V. A.; Raut, H. K.; Nair, A. S.; Ramakrishna, S. A Review on Self-Cleaning Coatings. *J. Mater. Chem.* 2011, 21, 16304−16322.

(28) Zhang, X. T.; Sato, O.; Taguchi, M.; Einaga, Y.; Murakami, T.; Fujishima, A. Self-Cleaning Particle Coating with Antireflection Properties. *Chem. Mater.* 2005, 17, 696−700.

(29) Damodar, R. A.; You, S.-J.; Chou, H.-H. Study the Self Cleaning, Antibacterial and Photocatalytic Properties of TiO_2 Entrapped Pvdf Membranes. *J. Hazard. Mater.* 2009, 172, 1321−1328.

(30) Anandan, S.; Rao, T. N.; Sathish, M.; Rangappa, D.; Honma, I.; Miyauchi, M. Superhydrophilic Graphene-Loaded TiO_2 Thin Film for Self-Cleaning Applications. *ACS Appl. Mater. Interfaces* 2013, 5, 207−212.

(31) Gao, Y.; Hu, M.; Mi, B. Membrane Surface Modification with TiO_2-Graphene Oxide for Enhanced Photocatalytic Performance. *J. Membr. Sci.* 2014, 455, 349−356.

(32) Hummers, W. S.; Offeman, R. E. Preparation of Graphitic Oxide. *J. Am. Chem. Soc.* 1958, 80, 1339−1339.

(33) Xu, C.; Chen, Z.; Fu, X. Graphene Oxide-Mediated Formation of Freestanding, Thickness Controllable Metal Oxide Films. *J. Mater. Chem.* 2011, 21, 12889−12893.

(34) Zhang, J.; Xu, Z.; Mai, W.; Min, C.; Zhou, B.; Shan, M.; Li, Y.; Yang, C.; Wang, Z.; Qian, X. Improved Hydrophilicity, Permeability, Antifouling and Mechanical Performance of Pvdf Composite Ultra-filtration Membranes Tailored by Oxidized Low-Dimensional Carbon Nanomaterials. *J. Mater. Chem. A* 2013, 1, 3101−3111.

(35) Jin, F.; Lv, W.; Zhang, C.; Li, Z.; Su, R.; Qi, W.; Yang, Q.-H.; He, Z. High-Performance Ultrafiltration Membranes Based on Polyethersulfone-Graphene Oxide Composites. *RSC Adv.* 2013, 3, 21394−21397.

(36) Zhao, C.-Q.; Xu, X.-C.; Li, R.-Y.; Chen, J.; Yang, F.-L. Highly Effective Permeability and Antifouling Performances of Polypropylene Non-Woven Fabric Membranes Modified with Graphene Oxide by Inkjet Printing and Immersion Coating Methods. *Water Sci. Technol.* 2013, 67, 2307−2313.

(37) Xu, C.; Wang, X. Fabrication of Flexible Metal-Nanoparticte Film Using Graphene Oxide Sheets as Substrates. *Small* 2009, 5, 2212−2217.

(38) Xiang, J.; Drzal, L. T. Electron and Phonon Transport in Au Nanoparticle Decorated Graphene Nanoplatelet Nanostructured Paper. *ACS Appl. Mater. Interfaces* 2011, 3, 1325−1332.

(39) Li, Z.; Wang, J.; Liu, X.; Liu, S.; Ou, J.; Yang, S. Electrostatic Layer-by-Layer Self-Assembly Multilayer Films Based on Graphene and Manganese Dioxide Sheets as Novel Electrode Materials for Supercapacitors. *J. Mater. Chem.* 2011, 21, 3397−3403.

(40) He, H.; Gao, C. Supraparamagnetic, Conductive, and Processable Multifunctional Graphene Nanosheets Coated with High-Density Fe_3O_4 Nanoparticles. *ACS Appl. Mater. Interfaces* 2010, 2, 3201−3210.

(41) Nethravathi, C.; Rajamathi, M. Delamination, Colloidal Dispersion and Reassembly of Alkylamine Intercalated Graphite Oxide in Alcohols. *Carbon* 2006, 44, 2635−2641.

(42) Jeong, H. K.; Lee, Y. P.; Lahaye, R. J. W. E.; Park, M. H.; An, K. H.; Kim, I. J.; Yang, C. W.; Park, C. Y.; Ruoff, R. S.; Lee, Y. H. Evidence of Graphitic Ab Stacking Order of Graphite Oxides. *J. Am. Chem. Soc.* 2008, 130, 1362−1366.

(43) Stanton, B. W.; Harris, J. J.; Miller, M. D.; Bruening, M. L. Ultrathin, Multilayered Polyelectrolyte Films as Nanofiltration Membranes. *Langmuir* 2003, 19, 7038−7042.

(44) Wang, L.; Travis, J. J.; Cavanagh, A. S.; Liu, X.; Koenig, S. P.; Huang, P. Y.; George, S. M.; Bunch, J. S. Ultrathin Oxide Films by Atomic Layer Deposition on Graphene. *Nano Lett.* 2012, 12, 3706−3710.

(45) Peng, X. S.; Karan, S.; Ichinose, I. Ultrathin Nanofibrous Films Prepared from Cadmium Hydroxide Nanostrands and Anionic Surfactants. *Langmuir* 2009, 25, 8514−8518.

(46) Chang, H.; Sun, Z.; Yuan, Q.; Ding, F.; Tao, X.; Yan, F.; Zheng, Z. Thin Film Field-Effect Phototransistors from Bandgap-Tunable, Solution-Processed, Few-Layer Reduced Graphene Oxide Films. *Adv. Mater.* 2010, 22, 4872−4876.

(47) Kim, I. Y.; Park, S.; Kim, H.; Park, S.; Ruoff, R. S.; Hwang, S.-J. Strongly-Coupled Freestanding Hybrid Films of Graphene and Layered Titanate Nanosheets: An Effective Way to Tailor the Physicochemical and Antibacterial Properties of Graphene Film. *Adv. Funct. Mater.* 2014, 24, 2288−2294.

(48) Williams, G.; Seger, B.; Kamat, P. V. TiO_2-Graphene Nanocomposites. Uv-Assisted Photocatalytic Reduction of Graphene Oxide. *ACS Nano* 2008, 2, 1487−1491.

(49) Chen, Y.; Chen, L.; Bai, H.; Li, L. Graphene Oxide-Chitosan Composite Hydrogels as Broad-Spectrum Adsorbents for Water Purification. *J. Mater. Chem. A* 2013, 1, 1992−2001.

(50) Wei, G.; Miao, Y.-E.; Zhang, C.; Yang, Z.; Liu, Z.; Tjiu, W. W.; Liu, T. Ni-Doped Graphene/Carbon Cryogels and Their Applications as Versatile Sorbents for Water Purification. *ACS Appl. Mater. Interfaces* 2013, 5, 7584−7591.

(51) Upadhyay, R. K.; Soin, N.; Roy, S. S. Role of Graphene/Metal Oxide Composites as Photocatalysts, Adsorbents and Disinfectants in Water Treatment: A Review. *RSC Adv.* 2014, 4, 3823−3851.

(52) Zhao, J.; Ren, W.; Cheng, H.-M. Graphene Sponge for Efficient and Repeatable Adsorption and Desorption of Water Contaminations. *J. Mater. Chem.* 2012, 22, 20197−20202.

(53) Akhavan, O.; Choobtashani, M.; Ghaderi, E. Protein Degradation and Rna Efflux of Viruses Photocatalyzed by Graphene−Tungsten Oxide Composite under Visible Light Irradi-ation. *J. Phys. Chem. C* 2012, 116, 9653−9659.

(54) Du, J.; Lai, X.; Yang, N.; Zhai, J.; Kisailus, D.; Su, F.; Wang, D.; Jiang, L. Hierarchically Ordered Macro−Mesoporous TiO_2−Graphene Composite Films: Improved Mass Transfer, Reduced Charge Recombination, and Their Enhanced Photocatalytic Activities. *ACS Nano* 2010, 5, 590−596.

(55) Jung, J. T.; Kim, J. O.; Choi, J. Y. Effect of Various Oxidants in a Photocatalysis/Filtration System for the Treatment of Contaminants. *Res. Chem. Intermed.* 2009, 35, 243−248.

(56) Djafer, L.; Ayral, A.; Ouagued, A. Robust Synthesis and Performance of a Titania-Based Ultrafiltration Membrane with Photocatalytic Properties. *Sep. Purif. Technol.* 2010, 75, 198−203.

(57) Huang, X.; Meng, Y.; Liang, P.; Qian, Y. Operational Conditions of a Membrane Filtration Reactor Coupled with Photocatalytic Oxidation. *Sep. Purif. Technol.* 2007, 55, 165−172.

(58) Sun, D.; Meng, T. T.; Loong, T. H.; Hwa, T. J. Removal of Natural Organic Matter from Water Using a Nano-Structured Photocatalyst Coupled with Filtration Membrane. *Water Sci. Technol.* 2004, 49, 103−110.

(59) Zhang, T.; Liu, J.; Sun, D. D. A Novel Strategy to Fabricate Inorganic Nanofibrous Membranes for Water Treatment: Use of Functionalized Graphene Oxide as a Cross Linker. *RSC Adv.* 2012, 2, 5134−5137.

(60) Crock, C. A.; Rogensues, A. R.; Shan, W.; Tarabara, V. V. Polymer Nanocomposites with Graphene-Based Hierarchical Fillers as Materials for Multifunctional Water Treatment Membranes. *Water Res.* 2013, 47, 3984−3996.

16123

dx.doi.org/10.1021/am5040945 | *ACS Appl. Mater. Interfaces* 2014, 6, 16117−16123