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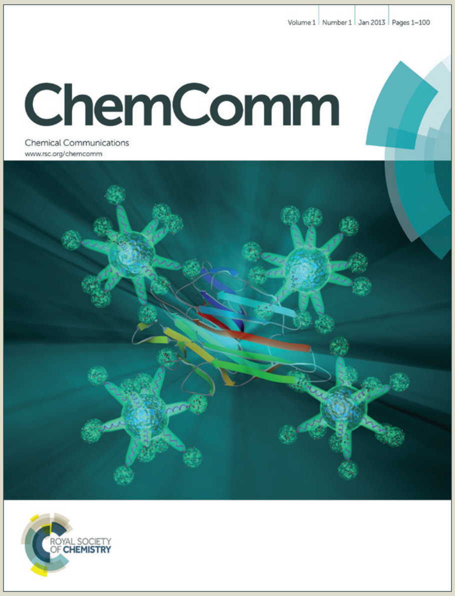

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Tuning underwater oleophobicity of graphene oxide coatings via UV irradiation†

Cite this: DOI: 10.1039/x0xx00000x

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Received xxth 2014,
Accepted xth 2014

DOI: 10.1039/x0xx00000x

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Ultraviolet (UV) was utilized to gradually modify the chemistry and structure of graphene oxide (GO) flakes, as confirmed by XPS and AFM. Ultrathin GO coatings/membranes, made from UV-irradiated flakes, showed tunable underwater oleophobicity. UV-treated, superoleophobic GO membrane exhibited excellent antifouling capability for oil/water separation

Surfaces with controllable underwater oil-adhesion have attracted great attention due to their potential applications in oil/water separation, oil-repellent materials, microfluidic devices, anti-bioadhesion materials, and robust antifouling materials.[1-4] Fish scales are well known to own the underwater superoleophoic/low oil adhesive properties. Studies on fish scales have shown hydrophilic mucus layer and micro/nanoscaled surface roughness are essential for their superior performance.[5] Consistently, underwater oil wettability on a solid surface has been found to depend strongly on the surface chemical composition and roughness.[5, 6] Graphene oxide (GO) is a well-known hydrophilic material due to its unique chemistry.[7] Oxygen-containing functional groups, such as carboxyl, carbonyl, hydroxyl and epoxy, are distributed at edges and structural defects of GO flakes. Therefore, GO flakes with fine-tuned chemistry and roughness are promising material for fabricating surfaces with desired underwater oleophobicity.

Oxidative etching has been proven as an effective way to create or enlarge structural defects on graphene-based materials.[8, 9] Generated defects increased the nano-scaled roughness on the single GO flakes.[10] In addition, oxidative etching also improved the hydrophilicity of GO, probably resulting from the introduced oxygen groups around the expanded and/or newly-generated defects.[7, 11] Oxidative etching, therefore, seems a viable way of controlling underwater oleophobicity of GO by modifying GO morphology and hydrophilicity. However, precise control of the hydrophilicity/ underwater oleophobicity of GO via oxidative etching has not been reported. One potential reason could be that etching reaction is in oxidative gas phase, which usually proceeds fast and is difficult to control.[8, 9] Also, only single or few-layered graphene-based suspended flakes or coatings, instead of powder, have been etched uniformly in gas phase,[8, 10] which may limit their large-scale productivity for potential applications. Here, we report the novel use of ultraviolet (UV) light to controllably modify the chemistry and structure of GO flakes in aqueous media. UV irradiation has been proved capable of either reducing or oxidizing graphene-based materials, depending on the reducing or oxidative nature of the surrounding environment.[12-18] We demonstrate that by simply controlling the UV etching time for dispersed GO flakes in water, the resulting GO coatings can be converted into underwater superoleophobic coatings. In addition, this method is very promising for large-scale production. The probable mechanism of UV oxidative etching can be that ozone molecules, generated by UV activation, adsorb onto the local pristine graphene region on GO and react with its surface to form oxygen-containing groups and create defects by breaking C-C bonds, as suggested by previous studies.[15-17] Cyclic oil/water separation tests of the UV-treated, superoleophobic GO coatings/membranes exhibited excellent antifouling and ease-of-cleaning performance. Such an effective and facile methodology to modify the chemistry and morphology of GO flakes may provide great opportunities to generate functional coatings/surfaces with drastically improved underwater oil repellence.

We prepared GO by an improved Hummers' method.[19] Dry GO powder was then well dispersed in deionized (DI) water by ultrasonication. After centrifugation, GO agglomerates were removed. The final GO flakes are ~1000 nm in size (Fig. 1a) and single-layered (Fig. 1b), as confirmed by atomic force microscopy (AFM). We then diluted the GO dispersion to a concentration of 0.0625 mg/mL. A UV lamp was applied as the light source to conduct etching treatment of the GO dispersion for different times, from 0 to 90 min (labelled as 0-GO, 10-GO, 30-GO, 60-GO and 90-GO for convenience). UV treatment in water, instead of in air, provides us better control of the GO etching process. This is because good dispersion of GO in water and vigorous stir ensure uniform UV irradiation for GO flakes. The GO dispersion was then used to fabricate 10-nm coatings/membranes onto flat anodic aluminium oxide (AAO) supports (20-nm pore size) by a vacuum filtration method, following a similar procedure from our previous work.[20] Water contact angle in air and oil contact angle in water measurements were subsequently performed for the GO coatings/membranes (see ESI† for experimental details). As shown in Fig. 1c, the water contact angle in air decreases gradually with the increase of UV treatment time, from 70.0° for 0-GO membrane to 32.4° for 90-GO membrane. From the underwater hexadecane (HD) contact angle measurements, slight contact angle increase from 0-GO to 30-GO could be noticed. Surprisingly, we found that when UV treatment time increased to 60 min, the underwater oil contact angle became 159.1°, which is considered to be superoleophobic (>150°).[21] The 90-GO membrane shows even higher oil contact angle (167.2°) than the 60-GO membrane. These results indicate that the oil-adhesion characteristics in oil-water-solid triple-phase system could be tuned by changing UV exposure time (see ESI† for details). The UV-treated GO flakes are stable in air, as suggested by Raman spectra shown in Fig. S2 (see ESI† for details).

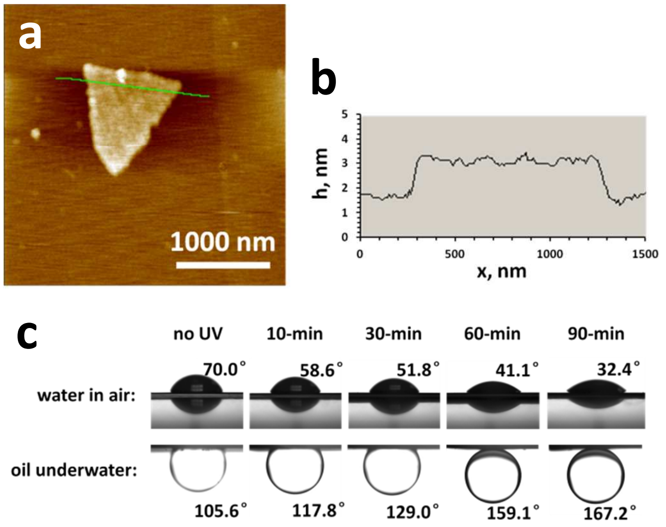

Fig. 1 (a) AFM image of a GO flake on a freshly cleaved mica. (b) The height profile across the green line in (a). h, height; x, position. (c) Water contact angle in air and hexadecane (HD) contact angle in water for GO membranes with different UV treatment times.

To explain the underlying mechanism, we further conducted x-ray photoelectron spectroscopy (XPS) and Raman spectroscopy measurements for GO dispersion after different UV treatment times. After deconvoluting the overlapping XPS peaks of C_1s (see Fig. S1 for C_1s XPS spectra), percentage of carbon in different chemical environments can be obtained, as shown in Fig. 2a. It is seen that as the UV treatment time increased, the percentage of oxidized carbon (including C-O, C=O and COOH) increased. This is because percentage of C in C=O and COOH increased, whereas that of C-O didn't change much. These groups on GO have been proved to have strong affinity to water molecules,[22] and thus would help form a thin layer of water barrier to lower the oil adhesion. Higher percentage of hydrophilic oxygen-containing functional groups after longer UV treatment time, therefore, may contribute to the better wettability of water in air and lower oil-adhesion underwater. Raman spectra (Fig. 2b) show that the I_D/I_G ratio increased as the UV treatment time increased, suggesting higher disorder of the planar structure of the GO flakes. This may be caused by the enlarged or newly-generated structural defects.[8] We then deposited thin coatings onto mica using GO dispersions with different UV exposure times and directly conducted AFM on them, as shown in Fig 3a-d. We can see that for the 0-GO coating, the surface is fairly flat and continuous. The 30-GO coating shows a surface decorated with defects from ~80 to 120 nm in size, while the 60-GO coating exhibits a very disordered surface with large holes from ~300 to 500 nm. The 90-GO coating seems more like isolated islands, apparently due to the over-etching.[9, 10] The generated defects eventually increased the nano-scaled surface roughness of the GO coatings, as indicated by the height profiles. Therefore, we conclude that both the chemical composition and structure changes after UV oxidative etching lead to the drastically improved underwater oleophobicity of GO coatings (see ESI† for details).

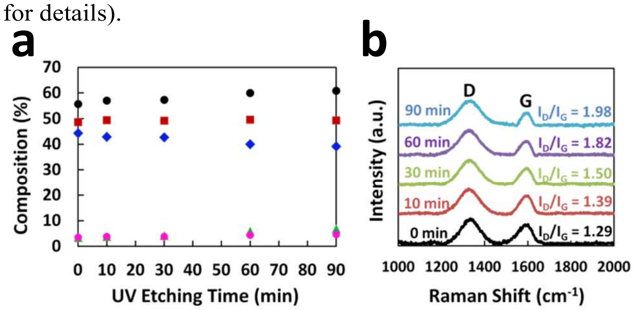

Fig. 2 (a) Percentage of differently bonded carbon on GO analyzed by XPS: ● Total oxidized carbon; ◆ Total unoxidized carbon; ■ C-O; ▲ C=O; ● COOH; (b) Raman spectra of GO after different UV treatment times from 0 to 90 min.

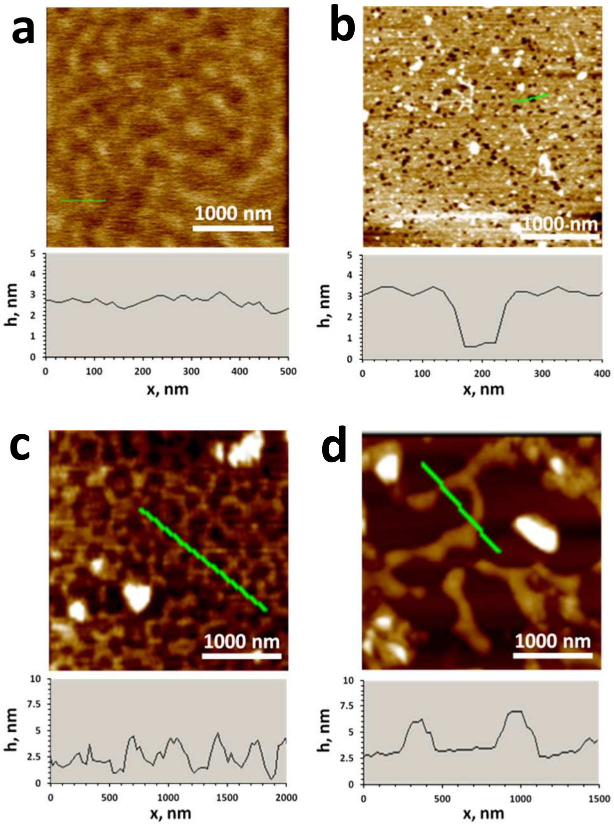

Fig. 3 AFM images and height profiles across the green lines for (a) 0-GO coating, (b) 30-GO coating, (c) 60-GO coating, and (d) 90-GO coating on mica. h, height; x, position

As is known, fouling of nano/ultrafiltration membranes in oil/water separation is a longstanding issue and a major economic barrier for their wide application.[23] Membranes with underwater superoleophobic surfaces are of great potential to realize antifouling in the oily wastewater treatment.[24] In order to utilize such excellent underwater superoleophobicity of our UV-treated GO, we prepared 10-nm GO membranes on polyamide (PA) supports using UV-treated GO (0, 30 and 60-GO) and conducted a series of oil emulsion filtration in a dead-end system to investigate their antifouling performance. 1500 ppm HD-in-water emulsion, stabilized by 100 ppm sodium dodecyl sulfate (SDS) after 1 hour sonication, was used as feed. The filtration process contains three cycles. In each individual cycle, a pure water filtration was performed, followed by an emulsion separation. During the interval between two neighboring cycles, a simple water flush cleaning process was applied to clean the membrane surface. Therefore, the recovery of pure water flux in each cycle could be an indicator of the membrane fouling degree. 60-GO membrane shows ~100% pure water recovery for all cycles (Fig. 4), suggesting superior antifouling performance. In stark contrast, 0-GO membrane (Fig. S3a) exhibits severe membrane fouling, since the pure water flux recovery for the 2nd cycle is only 51.7% and further decreases for the 3rd cycle. 30-GO membrane (Fig. S3b) shows improved antifouling performance with 2nd cycle pure water flux recovery of 90.1%. This again validates our methodology of utilizing UV to tune the chemical composition and structure of GO flakes to realize low oil-adhesion, underwater superoleophobic surface. The oil rejection for the tested membranes was all around 98.0%, (see ESI† for detailed experimental setup and discussion).

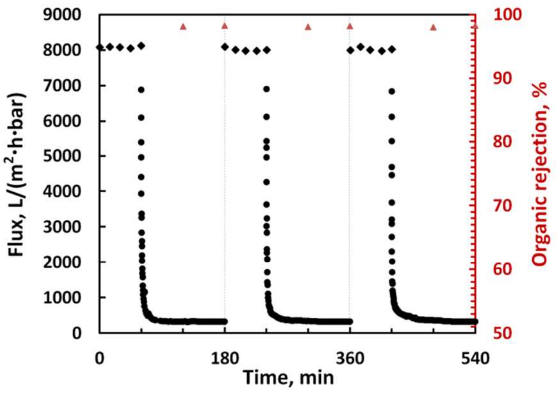

Fig. 4 Cyclic water/oil separation test for a 10-nm 60-GO membrane on PA support. (●) total flux in oil-in-water emulsion separation. (◆) pure water flux. (▲) total organic rejection,

Conclusions

In summary, UV-irradiation was utilized as an effective and facile approach to tune underwater oleophobicity of GO coatings/membranes by gradually modifying GO flake composition and surface morphology. Superoleophobic GO membranes, made from UV-treated GO flakes, showed excellent antifouling capability and greatly improved oil emulsion separation performance. We expect this facile strategy to tune underwater oleophobicity of GO may help design novel graphene-based materials/coatings for wide applications in oil contaminated environments.

We acknowledge the financial support from USC start-up funding and USC SPARC graduate student grant. We also thank Drs Shuguo Ma, Qian Wang and Xinyu Huang for their experimental assistance on XPS, contact angle and Raman, respectively.

Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, Fig. S1-S3 . See DOI: 10.1039/c000000x/

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