



## Facile coating of reduced graphene oxide and TiO<sub>2</sub> on floating polyurethane foams for photocatalytic water decontamination

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### Significance and Relevance

We developed a simple methodology to deposit a binder-free, aqueous-based coating containing reduced graphene oxide and TiO<sub>2</sub> onto polyurethane floating foams. The deposition only involves dip coating, compressed air blowing, and drying at 40 °C. Exposed to UV-Vis light, coated foams completely remove Rhodamine B from water in 90 min. The dye is firstly adsorbed and subsequently photodegraded on the foam surface. This study represents a novel approach to immobilize TiO<sub>2</sub> for photocatalytic water treatment, using commercial materials and a simple, low energy-consuming method. TiO<sub>2</sub> photoactivity is not only preserved, but possibly enhanced by the combination with reduced graphene oxide.

*Topic: Water treatment (preferred); Photocatalysis and photoelectrocatalytic approaches (2<sup>nd</sup> choice)*

*Preferred presentation: Oral preferred or Short Oral*

### Introduction and Motivations

TiO<sub>2</sub> is the most studied and used photocatalyst. However, its practical application in water treatment is still limited because: i) its 3.2 eV bandgap requires UV light, implying a significant energy consumption, ii) it is mainly employed as nanopowder, which tends to agglomerate, and is hardly recoverable after use<sup>1</sup>. Coupling TiO<sub>2</sub> with reduced graphene oxide (rGO) allows to reduce the material bandgap, improve the separation of charge carriers, and, being rGO an excellent adsorbent, keep contaminants in direct contact with the photocatalyst<sup>2</sup>. Because of its self-assembling properties, rGO can also be effective for immobilizing TiO<sub>2</sub> nanoparticles in macroscopic objects, as already demonstrated by our research group<sup>3</sup>.

### Materials and Methods

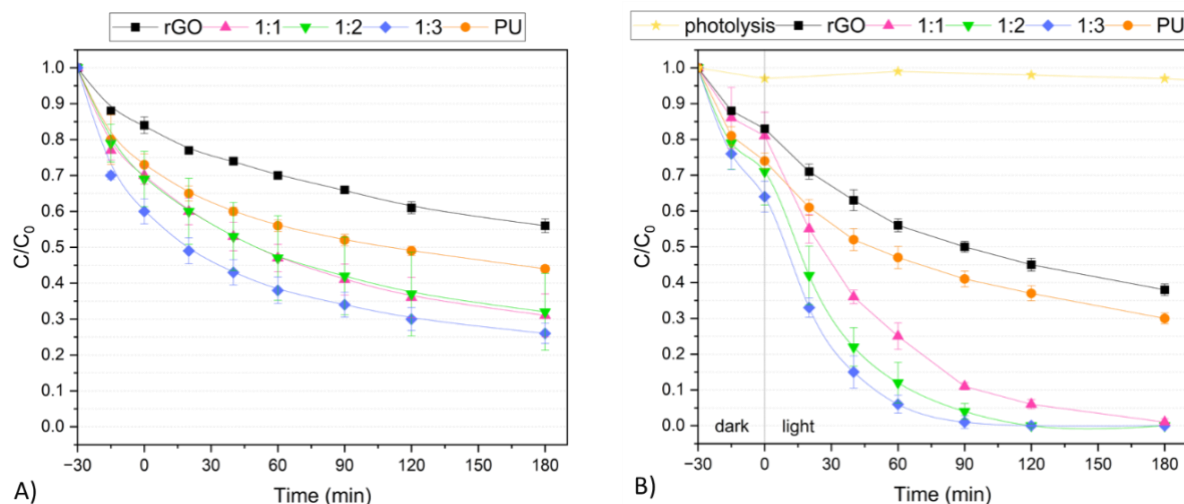
The slurry for the coating procedure was prepared by stirring at ambient temperature: i) a commercial graphene oxide (GO) aqueous dispersion, ii) ascorbic acid as reducing agent for GO, iii) TiO<sub>2</sub> Degussa P25. GO:TiO<sub>2</sub> mass ratios of 1:1, 1:2 and 1:3 were considered. A commercial polyurethane (PU) 20 PPI foam, cut into 0.5 cm-thick cylinders of 5.5 cm diameter, was used as substrate, without any pre-treatment. Foams were dip-coated, blown with compressed air to remove the excess coating, and dried at 40 °C for 2 h. For water decontamination tests, each foam was contacted with 100 mL of a 3 mg/L Rhodamine B (RhB) aqueous solution. The light source was a UV-Vis Osram Ultra Vitalux 300 W lamp. RhB concentration was monitored with UV-Vis spectroscopy.

### Results and Discussion

Foams coated with rGO/TiO<sub>2</sub> 1:1, 1:2, and 1:3 (w:w) were employed in decontamination tests both in dark and light conditions, comparing their behavior with the one of bare PU and rGO-coated foams. Experiments in dark (Fig. 1A) highlight that all the samples have a significant RhB adsorption capacity, reaching 55% of removal with bare PU, and 70-75% of removal with rGO/TiO<sub>2</sub>-coated foams after 180 min. Different results were obtained by exposing the samples to light (Fig. 1B). Curves related to rGO/TiO<sub>2</sub>-coated foams exhibit a marked change in the slope at 0 min, which corresponds to the activation of the UV-Vis lamp, after 30 min in dark. This suggests the shift from a pure adsorption to a photocatalysis-dominated process, which leads to 100% removal of RhB with the 1:1-coated foam after

180 min. However, the graph clearly indicates that an increase in  $\text{TiO}_2$  content determines an acceleration in the decontamination process. The complete RhB removal is indeed reached at 120 min using the 1:2-coated sample, and already at 90 min with the 1:3.

**Figure 1.** Normalized concentration of RhB during adsorption (A) and photodegradation (B) tests.



After the decontamination tests, foams were illuminated to reveal the possible presence of RhB through fluorescence. RhB can be clearly detected on all the foams employed in dark conditions. After photodegradation tests, instead, RhB is largely visible only on the rGO-coated foam. On rGO- $\text{TiO}_2$  coatings, limited pink areas can be seen on the 1:1 sample, which completely disappear as the  $\text{TiO}_2$  content increases. Thus, it can be hypothesized that RhB is firstly removed from water by adsorption on the foams surface, and successively photodegraded. Accordingly, after 180 min of test under light RhB can still be detected on the 1:1-coated foam, which features a slower degradation kinetics than 1:2 and 1:3-coated samples.

Foams were then immersed in deionized water, to assess the possible release of RhB. rGO-coated foams, both after adsorption and photodegradation tests, determine a slight water contamination with RhB, reaching the maximum after 24 h. However, the amount of released dye is remarkably lower than the one previously removed. The same behaviour was registered for the 1:3-coated sample used in dark conditions. The 1:3 foam employed in experiments under illumination, instead, does not release any RhB, even after 72 h.

The obtained results provide multiple confirmations of the photodegradation ability of  $\text{TiO}_2$ -containing coatings. An increase in the  $\text{TiO}_2$  content determined a faster RhB removal, thus new coating formulations with a higher quantity of  $\text{TiO}_2$  will be possibly prepared. Also, the photodegradation activity of coated foams will be assessed toward other organic contaminants, e.g. drugs or pesticides.

## References

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