



# Enhanced photocatalytic efficiency by layer-by-layer self-assembly of graphene and titanium dioxide on shrink thermoplastic film

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## Abstract

In this work, reduced graphene oxide/titanium dioxide (rGO/TiO<sub>2</sub>) composite material was immobilized on shrink thermoplastic film using layer-by-layer (LBL) self-assembly to remove pollutants in water, and the results were compared with immobilized TiO<sub>2</sub> on glass and shrink thermoplastic film. The structural and morphological properties of the immobilized photocatalysts were investigated using atomic force microscope and scanning electron microscope. The photocatalytic efficiency was measured by photodegradation of methylene blue under solar light illumination. The immobilized rGO/TiO<sub>2</sub> on shrink thermoplastic film showed doubled photocatalytic efficiency than TiO<sub>2</sub> on glass substrate, and no decrease of photocatalytic efficiency was shown after 5 h of operation. The use of shrink thermoplastic film and the introduction of graphene material contribute to an increase in catalytic efficiency of 63% and 28%, respectively. These results lead us to believe that the LBL self-assembled rGO/TiO<sub>2</sub> composite on shrink thermoplastic film could be used in photocatalytic degradation of other water pollutants.

## 1 Introduction

Water shortage is becoming a global challenge. Access to clean water is a problem not only in developing countries, but also in developed countries including the United States because of economic growth, demographic shift and climate change. There are approximately four billion people facing water scarcity, and water pollution makes their situation even more severe. In fact, the United Nations lists addressing water scarcity and water pollution as one of the goal challenges for sustainable development by 2030 (Desa 2016).

Photocatalytic technology based on titanium dioxide (TiO<sub>2</sub>) has gained wide attention in the past decades as a low-cost, environmentally friendly and sustainable water treatment technology. This technology uses semiconductor catalysts such as TiO<sub>2</sub> to mineralize refractory organic compounds, water pathogens and disinfection by-products (Pera-Titus et al. 2004). When TiO<sub>2</sub> is illuminated under photon energy greater than or equal to the bandgap energy of TiO<sub>2</sub>, the distinct lone electron in the outer orbital is

photoexcited to the empty conduction band, leaving a hole in the valence band. A series of redox reactions occur at the photo active surface and can remove the organics in water (Fujishima et al. 2008). However, low efficiency, catalyst agglomeration during operation, and the complex post-separation process are the primary barriers that prevent practical applications of this technology.

Graphene, a flat monolayer of *sp*<sup>2</sup>-bonded carbon atoms, is believed to be very effective in increasing photocatalytic efficiency because of the enhanced charge transfer rate (Zhang et al. 2010). Many approaches have been applied to synthesize graphene-based TiO<sub>2</sub> photocatalysts. For example, Guo et al. (2011) used an ultrasonic assisted chemical reaction to synthesize rGO/TiO<sub>2</sub> composite material and observed 2.57 times enhanced photocatalytic efficiency. Safardoust-Hojaghan and Salavati-Niasari (2017) synthesized rGO/TiO<sub>2</sub> composite material using a hydrothermal method, and it showed 2.13 times faster photodegradation speed than TiO<sub>2</sub>. All of these chemical methods require complex and expensive chemical reactions, and the final products are in powder form, which is difficult to be immobilized on the substrate.

As the slurry of TiO<sub>2</sub> and rGO/TiO<sub>2</sub> composite material requires a post-separation process and leads to catalyst agglomeration during operation, hindering the practical

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application of this technology (De Lasa et al. 2005), some researchers tried to deposit photocatalysts on different substrates using chemical vapor deposition (Alotaibi et al. 2018), atomic layer deposition (Klesko et al. 2018) and, most commonly, the sol–gel method (Al-Mathloom and Abed 2019). However, all of these methods start with a titanium precursor and require complex chemical reactions. In addition, the enhancement of graphene-based TiO<sub>2</sub> in photocatalytic efficiency becomes limited when the composite material is immobilized on the surface of the substrate due to the reduction of active sites involved in the reaction. For example, Padoin et al. (2016) immobilized rGO/TiO<sub>2</sub> composite material on the walls of microchannels, and only 29% enhancement was observed compared to immobilized pure TiO<sub>2</sub>.

Instead of using these chemical deposition methods, the physical LBL self-assembly is more convenient, and can produce a high-quality TiO<sub>2</sub> film on a substrate. The basic mechanism of LBL self-assembly is the electrostatic interaction between polymer or particles with opposite charges (De Villiers et al. 2011). Multilayered TiO<sub>2</sub> or rGO/TiO<sub>2</sub> films can be deposited onto an electrically charged substrate by dipping the substrate into alternating solutions with opposite charges. This deposition routine can be repeated many times to fabricate multilayer photocatalyst thin films. TiO<sub>2</sub>/Polymer nanocomposite films has been successfully fabricated since 1997, when Liu et al. (1997) fabricated as many as 120 layers of films on silicon, metal and plastic substrates. Yao et al. (2010) fabricated a graphene-based TiO<sub>2</sub> photocatalysts on glass substrate in a sequence of GO/PDDA/TiO<sub>2</sub> while Manga et al. (2009) fabricated the material in a sequence of PEI/TiO<sub>2</sub>/PEI/GO. Manga's group also used femtosecond transient absorption spectroscopy to demonstrate the ultrafast photocatalytic electron transfer between TiO<sub>2</sub> and graphene. Different substrate materials were used to increase the relative surface area of the photocatalyst, therefore increase the photocatalytic efficiency. For example, TiO<sub>2</sub> was deposited on glass spheres with a diameter of 5 mm, and then put in a lab scale compound parabolic collector to photodegrade methylene blue (MB) (Cunha et al. 2018). Wang et al. (2017) successfully fabricated carbon nanotubes and TiO<sub>2</sub> composite films on cotton fabrics to achieve high photocatalytic efficiency. However, their irregular shapes and material properties make them hard to use when fabricating microfluidic systems or flexible structures.

In this work, a shrink thermoplastic film was used as a substrate material as it can shrink more than 80% of its original size after heating. It has been successfully used in microsensors to enhance sensitivity and reduce the limit of detection (Li et al. 2015), but it has never been used in photocatalytic water treatment. TiO<sub>2</sub> films and rGO/TiO<sub>2</sub>

composite films were LBL self-assembled on shrink polymer films, respectively. The photocatalytic efficiency was measured and compared with TiO<sub>2</sub> films on a glass substrate, and the morphological properties were measured to explain the difference.

## 2 Experimental

### 2.1 Materials

Poly(sodium 4-styrenesulfonate) (PSS;  $M_w = 70,000$ ), Poly(diallyl dimethyl ammonium chloride) (PDDA; 20 wt% in water), and TiO<sub>2</sub> nanoparticle (P25, 30% rutile and 70% anatase phase) were obtained from Sigma-Aldrich, and monolayer graphene oxide water dispersion (4 mg/ml) was purchased from MSE Supplies LLC. Shrink thermoplastic films were acquired from Grafix Arts LLC.

### 2.2 LBL self-assembly process

The 1 wt% TiO<sub>2</sub> cationic solution was prepared by adding 1 g TiO<sub>2</sub> and 1 mL HCl (1 M) into 100 mL deionized water, followed by more than 24 h of continuous stirring until a stable colloid solution was formed. The GO solution was diluted to 1 mg/mL with deionized water, followed by slight sonication to prevent agglomeration. A shrink thermoplastic film was cut into 45 cm squares, and the 18 cm square glass was also used for comparison.

The schematic diagram of LBL self-assembly process is shown in Fig. 1. The substrates were first cleaned by deionized water and dried in air. Then the substrates were alternately immersed into cationic PDDA and anionic PSS solutions in a sequence of [PDDA + PSS + PDDA]. The long-chain polymers with charged branches helped to form a uniformly film on the substrates. Next, the PSS/TiO<sub>2</sub> bilayers or GO/TiO<sub>2</sub> bilayers were deposited on top of the substrates. Different numbers of composite photocatalyst bilayers were prepared. Deposition time for each process was 10 min, accompanied by the washing out of non-bound molecules after each layer was deposited.

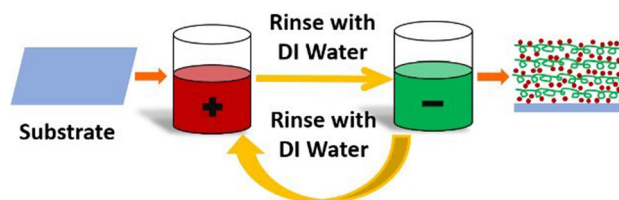
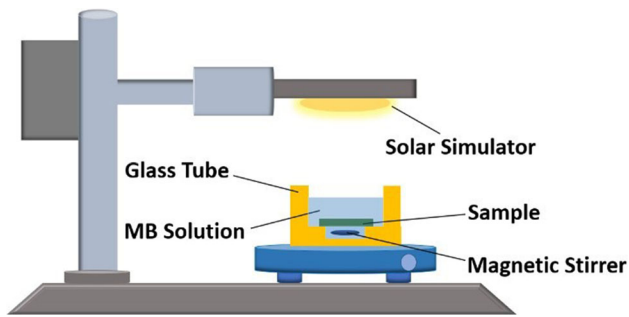


Fig. 1 Schematic diagram of LBL self-assembly process



**Fig. 2** Setup of the photocatalytic tests

The coated shrink thermoplastic films were heated in the oven under 150 °C. The film size after shrinking was 18 cm by 18 cm, the same as the cover glass. Then the Ultraviolet light illumination was applied to reduce GO into rGO (Williams et al. 2008).

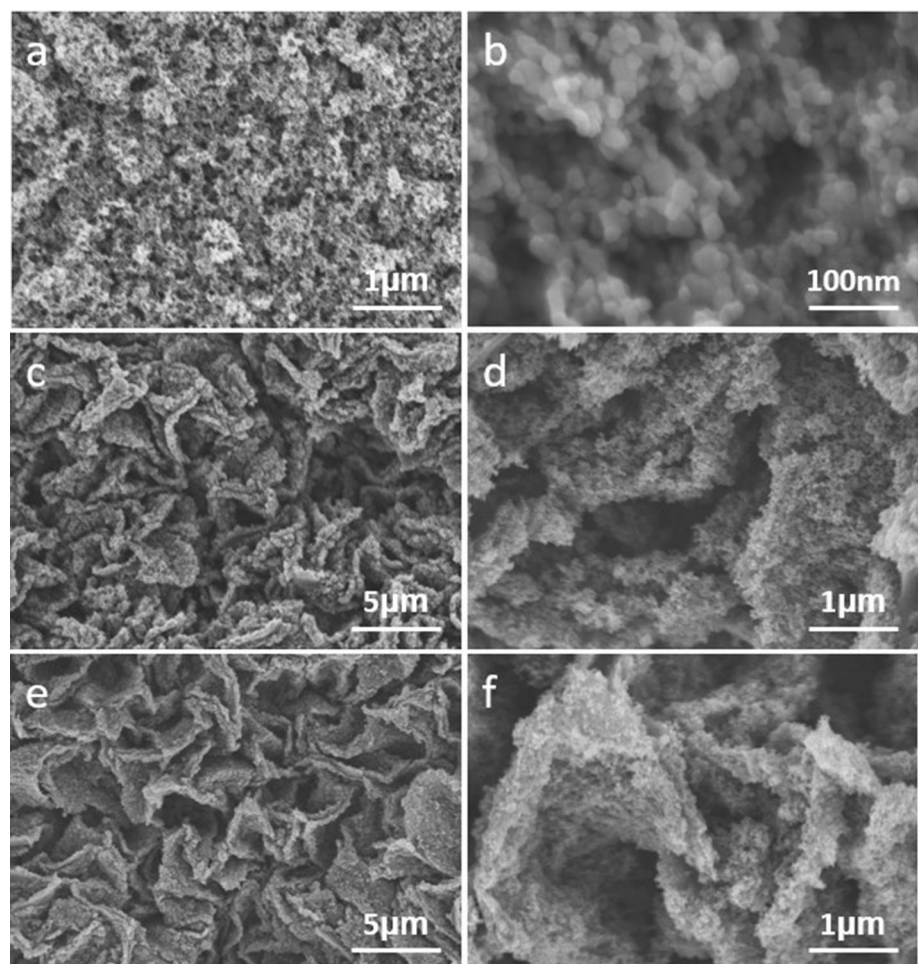
### 2.3 Measurement and characterization

The surface morphologies and elemental mapping of samples were observed by a Field Emission Gun Scanning

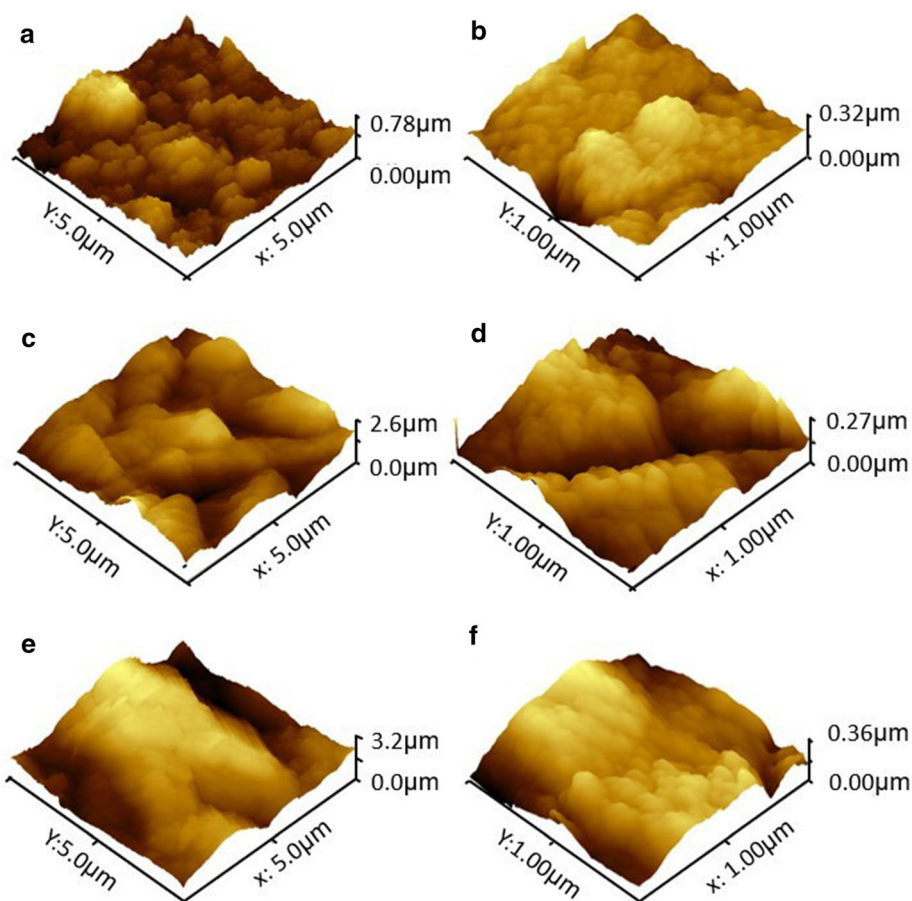
Electron Microscope (FEGSEM) (Hitachi SU8230). A thickness of 2.5 nm Iridium was deposited on each sample to increase the conductivity. The three-dimensional surface topography was measured by Atomic Force Microscopy (AFM) (MFP-3D Origin AFM, Asylum Research).

Photocatalytic efficiency of immobilized photocatalysts was evaluated by degrading MB. Figure 2 shows the setup of the photocatalytic experiments. The back of prepared samples was covered by waterproof tape, and the samples were placed in a customer designed glass tube with a volume of 12 mL. The magnetic stirrer was placed under the sample to increase the mass transfer from bulk solution to the surface of photocatalysts. 10 mL MB with a concentration of 100  $\mu\text{M}$  was used for photodegradation tests, and 10  $\mu\text{M}$  MB with the same volume was used for cycling tests. The tube was first placed in the dark for 1 h to reach the adsorption–desorption balance of MB from the photocatalysts. Then the tube was illuminated by solar light for 1 h. 100  $\mu\text{L}$  solution was taken from the tube every 10 min, and the concentration of MB was measured by UV/Visible

**Fig. 3** SEM images of different photocatalyst in different substrate **a** 4 PSS/TiO<sub>2</sub> bilayers on glass substrate, high resolution, **b** 4 PSS/TiO<sub>2</sub> bilayers on glass substrate, ultra-high resolution, **c** 4 PSS/TiO<sub>2</sub> bilayers on shrink polymer, low resolution, **d** 4 PSS/TiO<sub>2</sub> bilayers on shrink polymer, high resolution, **e** 4 rGO/TiO<sub>2</sub> bilayers on shrink polymer, low resolution and **f** 4 rGO/TiO<sub>2</sub> bilayers on shrink polymer, high resolution



**Fig. 4** AFM images of different photocatalyst in different substrate **a** 4 PSS/TiO<sub>2</sub> bilayers on glass substrate, low resolution, **b** 4 PSS/TiO<sub>2</sub> bilayers on glass substrate, high resolution, **c** 4 PSS/TiO<sub>2</sub> bilayers on shrink polymer, low resolution, **d** 4 PSS/TiO<sub>2</sub> bilayers on shrink polymer, high resolution, **e** 4 rGO/TiO<sub>2</sub> bilayers on shrink polymer, low resolution and **f** 4 rGO/TiO<sub>2</sub> bilayers on shrink polymer, high resolution



Spectrophotometer (Model SP-UV1100, DLAB Scientific Co., Ltd) under a wavelength of 664 nm.

### 3 Result and discussion

#### 3.1 LBL self-assembly and characterization

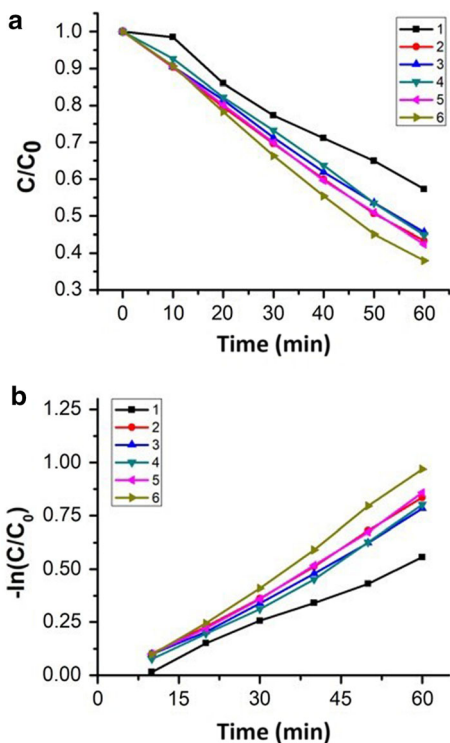
The morphology of immobilized photocatalysts was observed by SEM. Figure 3 shows the SEM images of 4 PSS/TiO<sub>2</sub> bilayers on both a glass substrate and a shrink thermoplastic film and 4 rGO/TiO<sub>2</sub> bilayers on the shrink thermoplastic film. It can be found that the PSS/TiO<sub>2</sub> bilayers on glass substrate were relatively flat, and the porous structure between photocatalysts was in nanoscale. The ultra-high-resolution image of glass sample clearly shows the TiO<sub>2</sub> nanoparticles. The size of TiO<sub>2</sub> nanoparticles were about 20–25 nm which matches the particle size of P25. Comparing the photocatalysts on the glass substrate with the shrink thermoplastic films, Fig. 3c, e show many folds produced by shrinking, which means a higher surface area can be expected on shrink thermoplastic films. It also leads to the microscale porous

structures on the substrate. The amount of folds was similar between PSS/TiO<sub>2</sub> and rGO/TiO<sub>2</sub> composite films on shrink thermoplastic films, but Fig. 3c, d show the surface of the folds was rougher than Fig. 3e, f. This is because there is more TiO<sub>2</sub> immobilized on PSS than rGO as the negatively charged functional groups on rGO is much less than PSS.

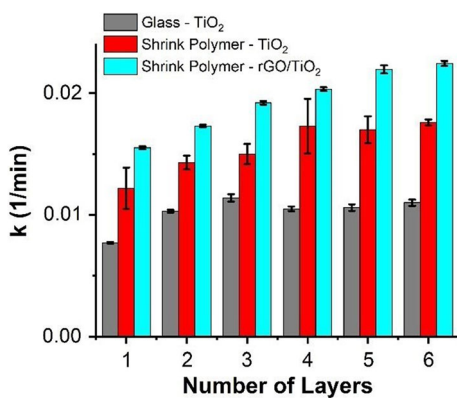
Figure 4 shows the AFM images of different photocatalysts on different substrates. Similar to the SEM images, the photocatalysts on a glass substrate were smoother than that on a shrink polymer substrate. In a square with a side of 5  $\mu\text{m}$ , the height difference of photocatalysts on the glass substrate was 783 nm, while the value on the shrink polymer substrate with different photocatalysts were 2.644  $\mu\text{m}$  and 3.315  $\mu\text{m}$ , respectively. The microscale folds on the shrink polymer were also visible in AFM images. The particle size shown in high resolution images were in a range from 20 to 25 nm, which matches the SEM results.

#### 3.2 Photocatalytic tests and efficiency

The photocatalytic efficiency was evaluated by photodegradation of MB solutions. Different numbers of PSS/



**Fig. 5** **a** Relative MB concentration versus irradiation time with different numbers of PSS/TiO<sub>2</sub> bilayers and **b** MB degradation kinetics for different numbers of PSS/TiO<sub>2</sub> bilayers

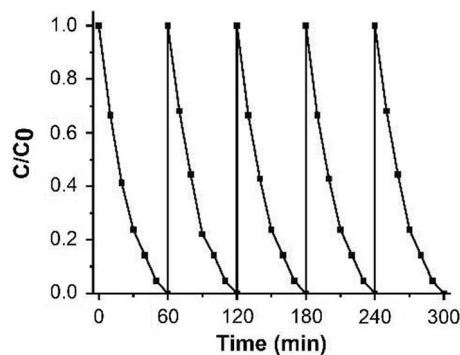


**Fig. 6** Pseudo first order kinetic constant for different number of PSS/TiO<sub>2</sub> and rGO/TiO<sub>2</sub> bilayers on different substrate

TiO<sub>2</sub> bilayers on shrink polymer films were first tested and compared. As shown in Fig. 5a, concentration of MB kept decreasing with increasing illumination time. The concentration change of MB slowed down when its concentration was lower, thus the kinetics of MB photodegradation can be described by the first order kinetics equation

$$\ln(C/C_0) = -kt \tag{1}$$

where  $C_0$  and  $C$  are the contaminant concentrations at the beginning and during light illumination, respectively,  $k$  is



**Fig. 7** Relative MB concentration versus irradiation time in cycling test

the reaction rate constant, and  $t$  is time (Raghavan et al. 2015). The photocatalytic efficiency can be represented by reaction rate constant,  $k$ , which is also the slope in Fig. 5b. It can be seen that when the number of PSS/TiO<sub>2</sub> bilayers is higher,  $k$  is also higher, and the value of  $k$  gets saturated when the number of bilayers is 4. This means a number of PSS/TiO<sub>2</sub> bilayers greater than 4 will not significantly change the photodegradation efficiency. This is because the bottom photocatalyst was covered by the upper photocatalyst, and only the upper photocatalyst could receive light illumination and photodegrade MB. When the number of PSS/TiO<sub>2</sub> is 4,  $k = 0.0173$ /min.

The same tests were done in different numbers of PSS/TiO<sub>2</sub> bilayers on a glass substrate and rGO/TiO<sub>2</sub> bilayers on a shrink polymer substrate. The results are shown in Fig. 6.

Figure 6 shows that the PSS/TiO<sub>2</sub> bilayers on a glass substrate always have the lowest photocatalytic efficiency, and the highest photocatalytic efficiency observed was  $k = 0.0106$ /min. The highest photocatalytic efficiency was obtained in shrink polymer with 6 rGO/TiO<sub>2</sub> bilayers. The highest reaction rate constant was  $k = 0.0222$ /min, 2.1 times higher than PSS/TiO<sub>2</sub> bilayers on glass substrate and 1.28 times higher than PSS/TiO<sub>2</sub> bilayers on a shrink polymer substrate.

The high photocatalytic efficiency for rGO/TiO<sub>2</sub> bilayers on a shrink polymer can be attributed primarily to two reasons: the high surface area induced by shrink and enhanced electron transfer due to graphene material. As the original size of shrink polymer is 6.25 times higher than the size after shrinking and covering the glass, the amount of immobilized photocatalyst is also higher than cover glass. The enhancement of photocatalytic efficiency by introducing graphene material has been verified by many publications. Even though the amount of TiO<sub>2</sub> in rGO/TiO<sub>2</sub> bilayers is less than PSS/TiO<sub>2</sub> bilayers, the enhanced electron transfer prevents photoexcited electron–hole recombination, and improves the photocatalytic efficiency even beyond PSS/TiO<sub>2</sub> bilayers.

The cycling tests were also performed to show the long-term stability of LBL self-assembled rGO/TiO<sub>2</sub> bilayers on shrink polymer. A sample with 4 rGO/TiO<sub>2</sub> bilayers on shrink polymer was used for this test. 10 mL MB solution with 10 μM concentration was fully degraded within 1 h. The process was repeated 5 times, and the result was shown in Fig. 7. It can be inferred from the figure that no decrease of photocatalytic efficiency was observed, which means that the bonding between photocatalyst and substrate is firm, and the result is repeatable.

## 4 Conclusions

This study shows that the photocatalyst can be firmly immobilized on glass substrates and shrink thermoplastic films using LBL self-assembly. The folds structure induced by shrinking helps increase photocatalytic efficiency by 63%, and the introduction of graphene material further enhances the photocatalytic efficiency to 2.1 times higher than pure TiO<sub>2</sub> immobilized on a glass substrate. Overall, more than 70% of 100 μM MB was removed in 1 h using rGO/TiO<sub>2</sub> bilayers immobilized on a shrink thermoplastic film, and the 10 μM MB can be fully removed within 1 h.

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