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## Graphene/TiO<sub>2</sub> composite films for efficient photocatalytic degradation of antibiotics in wastewaters

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### ABSTRACT

Graphene/oxide composite structures can be employed for advanced applications owing to their synergistic properties. We prepared mesoporous TiO<sub>2</sub> layers including (i) graphene oxide and (ii) reduced graphene oxide at various concentrations. The films deposited on glass were tested for photocatalytic degradation, in water and under UV light, of sulfathiazole, a model compound of an eco-persistent antibiotic. The results show the high photocatalytic activity of the TiO<sub>2</sub> layers. Moreover, a significant improvement in the photodegradation rate is found for graphene oxide with an optimum concentration of 2 wt. %. It is assigned to a favorable energy level combination that favors the photogenerated charge separation and increases the lifetime of the electron/hole pairs.

**Keywords:** TiO<sub>2</sub>, Nanocomposite layer, Photocatalysis, Sulfathiazole, Antibiotics.

### 1. INTRODUCTION

Graphene is a two-dimensional honeycomb carbon allotrope made of *sp*<sup>2</sup>-hybridized carbon atoms. It can be prepared with a single atomic layer thickness. It exhibits many interesting properties such as mechanical strongness with a breaking strength of 42 N.m<sup>-1</sup>, high thermal conductivity, and excellent electron conductivity of ~64 mS.cm<sup>-1</sup>. [1] Its theoretical specific surface area is 2600 m<sup>2</sup>.g<sup>-1</sup> and its lattice structure is thermally stable. Due to these singular properties, graphene has promising potential applications in various fields. [2-4]

TiO<sub>2</sub> is a widely studied photocatalytic material whose performance has been investigated in the degradation of many dyes and organic model pollutants. [5] It, as a wide-bandgap semiconductor, fulfills the principal requirements to be an efficient and robust photocatalyst in aqueous media with a top valence-band position above the oxidation potential of water. For industrial applications, TiO<sub>2</sub> offers the advantages of a low cost, high chemical stability, and rather harmlessness. The use of TiO<sub>2</sub>/Graphene composite allows for the enhancement of the photocatalytic properties of the oxide. [6-17] Its reported beneficial effects include improved adsorption of targeted molecules,[6,15] and a work function at -4.4 to -4.5 eV localized below the conduction band of TiO<sub>2</sub> (-4.2 eV). A faster and more efficient electron extraction and charge separation from TiO<sub>2</sub> can then be expected. [18]

Persistent aquatic pollutants represent a huge challenge to the environment. Among emerging pollutants in wastewater, a special role is played by antibiotics, which are highly toxic to aquatic and human life, even at very low concentrations. They are released in a rather large amount by human activities and intensive farming. By conventional methods, antibiotic organic pollutants are often insufficiently degraded and mineralized. Sulfathiazole, studied here (**Figure 1a**), belongs to the sulfonamide antibiotics group and is used in veterinary medicine. [19,20]

In the present work, we prepared by spin-coating composite mesoporous layers mixing TiO<sub>2</sub> nanoparticles with graphene oxide (GOSL) and reduced graphene oxide (rGO), the concentration of graphene being varied. Our results show the

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substantial effectiveness of the layers for the photocatalytic degradation of sulfathiazole under UV light at laboratory temperature.

## 2. EXPERIMENTAL SECTION

### 2.1 Layers preparation

Microscope glass slides (25 x 75 mm) were cleaned in Helmanex solution diluted to 2 vol% in deionized water using an ultrasonic bath for 1 h. They were then subsequently rinsed with acetone, ethanol, and deionized water in an ultrasonic bath for 30 min. Prior to the compact TiO<sub>2</sub> layer deposition, a 30 min UV-O<sub>3</sub> treatment was performed on the substrates. The compact TiO<sub>2</sub> layer, with a thickness of 20-30 nm, noted c-TiO<sub>2</sub>, was then prepared by aerosol spray pyrolysis as detailed in Ref. [21]. Anatase TiO<sub>2</sub> NR30-D paste (from Greatcell Solar Materials), made of nanoparticles with a mean diameter of 30 nm, was diluted in ethanol in a 1:6 w/w ratio and shaken for 5 min by hand. [22] For the composite layers, 1.5, 2, and 3 wt% of GOSL (graphene oxide single layer from US Research Nanomaterials) and rGO (from Nanographi) relative to the total mass of the composite were mixed to the diluted paste after the 5 min shaking. All suspensions were stirred at room temperature for at least 24 h prior to use. The composite suspensions were also sonicated for 15 min every 4 h to improve GOSL/rGO dispersion. A 25x25 mm<sup>2</sup> area was delimited with Kapton tape. For pristine TiO<sub>2</sub> layers, 45 μL of the corresponding suspension was dropped on top of the compact TiO<sub>2</sub> layer and spin-coated at 2000 rpm for 15 s. For the composite layers, 130 μL of the composite suspension was dropped on top of the compact TiO<sub>2</sub> layer and thoroughly spread with the tip of the micropipette on the whole surface, then spin-coated at 2000 rpm for 15 s. The layer was then dried on a hotplate at 70 °C for at least 10 min, heated at 500 °C under an air flux for 30 min, followed by cooling down to 200 °C, and finally removed from the hotplate. The films were characterized by Raman spectroscopy, using a 532 nm excitation laser.

### 2.2 Photoactivity test

The photocatalytic experiments were performed using a custom-made set-up consisting of 25 mL cuvettes, whose contents was homogenized by a magnetic stirrer and kept at constant temperature by cooling coils attached to an external thermostat, and UV lamp holders, equipped with UV lamps with a dominant wavelength of 365 nm (Philips). The irradiation intensity was 6 mW cm<sup>-2</sup>, as measured with a radiometer (ILT 1400 A, International Light Technologies). To eliminate the potential influence of solar light, the photocatalytic experiments were performed in a dark room illuminated only by a sodium lamp. All solvents were of HPLC grade. Demineralized water used as a matrix for the photocatalytic experiment was obtained by reverse osmosis. The concentration of the sulfathiazole (sodium salt, ≥99.0% from Sigma-Aldrich) solution was 10<sup>-4</sup> M. The slide, with a 25x25 mm<sup>2</sup> active oxide or composite porous layer area, was fixed inside the cuvette and completely immersed in the test solution, which was vigorously stirred (450 rpm). To monitor the reaction, aliquots were taken at 30, 60, 90, 120, 180, 240, 300, and 1440 min after the beginning of the reaction.

The aliquots were then analyzed using a HPLC Agilent Technology 1200 Series instrument with DAD detector. A LiChroCART® 125-4 LiChrospher® 100 RP-18 (5 μm; Merck KGaA, Darmstadt, Germany) was used with isocratic elution. The column temperature was 25 °C. A methanol/water (15:85 vol.) solvent mixture was used at the flow rate of 1 mL.min<sup>-1</sup>. The injection volume was 50 μL, and the detection wavelength was set to 254 nm.

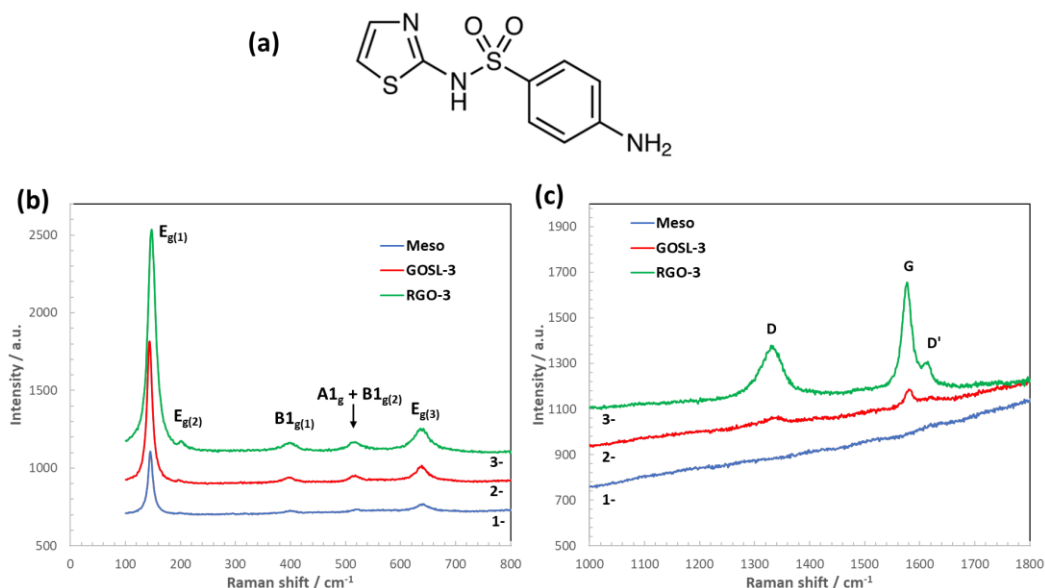
The reaction rate constants were obtained by non-linear fitting using an exponential function corresponding to the pseudo-first-order kinetics.

## 3. RESULTS AND DISCUSSION

To distinguish the TiO<sub>2</sub> allotropic phases and identify the presence of graphene, Raman spectroscopy was used. [23] In **Figure 1b**, the spectra are characteristic of anatase TiO<sub>2</sub>. This phase gives rise to six Raman active modes, A<sub>1g</sub> + 2B<sub>1g</sub> + 3E<sub>g</sub>. [24,25] Raman bands at 632, 197 and 146 cm<sup>-1</sup> are assigned to the E<sub>g</sub> modes, those at 398 cm<sup>-1</sup> to a B<sub>1g</sub> mode and at 519 cm<sup>-1</sup> to the A<sub>1g</sub> and B<sub>1g</sub> modes. The Raman band at 144 cm<sup>-1</sup> is very intense and sharp. Extra-bands are found for the

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composite layers (**Figure 1c**). In graphene, the Stokes phonon energy shift caused by laser excitation creates two main peaks in the Raman spectrum. The G band at around 1585 cm<sup>-1</sup> is a primary in-plane vibrational mode, and is close to that for well-ordered graphite. The bands at 1272 cm<sup>-1</sup> and 1614 cm<sup>-1</sup> are assigned to disordered sp<sup>2</sup> carbon and are called the D and D' bands, respectively. The Raman spectra show that, in both cases, the composite layers are based on anatase and graphene. They also point out the disorder of the carbon in the GOSL and rGO employed, the intensity of the GOSL signal being much stronger than the rGO one.



**Figure 1.** (a) Molecular structure of sulfathiazole. (b, c) Raman spectra of mesoporous TiO<sub>2</sub> layer (1), TiO<sub>2</sub>/GOSL-3 (2) and TiO<sub>2</sub>/rGO-3 (3) composites. The spectra are offset vertically for clarity.

**Table 1.** Sulfathiazole degradation after 5h and 24 h of experiments. The number behind the graphene component designation shows its mass content.

Sample	% degradation 5 h	% degradation 24 h
Blank (spray)	0	0
Meso	12.5	33.4
GOSL 1.5	13.8	46.2
GOSL 2	14.6	53.2
GOSL 3	14.0	47.4
rGO 1.5	12.8	36.5
rGO 2	9.5	36.9
rGO 3	11.0	45.7

These films were tested for the photodegradation of sulfathiazole under UVA light ( $\lambda = 365$  nm). Sulfathiazole degradation was followed during 24h by measuring its concentration by HPLC technique. The blank experiment performed using a glass slide coated with a compact TiO<sub>2</sub> layer deposited by spray pyrolysis showed no significant sulfathiazole degradation. After 24h, the presence of the graphene species favored the degradation of the antibiotic (**Table 1**).

The reaction rate constants were obtained by fitting of the experimental points using an exponential function corresponding to the pseudo-first-order kinetics (**Figure 2**). This parameter shows the beneficial effect of the addition of the graphene components. While for the mesoporous TiO<sub>2</sub> layer, the degradation rate constant was  $3.2 \cdot 10^{-4} \text{ min}^{-1}$ , a significant increase was found composite photocatalysts containing GOSL, the constant reaching  $5.27 \cdot 10^{-4} \text{ min}^{-1}$  for 2

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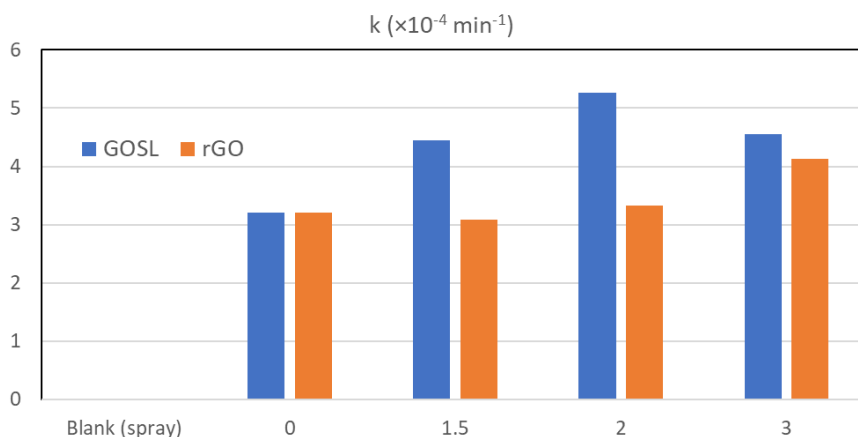


Figure 2. Degradation rate constants for the various samples.

#### 4. CONCLUSION

A method for the deposition of stable porous layers of anatase TiO<sub>2</sub>, either pristine or containing a graphene component, was developed based on spin coating on glass substrates with a sprayed compact TiO<sub>2</sub> layer as an adhesion underlayer. The addition of graphene oxide and reduced graphene oxide species had generally beneficial effect on the efficiency of the sulfathiazole degradation. For GOSL, the best-performing concentration was 2 %, however, all materials containing GOSL exhibited higher activity than pure mesoporous TiO<sub>2</sub>. As the GOSL concentration did not have a significant impact on the photocatalytic performance, the percentage of GOSL can be decreased to 1.5 wt%, which is beneficial regarding the application in a larger extent. For rGO, only the highest concentration provided the desired increase in activity, however, this increase was still lower than in all the GOSL samples. The best performance of GOSL can be assigned to the presence of functional groups (carboxylic, epoxy, and hydroxyl groups) that favor the anchoring of graphene onto TiO<sub>2</sub>, which is necessary for the charge transfer from TiO<sub>2</sub>. It improves the charge separation and the production of highly reactive oxidizing species from water. It seems that the physical interactions (Van der Waals, electrostatic, and charge transfer ones) dominate over the chemical bonds. [26] Therefore, to obtain even more efficient photocatalyst, the ways to intensify the interactions between oxide semiconductor and graphene components should be sought after.

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