

# TiO<sub>2</sub>/Graphene Oxide Heterostructures for Photocatalytic Applications

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## Abstract

In the present work, TiO<sub>2</sub>/graphene oxide (GO) heterostructures with different concentrations of GO were synthesized by hydrothermal transformation of Na-titanate in basic solution. The morphology of the prepared materials was observed by X-ray diffraction analysis (XRD) and transmission electron microscopy (TEM). The transient absorption spectra of the pure TiO<sub>2</sub> and composite TiO<sub>2</sub>/GO materials were collected using laser flash photolysis technique in order to assess photoinduced charge transfer kinetics. Finally, the materials were tested for photocatalytic hydrogen production under solar light irradiation.

**Keywords:** graphene oxide, TiO<sub>2</sub>, heterostructure, photocatalysis, H<sub>2</sub> production

## 1. Introduction

Hydrogen (H<sub>2</sub>) is considered an efficient solar fuel for green energy applications. Among different methods of H<sub>2</sub> production, photocatalysis is one of the most interesting and intensely investigated in the last few years (Chen 2010). However, the energy conversion efficiency from solar to H<sub>2</sub> via TiO<sub>2</sub> photocatalytic water-splitting is still low. Usually, noble metals are employed to reduce charge carriers' recombination. In the present work, 2D heterostructures based on TiO<sub>2</sub> nanorods/GO co-catalyst were proposed. The reduced charge carriers' recombination was evidenced by increased electron/hole lifetimes using laser flash photolysis, that is a well-known technique to investigate charge carriers' trapping and lifetime (Schneider 2016). This is due to electron transfer being facilitated from TiO<sub>2</sub> to GO in TiO<sub>2</sub>/GO heterostructures. The obtained results were directly correlated with the outcome of the photocatalytic tests.

## 2. Experimental

Graphite oxide was synthesized via a modified Hummer's method. It was further used for preparation of stable aqueous GO solution by ultrasonic treatment. Then, TiO<sub>2</sub> nanorods were prepared by two-step hydrothermal procedure. Specifically, P25 was initially transformed into Na-titanate which then acted as a precursor for the TiO<sub>2</sub> nanocomposites. The weight

percentages of GO to Na-titanate were 0.1%, 0.5%, 1% and 2%.

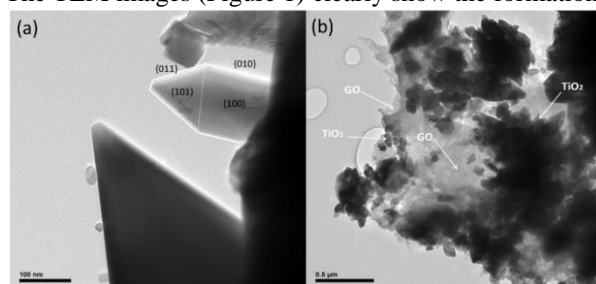
The morphology and crystalline structure of the prepared nanocomposites were investigated by XRD and TEM. The electron/hole lifetimes were assessed by LKS 80 time-resolved laser flash photolysis spectrometer from Applied Photophysics. The sample excitation was realized with the help of Brilliant b Nd:YAG laser from Quantel that generated the third harmonic with a wavelength of 355 nm and a pulse duration of 4 ns. The probing beam from a 150 W Xe arc lamp was used to produce transient absorption spectra of the photo-generated species.

The hydrogen production tests were carried out on experimental set-up consisting of a gas supply, a mass flow controller, a 100 cm<sup>3</sup> double jacket quartz reactor and Hiden HPR 20 mass spectrometer. Methanol and H<sub>2</sub>PtCl<sub>6</sub>·H<sub>2</sub>O were used as sacrificial agent and Pt precursor, respectively. The intensity of the Osram 1000 W Xe lamp irradiation on the reactor surface was 60 mW/cm<sup>2</sup>.

## 3. Results and Discussion

The XRD diagrams reveal gradual transformation from P25 TiO<sub>2</sub> to Na-titanate and then to a new TiO<sub>2</sub> nanostructure with two polymorphs attributed to anatase (PDF #021-1272) and brookite (PDF #76-1934). The calculated phase content of anatase and brookite was 68.7 and 31.3 wt% with average crystallite diameter 32.23 and 27.17 nm, respectively.

The TEM images (Figure 1) clearly show the formation

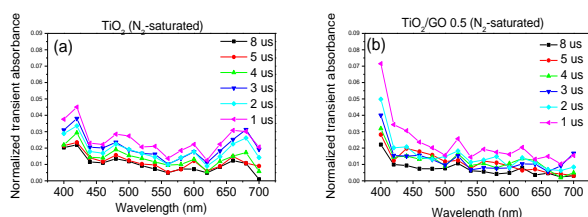


**Figure 1.** TEM micrographs patterns of TiO<sub>2</sub> (a) and TiO<sub>2</sub>/GO 1% heterostructures (b).

It can be seen that the synthesized TiO<sub>2</sub> nanorods are growing along the [010] direction with exposed {100} facets (Figure 1a). The micrograph

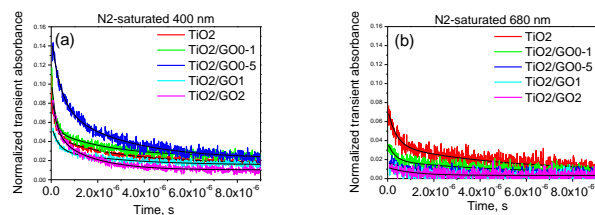
of TiO<sub>2</sub>/GO 1% (Figure 1b) displays the attachment between GO and TiO<sub>2</sub> and confirms that the presence of GO does not hinder the nanorods' growth.

The transient absorption spectra of the prepared samples measured in N<sub>2</sub> atmosphere (Figure 2) exhibit two maximums at 400 and 680 nm that strengthen with the increase of TiO<sub>2</sub>/GO ratio up to the value of 0.5-1%. Also, the absorption is evident within the first  $\mu$ s and weakens noticeably after the next 7  $\mu$ s. According to the literature (Schneider 2016), the pronounced peak near 400 nm is attributed to the trapped holes while wide and low one near 700 nm is connected to the electrons.



**Figure 2.** Transient absorbance spectra collected at delay times of 1, 2, 3, 4, 5 and 8  $\mu$ s after laser excitation for pure TiO<sub>2</sub> (a) and TiO<sub>2</sub>/GO0.5 sample (b) N<sub>2</sub> saturated.

The transient absorbance decay curves at 400 and 680 nm (Figure 3) gives information about holes and electrons' lifetimes, respectively. The decays at 400 nm



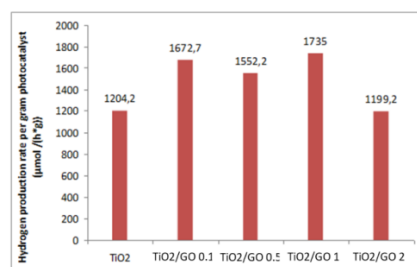
**Figure 3.** Transient absorbance decay for charge carriers (holes and electrons) at 400 (a) and 680 nm (b) for TiO<sub>2</sub> and TiO<sub>2</sub>/GO samples N<sub>2</sub> saturated.

were successfully fitted by a double exponential function with two t<sub>1</sub> and t<sub>2</sub> parameters that concern lifetime of holes trapped at different trapping centres. The decays at 680 nm for TiO<sub>2</sub> and TiO<sub>2</sub>/GO heterostructures with 0.1% GO content could be fitted with a double exponential function while those for larger GO content were successfully fitted with a single exponential function. It can be concluded that deeper trapping centres corresponding to longer electron lifetimes (t<sub>2</sub>) were not activated in the corresponding composites. The fitting results are presented in Table 1. The photocatalytic tests (Figure 4) demonstrate that the Pt-loaded TiO<sub>2</sub>/GO composites exhibit improved photocatalytic activity in comparison to Pt-loaded pure TiO<sub>2</sub>. The TiO<sub>2</sub>/GO nanocomposite with 1% GO content shows the highest hydrogen production rate reaching the value of 1735  $\mu$ mol/(h\*g), which is about 44% more than that for pure TiO<sub>2</sub> (1204.2  $\mu$ mol/(h\*g)). Higher GO percentage (2%) leads to lower hydrogen

**Table 4.** Hole and electron lifetimes received via double/single exponential function fitting of decay curves for TiO<sub>2</sub> and TiO<sub>2</sub>/GO heterostructures.

Sample	hole t1 ( $\mu$ s)	hole t2 ( $\mu$ s)	electron t1 ( $\mu$ s)	electron t2 ( $\mu$ s)
TiO <sub>2</sub>	0.17	2.64	0.36	4.71
TiO <sub>2</sub> /GO 0.1	0.14	2.33	0.34	4.99
TiO <sub>2</sub> /GO 0.5	0.40	2.76	1.29	-
TiO <sub>2</sub> /GO 1	0.27	2.82	1.02	-
TiO <sub>2</sub> /GO 2	0.22	1.59	1.08	-

production rate of 1199.2  $\mu$ mol/(h\*g). So, the contribution of GO is considered essential as it enhances the photocatalytic performance of TiO<sub>2</sub> by more efficient electron-hole separation. However, there exists a certain optimum value of the GO concentration above which the deterioration of the H<sub>2</sub> production rate takes place. This is because the GO sheets shield the active sites on the photocatalyst surface and decrease the intensity of light, hindering this way the efficiency of the TiO<sub>2</sub>/GO catalysts.



**Figure 4.** Hydrogen production rates of the synthesized photocatalysts.

#### 4. Conclusions

The best photocatalytic H<sub>2</sub> production rate belongs to Pt-loaded TiO<sub>2</sub>/GO heterostructures with 1% GO content reaching the value of 1735  $\mu$ mol/(h\*g). Thus, GO plays a significant role in enhancing the H<sub>2</sub> production yield of composites (up to 44% compared to pure TiO<sub>2</sub>). The results for H<sub>2</sub> production are consistent with those of flash photolysis since the latter provides longer electrons'/holes' lifetimes for the composites with 0.5 and 1% GO content.

#### References

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