



# Photocatalytic conversion of terephthalic acid preparation wastewater to hydrogen by graphene-modified TiO<sub>2</sub>



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## ARTICLE INFO

### Article history:

Received 12 October 2015

Received in revised form 5 January 2016

Accepted 5 February 2016

Available online 26 February 2016

### Keywords:

GN-TiO<sub>2</sub>

H<sub>2</sub> production

Wastewater

## ABSTRACT

Using wastewater as sacrificial reagent to transfer solar energy and water as clean energy has attracted significant attention because of increasing concerns on environmental pollution and depletion of fossil fuels. In this study, wastewater from terephthalic acid preparation process was used as sacrificial reagent, and raw components and intermediates were identified by GC–MS, IC, and TOC analyzer. The characterizations of the catalyst were analyzed by XRD, TEM, and XPS. Results showed that the metal and metallic ions (Fe<sup>2+</sup> and Fe) in wastewater were more feasible for electron provision than organics. The final products of Fe<sup>3+</sup> were also confirmed by XPS on the surface of the catalyst. By contrast, the rate of photocatalytic H<sub>2</sub> production did not changed with the addition of terephthalic acid. The H<sub>2</sub> production rate could reach 1.8 mmol g<sup>-1</sup> h<sup>-1</sup> through the use of wastewater and acetic acid as sacrificial reagents.

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## 1. Introduction

As environmental pollution and the depletion of fossil fuels have raised considerable public concern in recent decades, storing unlimited solar energy for use as clean fuel (e.g., H<sub>2</sub>) has been considered as a method to resolve these issues and ensure sustainable development. Among all renewable types of energy, H<sub>2</sub> splitting from water has been the most popular topic since the first report of Fujishima and Honda in 1972; the method uses TiO<sub>2</sub> electrodes in an electrochemical photocatalytic system [1]. Over the past decade, significant efforts have been exerted to improve H<sub>2</sub> generation from water through light energy. Despite these efforts, some sacrifice (except water) is still necessary to provide electrons during the chemical reaction. Sacrificial reagents include organic and inorganic materials, such as Na<sub>2</sub>S–Na<sub>2</sub>SO<sub>3</sub> aqueous solution [2], Na<sub>2</sub>SO<sub>4</sub> solution [3], methanol [4–6], ethanol [7], and ethylene glycol [3].

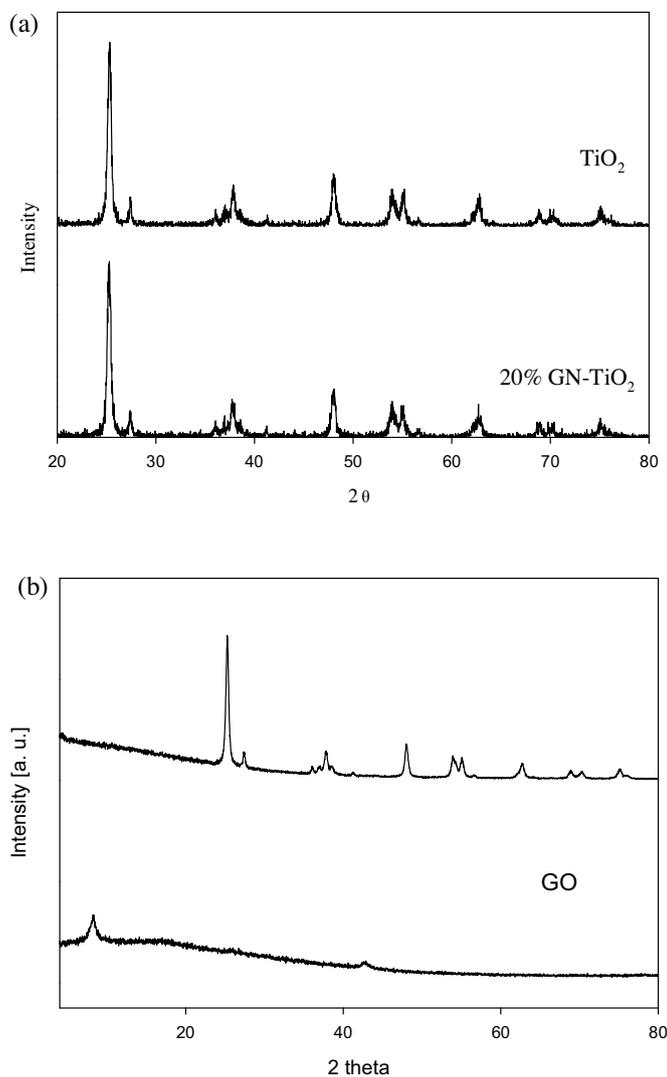
Even if H<sub>2</sub> could be produced successfully through the use of these sacrificial reagents, the cost and energy benefits of the reaction would be decreased. Using wastewater as sacrificial reagent to generate H<sub>2</sub> is a promising method to solve this problem. However, because of the complicated characteristics of wastewater, model contaminants are mostly used instead of real wastewater.

In previous studies, ethylenediaminetetraacetic acid (EDTA) [8], acetic acid [9], sucrose [10], triethanolamine [11], and glucose solution [12] were used to model EDTA wastewater, organic pollutants from anaerobic treatment, sugar industry wastewater, drycleaning wastewater, and organic wastewater, respectively. The H<sub>2</sub> generation rate of these studies could reach 6–7 mmol h<sup>-1</sup> g<sup>-1</sup>, 1–3 mmol h<sup>-1</sup>, 8–12 μmol, 120 μmol h<sup>-1</sup>, and 8–10 mmol h<sup>-1</sup> g<sup>-1</sup>. For real wastewater utilization, Andrea et al. [13] successfully used swine sewage as sacrificial biomass for H<sub>2</sub> production. In a study by Haldorai et al. [14], methylene blue dye and Cr(VI) mixture were treated simultaneously by H<sub>2</sub> generation using graphene-TiO<sub>2</sub>. In the process, graphene-TiO<sub>2</sub> exhibited high methylene blue dye degradation rate (94.2%), Cr(VI) reduction conversion rate (47%), and H<sub>2</sub> production rate (203 μmol/h).

Despite great efforts, the varying effects of sacrificial reagents on real wastewater remain open for discussion. To clarify this problem, we initially analyzed the components of terephthalic acid preparation wastewater by GC–MS (Gas Chromatography–Mass Spectrometer), IC (Ion Chromatography), and TOC analyzer. The H<sub>2</sub> production efficiency of wastewater indicated that some components of wastewater showed better performance than pure acetic acid. In clarifying this phenomenon, each organic and inorganic component (Fe<sup>2+</sup>, Fe, and acetic acid) was analyzed separately through the use of graphene-TiO<sub>2</sub> as catalyst. The H<sub>2</sub> production rate could reach up to 1.8 mmol g<sup>-1</sup> h<sup>-1</sup> through the use of terephthalic acid preparation wastewater as sacrificial reagent. The

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**Fig. 1.** XRD patterns of various catalysts (a) commercial  $\text{TiO}_2$  and self-prepared 20 wt% GN- $\text{TiO}_2$  (20–80°); (b) graphite oxide and self-prepared 20 wt% GN- $\text{TiO}_2$  (4–80°).

characterizations of the catalyst were also analyzed by XRD, TEM, and XPS.

## 2. Experimental method

### 2.1. Preparation of graphite oxide

As the precursor of graphene, graphite oxide was prepared by modified Hummer's method in this study. Initially, the mixture of  $\text{NaNO}_3$  (extra pure reagent, Japan Reagent, 2.5 g),  $\text{H}_2\text{SO}_4$  (analytical reagent, Ke Hua Company, 120 mL), graphite powder (>99.8%, Alfa Aesar, 5 g), and  $\text{KMnO}_4$  (extra pure reagent, ACROS Organics, 15 g) was stirred continuously at 5 °C. During this process, the edge oxidation of graphite would facilitate the penetration of  $\text{H}_2\text{SO}_4$  into the space of two layers of graphite. Thereafter, the temperature was increased to 35 °C to induce the oxidation between the graphite and the penetrated  $\text{H}_2\text{SO}_4$ . Finally, the temperature was further increased to 95 °C to complete the oxidation. The final products were washed with 1 M  $\text{HNO}_3$  and deionized water.

### 2.2. Preparation of graphene- $\text{TiO}_2$

20 wt% graphene- $\text{TiO}_2$  was prepared through the hydrothermal method. Initially, pre-prepared GO (0.2 g) was physical mixed with

commercial  $\text{TiO}_2$  (Degussa P25, 1 g) in 200 mL deionized water and ultrasonicated for 1 h. Thereafter, the mixture was charged into a Teflon-lined autoclave and oven-heated to 120 °C for 3 h to reduce the graphite oxide to graphene. The final precipitation was washed by deionized water and dried at 60 °C.

### 2.3. Characterization of catalysts

The inner structure of the film was analyzed by high-resolution transmission electron microscopy (HR-TEM, JEOL, JEM-2000 FXII). The crystal phase of the catalysis was determined by an X-ray diffraction (XRD, X'Pert PRO) instrument using  $\text{Cu K}\alpha$  radiation ( $\lambda = 0.1541$  nm). X-ray photoelectron spectroscopy (XPS, PHI Quantera, AES 650) was used to analyze the elements, bond, and valence of the material. Invia Raman Microscope (RENISHAW) was used to identify the defects of graphene and graphite oxide.

### 2.4. Hydrogen production

In this study, hydrogen production was conducted by a self-designed quartz reactor at room temperature. The wastewater, which was obtained from Formosa Chemicals Fiber Corporation (Mailiao), was generated in the terephthalic acid preparation process. Before the reaction, 0.5 g  $\text{L}^{-1}$  catalyst was suspended in 300 mL

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