



Incorporating nitrogen-doped graphene oxide dots with graphene oxide sheets for stable and effective hydrogen production through photocatalytic water decomposition



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ABSTRACT

This study proposes incorporating nitrogen-doped graphene oxide dots (NGODs) with graphene oxide (GO) sheets to form a stable and effective NGOD:GO composite for photocatalytic H₂ production through water splitting under visible light illumination. Although Pt-deposited NGOD catalysts were active in the photocatalytic H₂ production reaction, they were only moderately stable. Introducing GO sheets in light-absorbing NGODs effectively mediated the transfer of photogenerated electrons from the NGODs to the GO sheets. This vectorial electron transfer, confirmed by a photoluminescence spectroscopy analysis, led to the relocation of the reaction sites from the NGODs to the GO sheets, protecting the NGODs from attack by reaction intermediates. Moreover, the GO sheets acted as an electron sink, facilitating charge separation in the NGODs. When 3 wt% Pt was deposited on the developed NGOD:GO catalyst, the catalyst steadily catalyzed H₂ production from a 10 vol% aqueous solution of triethanolamine under visible light illumination for 96 h, unlike a NGOD catalyst that exhibited an activity decay of 50% within 96 h. The apparent quantum yield of H₂ under 420-nm light irradiation was 16.0%, demonstrating the high activity of the NGOD:GO catalyst.

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1. Introduction

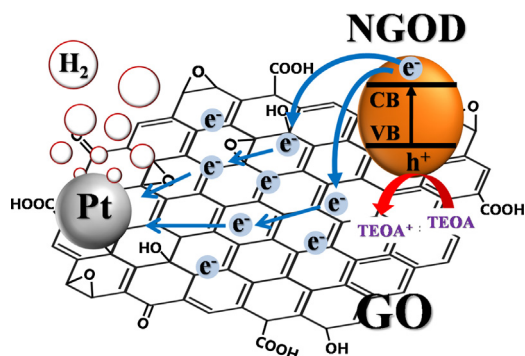
Graphene oxide (GO)-based materials have been widely researched for use as photocatalysts for water splitting because they have structural features similar to those of inorganic materials and behave like a molecular species having high affinity for water [1–5]. GO sheets, which play an auxiliary role in photocatalysis, are derived through the chemical oxidation of graphite powder and contain oxygen functional groups that provide linkages between the catalysts and the GO sheets. In such catalyst:GO composites, the GO sheets have three functions: (I) narrowing the band gap of oxide photocatalysts to extend the light-absorption spectrum, (II) mediating electron transfer to facilitate charge separation, and (III) serving as a charge sink to relay the separated charges [6]. A previous study demonstrated the high activity of nitrogen-doped graphene oxide dots (NGODs) in photocatalytic

water splitting under visible light illumination [5]. The directly depositing a Pt cocatalyst on NGODs may cause extensive interactions between the NGODs and the reaction intermediates, which would result in the catalyst structure being damaged and the catalyst activity consequently being reduced. A promising strategy to increase the chemical stability of NGODs in photocatalysis is to modify the charge transfer in the NGODs by using GO sheets as a charge mediator.

Graphene is a semiconductor with bonding π and antibonding π^* orbitals that act as the valence band maximum (VBM) and conduction band minimum (CBM), respectively. The infinite size and high symmetry of the constituent carbon atoms render graphene a high-conductivity and zero-gap material [7,8], and chemical modification and size reduction can lead to a finite band gap [1–6,9]. Chemical modification of graphene for functionalization can be achieved using GO as the starting materials [10]. Functionalities on graphene can withdraw (e.g., oxygen functionalities) or donate (e.g., nitrogen functionalities) electrons, leading to p-type or n-type conductivity, respectively [11–13]. A previous study revealed that NGODs with oxygen and nitrogen functionalities exhibited an apparent quantum yield (AQY) of 12.8% for H₂ production from an

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Scheme 1. Schematic structure of NGOD:GO composite and possible H_2 evolution process. During visible light illumination, photogenerated electrons can inject from the CBM of NGODs to GO sheets. The photogenerated electrons stored in GO are subsequently transferred to the reactive sites (Pt) for H_2 production. The remained holes in the VBM of NGODs do not interact with the water molecules for O_2 generation, but are exhausted to the hole scavenger (TEOA) instead.

aqueous solution of triethanolamine (TEOA) under 420-nm light irradiation [5].

In the present study, we fabricated a highly efficient, stable, and visible-light-driven photocatalytic H_2 evolution system, a NGOD:GO composite. In this system, NGODs act as a light absorber, and GO sheets act as an electron mediator; the GO therefore facilitates efficient charge separation and transport. Because of the large work function of the GO sheets, photogenerated electrons can be transferred from the CBM of the NGODs to the GO sheets, because there is no barrier [14]. The photogenerated electrons stored in GO are subsequently transferred to reactive sites (such as those on co-catalysts) for H_2 production [14–16]. We used Pt nanoparticles as a cocatalyst, and the nanoparticles were deposited on the surface of the GO sheets in the NGOD:GO composite (Scheme 1). The resulting NGOD:GO composite demonstrated high stability during photocatalysis and achieved an AQY of 16.0% for H_2 production from an aqueous solution of TEOA under 420-nm light irradiation. Our results support a conceptual design for GO-based photocatalysts used for H_2 production, in which vectorial electron transfer increases the activity and stability of the photocatalysts.

2. Experimental

2.1. Synthesis of photocatalysts

GO was prepared using natural graphite powder (Bay Carbon, SP-1, USA) through a modified version of Hummers' method [10]. The graphite powder (5 g) and $NaNO_3$ (2.5 g; Merck, Germany) were added to a solution of concentrated H_2SO_4 (18 M, 150 mL; Wako, Japan) in an ice bath. $KMnO_4$ (15 g; J.T. Baker, USA) was gradually added with stirring; therefore, the temperature of the mixture remained below 20 °C. The mixture was stirred at 35 °C for 4 h to oxidize it, and subsequently, deionized water (230 mL) was slowly added with stirring at 98 °C for 15 min. The mixture was further diluted to 700 mL and stirred for 30 min. The reaction was terminated by adding H_2O_2 (12 mL, 30 wt%; Shimadzu, Japan) with stirring at room temperature. The precipitate of the final solution was washed several times with deionized water (3×500 mL), and it was then dried at 40 °C for 24 h to obtain GO.

Nitrogen-doped graphene was synthesized by exposing as-prepared GO to NH_3 gas at 500 °C for 3 h. The synthesized nitrogen-doped graphene (0.1 g) was oxidized in concentrated HNO_3 (30 mL, 60%, Showa, Japan) at room temperature for 12 h. The solution was subsequently ultrasonically agitated for 10 h. The mixture was heated to 140 °C in a vacuum oven to remove the residual HNO_3 . The product was dispersed in deionized water

and centrifuged to remove the precipitate and form a NGOD suspension. 3 wt% Pt-deposited NGOD suspension was prepared by mixing a NGOD powder (0.4 g) with $H_2PtCl_6 \cdot 6H_2O$ (0.033 g, 99.9%, Alfa Aesar, USA) in a 10 vol% TEOA aqueous solution (250 mL) and subsequently illuminating the mixture. The 3 wt% Pt-deposited NGOD:GO composite was prepared by mixing NGODs (0.4 g), GO sheets (0.012 g), and H_2PtCl_6 (0.033 g) in a 10 vol% TEOA aqueous solution (250 mL) and then illuminating the mixture.

2.2. Characterization of photocatalysts

X-ray photoelectron spectroscopy (XPS; Kratos AXIS Ultra DLD, UK) with Al $K\alpha$ radiation was used to quantitatively determine the chemical composition of the GO-based samples. The C 1s and N 1s spectra were decomposed into several peaks fitted using a Gaussian function. High-resolution transmission electron microscopy (HRTEM; Jeol 2100F, Japan) was used to explore the microstructure of the samples. Raman spectra were recorded using a DXR Raman microscope (Thermo Fisher Scientific Inc., USA) at room temperature and a laser beam with an excitation wavelength of 532 nm. The double-resonant 2D band at 2710 cm^{-1} of NGODs consisted of two peaks, which were de-convoluted using a Gaussian function. The distance between the two peaks was used to estimate the number of graphene sheets contained in NGODs [17]. The optical absorption spectra of NGOD and NGOD:GO aqueous suspensions (both at 0.18 mg mL^{-1}) were obtained by placing the solution in a 1-cm quartz cuvette for analysis with a Hitachi U-4100 (Japan) spectrophotometer. The photoluminescence (PL) spectra of the NGOD and NGOD:GO suspensions were measured at ambient temperature by using a fluorescence spectrophotometer (Hitachi F-700, Japan). The Fourier transform infrared (FTIR) spectra were recorded using a Nicolet 6700 spectrometer (Thermo Fisher Scientific Inc., USA) at room temperature. For electrochemical analysis, NGODs and GO electrodes were prepared by drop-casting these samples on a glassy carbon electrode. These electrodes were subjected to electrochemical analysis in 1 M H_2SO_4 solution with a Pt foil counter electrode and an Ag/AgCl reference electrode. Linear potential scanning (5 mV s^{-1}) was conducted to determine the CBM of NGODs and GO.

2.3. Photocatalytic activity measurements

Photocatalytic reactions were conducted at approximately 25 °C in a gas-enclosed side irradiation system. The GO-based catalysts were suspended in a 10 vol% aqueous solution of TEOA in a Pyrex vessel irradiated from one side by a 300-W xenon lamp (Oriental Instruments, model 66901, USA) with an irradiation intensity of 45 mW cm^{-2} . The wavelength of the incident light was limited to 420–800 nm by using an ultraviolet (UV) cutoff filter (Asahi Spectra, XUL0422, USA) and an infrared cutoff filter (Asahi Spectra, XIS0810, USA). For quantum yield measurements, we used 420-, 450-, and 500-nm band-pass filters (Newport, 20BPF10 series, USA) to obtain monochromatic radiation. The intensity of the light irradiated on the reacting system was obtained using a photodetector (Oriental Instruments, model 71964, USA). The amount of H_2 produced was determined using gas chromatography (Hewlett–Packard 7890, USA; molecular sieve 5A column, thermal conductivity detector, argon carrier gas).

3. Results and discussion

3.1. Morphology and chemical structure of photocatalysts

Fig. 1a shows the full-range XPS spectrum of the NGODs, indicating that the C 1s, N 1s, and O 1s peaks are located at binding energies of 284, 400, and 532 eV, respectively. The atomic ratios (O 1s)/(C

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