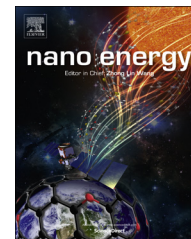




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# Synergistic effect of oxygen and nitrogen functionalities for graphene-based quantum dots used in photocatalytic H<sub>2</sub> production from water decomposition

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## Abstract

Surface intact nitrogen-doped graphene oxide quantum dots (iNGO-QDs), which are based on the abundant elements C, H, O, and N, exhibit outstanding photocatalytic performance in H<sub>2</sub> production through water decomposition. In this study, we synthesize the iNGO-QDs by thermally treating graphene oxide sheets in NH<sub>3</sub> with subsequent ultrasonic exfoliation. The iNGO-QDs exhibit sizes of 2 to 6 nm and consist of approximately 3 graphitic layers. Nitrogen doping in QD synthesis repairs the vacancy-type defects of GO and introduces n-type conductivity to compensate for the unbalanced charges on p-type GO, thereby suppressing leaks of photogenerated charges. Coexistence of p- and n-domains in the iNGO-QDs may form photochemical diodes to facilitate charge separation. Under visible light illumination, the iNGO-QDs steadily catalyze the production of H<sub>2</sub> from an aqueous solution containing triethanolamine. When deposited with Pt as the cocatalyst, the iNGO-QDs exhibit high activity in H<sub>2</sub> generation at an apparent quantum yield of 12.8% under monochromatic light (420 nm) irradiation. The high activity of the iNGO-QDs can be attributed to the synergistic effect of the oxygen and nitrogen functionalities in facilitating charge separation and transfer.

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## Introduction

The use of solar light to catalyze the cleavage of water into hydrogen for use as fuel is a sustainable and environment-friendly approach to overcome issues related to increasing energy consumption [1-6]. Ideally, a photocatalyst should enable light absorption across a wide band of the solar spectrum and should have adequate conduction band minimum (CBM) and valence band maximum (VBM) levels as well as a high degree of stability in order to sustain water redox reactions [5]. A variety of organic as well as inorganic semiconductors have been used as photocatalysts [7-10]. Organic semiconductors enable facile engineering of the electronic structure by varying the constituents of the conjugated systems [11-13]; however, they are susceptible to photocorrosion.

Carbon nitride [14] and graphene oxide (GO) [15-17] have a crystal structure similar to that of inorganic materials but exhibit electronic properties similar to those of organic conjugated systems. As a result, they have emerged as an alternative to conventional photocatalysts. These materials remain stable under irradiation by light and are easily modifiable through chemical doping to vary their electronic properties. In particular, GO sheets have a unique 2D structure that allows extensive modification through substitutional and/or surface-transfer doping treatments [7,18]. This study succeeded in synthesizing stable GO photocatalysts capable of splitting water to produce  $H_2$  without the need for cocatalysts [15,16,19,20].

In the synthesis of GO photocatalysts, the tunable electronic properties of graphene are particularly important. These adjustments can be made via size modulation and chemical modification (see Scheme 1) [21-23]. The bonding  $\pi$  (VBM) and antibonding  $\pi^*$  (i.e.,  $\pi^*$ ; CBM) orbitals of graphene degenerate in the Brillouin zone corners, which renders graphene a zero band-gap material [24,25]. Novoselov et al. were the first to form graphene into QDs using electron-beam lithography, which resulted in materials with a finite band gap and demonstrated the quantum confinement effect in graphene with lateral dimensions of less than 100 nm [21]. Scheme 1 reveals that band-gap creation can also be achieved through chemical modification, resulting in the formation of  $sp^3$  carbon orbitals that disrupt the  $sp^2$  conjugated network of graphene. For example, the C-O covalent bonds in GO break the extended  $sp^2$  conjugated network and confine the  $\pi$ -electrons within the isolated  $sp^2$  domains, resulting in a finite band gap [26,27]. This kind of chemical functionalization (also known as surface transfer doping) withdraws or donates electrons to create p- or n-type conductivity, respectively, on the functionalized graphene [23]. In addition to surface

transfer doping, the substitutional doping of heteroatoms into the graphene lattice opens the band gap by destroying the symmetry of the two carbons in the graphene unit cell [28]. The valence number of the doped heteroatoms (relative to that of carbon) determines the type of conductivity in the doped graphene [23,29,30].

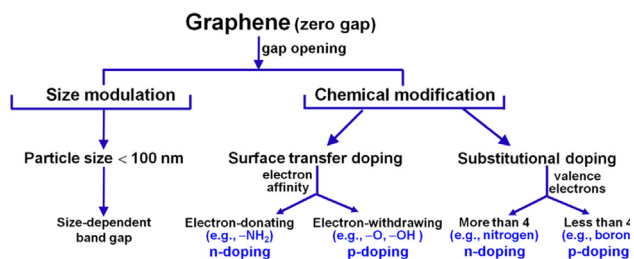
In graphene  $sp^2$  domains with conjugated  $\pi$  orbitals, photo-generated molecular excitons (known as Frenkel excitons) have large Coulombic binding energy (due to a small material dielectric constant), making them prone to recombination [31]. The probability of charge separation governs the performance of photocatalysis systems using  $\pi$ -conjugation in the light-absorbing media. Analogous to biological photosynthesis [32], forming a photochemical diode, which comprises p- and n-type semiconductors connected through ohmic contact, is generally adopted to dissociate Frenkel-type excitons [33]. The 2D feature of graphene, which is directly susceptible to chemical modification, provides a platform for the creation of electronic domains and junctions to induce vectorial displacement and the subsequent separation of opposite charges in Frenkel-type excitons. Furthermore, the substitutional doping of heteroatoms in the honeycomb lattice of graphene can be used to repair vacancy defects and compensate for unbalanced charges caused by surface transfer doping [34].

In previous studies, we demonstrated the ability of GO and nitrogen-doped GO to catalyze water-splitting under illumination, even in the absence of cocatalysts [15,16,19,20]. The surface defects created during GO synthesis may serve as charge-trapping states, which facilitate water redox reactions [35]. However, surface defects also provide a center for charge recombination, which reduces the quantum efficiency of photocatalytic water-splitting [20]. In the present study, we prepared surface-intact nitrogen-doped GO quantum dots (iNGO-QDs) using a mild oxidation process to minimize the density of surface defects on the QDs. Lacking the surface state required to facilitate charge injection into the solution phase, the iNGO-QDs must undergo surface treatment with a cocatalyst to achieve photocatalytic water splitting. The iNGO-QD photocatalyst in this study features a synergistic combination of oxygen and nitrogen functionalities capable of catalyzing the generation of  $H_2$  from water with an apparent quantum yield of 12.8% under monochromatic irradiation at  $\lambda=420$  nm.

## Experimental

### Synthesis of photocatalysts

GO was prepared using a natural graphite powder (Bay carbon, SP-1, USA) according to a modified version of Hummers' method [36]. Graphite powder (5 g) and  $NaNO_3$  (2.5 g; Merck, Germany) were introduced to a solution of concentrated  $H_2SO_4$  (18 M, 115 mL; Wako, Japan) in an ice bath.  $KMnO_4$  (15 g; J.T. Baker, USA) was gradually added with stirring with the temperature of the mixture held below 20 °C. The mixture was then stirred at 35 °C for 4 h to allow oxidation. Deionized water (230 mL) was then slowly added to the mixture and stirred at 98 °C for 15 min. The mixture was further diluted to 700 mL and stirred for 30 min. The reaction was concluded with the addition of  $H_2O_2$  (12 mL, 35 wt%; Shimadzu, Japan) while being stirred at room temperature. Multiple washings



**Scheme 1** Approaches for manipulating the electronic structure of graphene: size modulation and chemical modification.

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