



Full Length Article

Graphitic carbon nitride/graphene oxide/reduced graphene oxide nanocomposites for photoluminescence and photocatalysis



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ABSTRACT

The study presents a modification of graphitic carbon nitride ($g\text{-C}_3\text{N}_4$) with graphene oxide (GO) and reduced graphene oxide (rGO) and investigation of photoluminescent and photocatalytic properties. The influence of GO and rGO lateral sizes used for the modification was investigated. The nanomaterials were characterized with atomic force microscopy (AFM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), diffuse reflectance UV–vis spectroscopy (DR–UV–vis) and photoluminescence spectroscopy (PL). PL revealed that pristine graphitic carbon nitride and its nanocomposites with GO and rGO emitted up-converted photoluminescence (UCPL) which could contribute to the improvement of photocatalytic activity of the materials. The photoactivity was evaluated in a process of phenol decomposition under visible light.

A hybrid composed of rGO nanoparticles (rGONPs, 4–135 nm) exhibited the highest photoactivity compared to rGO with size of 150 nm–7.2 μm and graphene oxide with the corresponding sizes. The possible reason of the superior photocatalytic activity is the most enhanced UCPL of rGONPs, contributing to the emission of light with higher energy than the incident light, resulting in improved photogeneration of electron-hole pairs.

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1. Introduction

Potential applications of photocatalysis are focused on the photocatalytic disinfection of water, production of self-sterilizing and self-cleaning surfaces and the conversion of hydrogen due to the photocatalytic water splitting [1–4]. A photocatalytic activity depends on the ability of the catalyst to form electron-hole pairs that generate free radicals, which can undergo subsequent reactions [5]. Therefore, efficient photocatalyst should fulfil several conditions and requirements, such as well-arranged band gap, photostability, chemical stability, and high affinity to the light. Recently, it has been shown that graphitic carbon nitride exhibits unexpected catalytic activity for various reactions, for example activation of benzene, trimerization reactions, and the activation of carbon dioxide [6]. It is a family of compounds of general formula C_3N_4 and structure-based heptazine units, which depending on the reaction conditions, exhibit different degrees of condensation, properties, and reactivity. Recently, graphitic carbon nitride has been reported as a photocatalytic and photovoltaic material with

a potential use for hydrogen production, oxygen reduction reaction (ORR), for fuel cells, and as metal-free heterogeneous catalyst [7–9]. For example Su et al. described catalyzed selective oxidation of alcohols using O_2 and visible light with high conversion [10]. Pristine $g\text{-C}_3\text{N}_4$ presents semiconductor band gap of 2.7 eV corresponding to an optical wavelength of 460 nm [10]. This band gap is especially relevant for applications in photochemistry and photocatalysis [11]. Unfortunately photocatalytic efficiency of pristine $g\text{-C}_3\text{N}_4$ is still not satisfactory and scientists search for a route to improve it.

One of methods is doping with metallic (e.g. Cr, Fe, V) and non-metallic elements (e.g. N, C, B). Such treatment creates localized/delocalized states in the band gap and thus extends its optical absorption to the visible region. Doping with heteroatoms into the matrix slightly modifies the molecular structure and consequently improves the photocatalytic activity [7]. Boron- and fluorine-enriched polymeric carbon nitride has been successfully synthesized and exhibited good catalytic performance for the selective oxidation of cycloalkanes and improved photoactivity under visible-light illumination [12]. Doping with sulphur increases hydrogen-evolution half-reaction and oxygen producing half-reaction driven by the light irradiation [13].

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Recently, graphene and its derivatives, graphene oxide (GO) and reduced graphene oxide (rGO), have been widely explored for the applications in photocatalysis. The reduced graphene oxide have good photoelectric and photocatalytic properties. It has been found that the most popular photocatalyst, titanium dioxide, modified with graphene and its derivatives has enhanced response of pristine TiO₂. It reveals superior adsorption and photocatalytic performance under both UV and visible radiation. Gradual increase of the content of graphene oxide up to 10 wt% promoted the removal efficiency and correspondingly, facilitated the photodegradation rate of methylene blue [14]. Hence, one of the promising ways to increase the photocatalytic activity of the carbon nitride is a modification with graphene and its derivatives. For instance, Changyoon Song and Seok Kim reported utilization of rGO-modified g-C₃N₄ as fuel cell catalysts [15]. Xiang et al. proved that graphene sheets act as electronic conductive channels to efficiently separate the photogenerated charge carriers and, consequently, to enhance the visible-light photocatalytic H₂-production activity of g-C₃N₄. The optimal graphene content was determined to be ~1.0 wt%, and the corresponding H₂-production rate was 451 μmol h⁻¹ g⁻¹, which exceeded that of pure g-C₃N₄ by more than 3 times. The proposed mechanism for the enhanced visible-light photocatalytic activity of g-C₃N₄ modified with graphene was further confirmed by the photoluminescence spectroscopy and transient photocurrent response. The metal-free graphene/g-C₃N₄ composites showed high visible-light photocatalytic activity, which makes them promising nanomaterials for further applications in water treatment and dye-sensitized solar cells [30]. Li et al. described composite of C₃N₄ and graphene as layer-by-layer and revealed a high catalytic activity towards molecular oxygen activation for the selective oxidation of secondary C–H bonds with a good conversion rate and high selectivity to the corresponding ketones. They contributed to the high-performance of selective oxidation on the composite to the synergistic effect of graphene and g-C₃N₄. The introduction of graphene could shift the highest occupied molecular orbital (HOMO) of g-C₃N₄ to the lower energies via π–π* or charge-transfer interactions to ensure the selectivity of the catalytic reaction [16].

This contribution presents a method of g-C₃N₄ modification with graphene oxide and reduced graphene oxide nanosheets with different lateral sizes. Furthermore, study on influence of the GO and rGO flakes size on a photocatalytic activity of the obtained nanocomposites in the process of phenol decomposition is presented.

2. Materials and methods

2.1. Preparation

2.1.1. Synthesis of graphene oxide

Graphene oxide was obtained by modified Hummers' method [17]. Briefly, graphite powder (1 g) was oxidized by a mixture of concentrated H₂SO₄ and H₃PO₄ acids (120:15 mL) and KMnO₄ (6 mg) under a reflux at 50 °C. After 24 h reaction, the mixture was poured into ice (150 mL) containing 1 mL of 30% H₂O₂. Then, GO was washed in succession with water, 30% HCl and ethanol and separated through centrifugation. Finally, the GO was dried in air at 60 °C.

Graphene oxide was dispersed in water with a concentration of 0.3 mg mL⁻¹ and sonicated for 1 h in bath sonicator to achieve homogeneous suspension. For graphene oxide nanoparticles (GONPs) preparation, GO water suspension (0.3 mg mL⁻¹) was additionally sonicated with horn sonicator for 4.5 h.

2.1.2. Synthesis of graphitic carbon nitride

Pristine graphitic carbon nitride (g-C₃N₄) was synthesized via pyrolysis of melamine at 550 °C for 2 h in a tubular furnace in an inert atmosphere of argon. The temperature was achieved with a heating rate of 2 °C min⁻¹. After the reaction, the furnace was cooled to room temperature in argon atmosphere.

2.1.3. Synthesis of graphitic carbon nitride modified with graphene oxide

GO and GONPs were sonicated for 0.5 and 4.5 h, respectively, to achieve homogeneous suspensions in isopropanol with concentration of 0.1 mg/mL. Simultaneously, g-C₃N₄ was added to isopropanol (0.5 mg/mL), followed by sonication for 4 h. Next, GO or GONPs suspensions were mixed with g-C₃N₄ dispersion (1:2 vol. ratio) and stirred at room temperature for 24 h.

2.1.4. Synthesis of graphitic carbon nitride modified with reduced graphene oxide

Before pyrolysis process, 1 mL of GO or GONPs water suspension was added to 1.5 mg melamine and put into an alumina crucible. Next, the furnace was heated (2 °C min⁻¹) to 550 °C for 2 h under argon atmosphere. After the reaction, the furnace was cooled to room temperature in argon atmosphere.

2.2. Characterization

The morphology of the samples was examined via transmission electron microscopy (TEM, Tecnai F30), scanning electron microscopy (VEGA3 TESCAN) and atomic force microscopy (Nanoscope V MultiMode 8, Bruker). X-ray diffraction (XRD) patterns were carried out using X'Pert Philips Diffractometer with Cu lamp (Kα1 = 1.54056 Å) to investigate the crystal composition of the samples. FT-IR absorption spectra were recorded on Nicolet 6700 FT-IR Spectrometer. Raman spectra were performed using in Via Raman Microscope (Renishaw), with the excitation wavelength of 785 nm. The room temperature photoluminescence (PL) spectroscopy measurements at 650 nm excitation were performed using fluorescence spectrophotometer F 7000 (Hitachi). The optical properties of the materials were investigated by means of the diffuse reflectance DR-UV-vis technique, using a Jasco (Japan) spectrometer. UV-vis absorption spectra of phenol solution were recorded in Jasco V-570 UV-vis spectrometer to determine the degree of phenol decomposition during the photocatalytic process.

2.3. Photocatalytic phenol decomposition

The photocatalytic activity of the materials was examined in the process of phenol decomposition. In a typical procedure, 80 mg of a photocatalyst was dispersed in a 160 mL phenol solution with the starting concentration of 10 mg L⁻¹ and next, poured into a reactor followed by stirring in darkness for 1 h (for adsorption of phenol onto photocatalyst surface). Then, the lamp was turned on and the mixture was irradiated for 72 h. The halogen lamp provided light of wavelength ranging from 400 to 900 nm with the maximum intensity of

650 nm. During the processes, the samples were taken from the mixture every 24 h to determine the concentration of phenol in the reaction solution using UV-vis spectroscopy with a calibrated curve at 270 nm.

3. Results and discussion

The topography of the starting graphene oxide and graphene oxide nanoparticles used for graphitic carbon nitride modification was examined with atomic force microscopy. The images

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