Molecular Catalysis 433 (2017) 274–281

Contents lists available at ScienceDirect

Molecular Catalysis

journal homepage: www.elsevier.com/locate/mcat

MCAT

Editor's choice paper

Graphitic carbon nitride coupled with perylene nanoparticles as efficient solar photocatalyst

Jesty Thomas[a,*], S. Radhika[a], Minjoong Yoon[b,c]

[a] Research Department of Chemistry, Kuriakose Elias College, Mannanam, Kottayam, Kerala, 686561, India
[b] Department of Chemistry, Chungnam National University, Daejeon, Korea
[c] KD Chem-JNT Inc., Ltd., 41-14 Moonpyong dong-ro, Daedok-gu, Daejeon, South Korea

ARTICLE INFO

Article history:
Received 19 October 2016
Received in revised form
23 December 2016
Accepted 24 December 2016

Keywords:
Graphitic carbon nitride
perylene nanoparticles
solar photocatalysis
pollutant degradation

ABSTRACT

Graphitic carbon nitride (CN), a two dimensional (2D) soft nanomaterial is becoming increasingly popular in the field of solar photocatalysis as its surface is modified by incorporating various organic and inorganic guest species. In this study, as a new guest species quasi spherical perylene nanoparticles (PeNPs) were prepared by chemical reduction of perylene-3,4,9,10-tetracarboxylic dianhydride using D-glucosamine hydrochloride, and they were incorporated into CN to form the PeNPs-coupled CN (PeNPs-CN). The prepared PeNPs-CN and CN were characterized in terms of their structural and optical properties, followed by evaluation of their photocatalytic efficiencies by measuring the photodegradation of different dyes like rhodamine B (RhB), eosin yellow (EY) and malachite green (MG) under solar simulator. The PeNPs-CN exhibited higher photocatalytic activity than Degussa P25 (TiO_2) and CN under sunlight, indicating that the solar photocatalytic performance of CN was significantly improved by the addition of PeNPs. Analysis of the UV–vis diffuse reflectance and photoluminescence spectra of PeNPs-CN and CN supported that the improved solar photocatalytic efficiency of PeNPs-CN is attributed to both enhancement of visible light absorption and reduction of the charge recombination rates through sensitization by PeNPs. Both superoxide anion radials and hydroxyl radicals formed by the electron holes were observed to play major roles in the solar photocatalytic degradation of pollutant dyes as identified using different radical scavengers.

1. Introduction

Nowadays, overriding themes of scientific research are mineralization of environment pollutants and the development of efficient solar energy utilization techniques. Semiconductor photocatalysis is recognized as an environmentally benign technology to remediate organic pollutants from aqueous environment and also for effective solar energy conversion. Research is focused in this area using metal nitrides [1], metal oxides [2] etc. However, due to the wide band gap, these catalysts are active only under UV light, restricting their practical applications under solar light [2]. Intense efforts have been devoted to photocatalysts which respond to visible light for the development of systems which utilize solar energy.

Graphitic carbon nitride (CN), a metal-free organic semiconductor has attracted much interest towards the field of photocatalysis since the innovative work on carbon nitride for visible light photocatalytic water splitting [3,4] in the year 2009. CN consists of 2D sheets of tri-s-triazines interconnected via tertiary amines and is the most stable allotrope of various carbon nitrides under ambient conditions [5]. Pure CN presents a bandgap of 2.75 eV, corresponding to visible light absorption up to ~450 nm, which is relevant to the application in solar photocatalysis. CN shows excellent thermal, chemical and photochemical stability due to its s-triazine structure and high degree of condensation. Also it can be synthesised using low cost nitrogen-rich compounds like urea, thiourea, melamine etc. by calcination at high temperatures [6]. Even though CN is visible light active, high recombination rate of photogenerated charge carriers makes its photocatalytic activity very low [7]. Since the graphitic nature of CN allows it to act as a host to incorporate various inorganic and organic guest species, efforts are taken to improve the photocatalytic performance. Several approaches like doping with metals [8] or non-metals [9], coupling with narrow band gap semiconductors [10], formation of hetero structures with organic dyes [11] and molecules like metal phthalocyanine and phosphotungstic acid [12–16] have been recognized to enhance the visible light photocatalytic performance of CN. However, it is known that dye sensitization for the photocatalytic activity of CN is not effective without oxygen doping [11]. Further there are hardly

* Corresponding author.
E-mail address: jestyk@gmail.com (J. Thomas).

http://dx.doi.org/10.1016/j.mcat.2016.12.016
1381-1169/

any reports of sensitization of CN using organic dye nanoparticles. Actually organic dye nanoparticles such as perylene nanoparticles (PeNPs) exhibit distinctive optoelectronic properties superior to their bulk counter parts, and they are of significant use in areas such as biolabelling, novel luminescent materials, non linear optics, chemical sensors [17–19] etc. Thus, they are expected to have higher photosensitization of CN. Nevertheless, the applications of PeNPs in photocatalysis are limited probably due to the poor stability in deionised water [19,20].

Hence we used new approaches to synthesize stable PeNPs from perylene-3,4,9,10-tetracarboxylic dianhydride using D-glucosamine hydrochloride which acts both as reducing and stabilizing agent. The as-prepared PeNPs are incorporated into CN, and the resulting CN-based nanocomposites show greatly enhanced photocatalytic activity under illumination of simulated solar light as compared to those of free CN and TiO_2 (Degussa P25).

2. Experimental details

2.1. Materials

Urea [NH_2CONH_2] was purchased from Merck. Perylene-3,4,9,10-tetracarboxylic dianhydride [PTCDA or Pigment red 224, $C_{24}H_8O_6$], glucosamine hydrochloride [GAH, $C_6H_{14}ClNO_5$], rhodamine B [RhB, $C_{28}H_{31}ClN_2O_3$], eosin yellow [EY, $C_{20}H_6Br_4Na_2O_5$] and malachite green [MG, $C_{23}H_{25}ClN_2$] were procured from Sigma Aldrich. All other chemicals are of analytical grade and used without further purification. Distilled water was used throughout the experiments.

2.2. Preparation of perylene nanoparticles (PeNPs)

Perylene nanoparticles (PeNPs) were prepared in a single step from PTCDA by chemical reduction technique employing a biologically active molecule D-glucosamine hydrochloride (GAH). 1 ml solution of PTCDA in acetone (1.3 mM) was injected by a micro syringe into 30 ml of GAH aqueous solution (25 mM) with vigorous stirring under room temperature. The mixture was stirred well to disperse the perylene nanoparticles in water. The formation of perylene nanoparticles was identified by the development of fluorescent yellow colour.

2.3. Preparation of CN and PeNPs-CN

CN was synthesized from urea by a facile template free method. 10 g of urea was calcinated at 450 °C for 60 minutes in a muffle furnace by placing in a silica crucible covered with lid. After cooling, the light yellow colored powder obtained was collected and is designated as CN.

To synthesize CN coupled with PeNPs (PeNPs-CN), 0.2 g of CN was dispersed in the as-prepared PeNPs. To this 20 ml of distilled water was added and the mixture was stirred well for 60 minutes and dried.

2.4. Characterizations

X-ray diffraction patterns (XRD) of the synthesized samples were obtained on a Rigaku Miniflex 600 diffractometer using Cu Kα (λ = 0.15418 nm) radiation. Photoluminescence (PL) spectral measurements were made using spectrofluorophotometer SL174 at an excitation wavelength of 380 nm using 150W Xe lamp as excitation source. FT-IR spectra of samples were obtained on a Brucker Alpha FT-IR/NIR spectrometer. UV–vis diffuse reflectance (DRS) spectra of the samples were analyzed using Jasco V-770 spectrophotometer. Scanning electron microscopic (SEM) and high resolution transmission electron microscopic (HR-TEM) images of samples were obtained on a JEOL JSM-6700 field emission scanning electron microscope and JEOL 3010 field emission electron microscope.

2.5. Evaluation of solar photocatalytic performance

Solar photocatalytic performances were measured using Heber solar simulator (Heber Scientific, model no: HMV-88123). The solar simulator consists of tungsten halogen lamp (as visible light source) and mercury vapour lamp (as UV light source) along with A.M 1.5G filter. A.M 1.5 G gives standard solar spectrum measured on earth.

The photocatalytic activity of the prepared photocatalysts and commercial photocatalyst such as Degussa P25 (TiO_2) was assessed by measuring the photocatalytic degradation of xanthene fluorene dye, rhodamine B (RhB). For a typical photocatalytic experiment, 0.01 g of synthesized sample was suspended in 20 ml of 15 ppm RhB aqueous solution. The resulting suspension was equilibrated by stirring in the dark for 30 minutes. To study the photocatalytic degradation under sunlight, RhB-photocatalyst suspension was irradiated under solar light at room temperature. The samples were withdrawn at different time intervals and centrifuged at 6000 r.p.m. to separate the photocatalyst. The absorbance of RhB was measured at 553 nm using a Systronics 2203 Double beam spectrophotometer. It was observed that no detectable degradation of RhB occurs without photocatalyst or solar irradiation alone. The photocatalytic degradation of eosin yellow (EY, 20 ppm) and malachite green (MG, 100 ppm) dyes were also studied using synthesised samples and changes in concentration of EY and MG were monitored at 515 and 616 nm, respectively.

Presence of active radical species and their role on photocatalysis was tested by trapping the active species by using some sacrificial agents. Isopropyl alcohol (IPA), ascorbic acid (AA) and triethanolamine (TEOA) were used as hydroxyl free radical ($^{\cdot}OH$), superoxide anion radical ($^{\cdot}O_2^-$) and hole (h^+) scavenger, respectively. The experimental procedure involves the addition of 1 mM of scavengers to photocatalyst-dye solution (0.01 g, 20 ml of 15 ppm RhB). The mixture was then exposed to solar irradiation and the changes in the concentration of RhB were monitored at 553 nm.

3. Results and discussion

3.1. Formation and characterization of PeNPs and PeNPs-CN

Fig. 1(a) shows the UV–vis absorption spectra of mixture solution of PTCDA and GAH at different reaction time intervals. Immediately after mixing PTCDA in acetone and the GAH aqueous solution, only the peak at 265 nm was observed, which is attributed to the intense band system of perylene aggregates [21]. As the reaction time increases, the intensities of visible region peaks (437 and 465 nm) [Fig. 1(a) inset] increased while the intensity of absorption peak in UV region (at 265 nm) decreased. The increase in the intensities of these bands is due to the generation of PeNPs [19,20,22]. These observations clearly indicate that the perylene nanoparticles (PeNPs) are formed at the expense of perylene aggregates [22,23].

The formation of PeNPs was also supported by observation of photoluminescence (PL) emission spectrum (Fig. 1(b)) showing strong emission around 483 and 513 nm originated from free exciton (F-exciton) states [24,25] of quasi-spherical PeNPs [26]. In fact the development of fluorescent yellow colour in the reaction mixture was identified as seen from (Fig. 2(a)). On the other hand 550–600 nm emission attributed to perylene aggregates was weakly observed. Hence PeNPs nanoparticles are formed from monomers rather than perylene aggregates according to the mechanism as illustrated in Scheme 1 and Fig. 2(b). The synthesised PeNPs are stable in aqueous solution as their synthesis involves