



Photocatalytic activity and NIR laser response of polyaniline conjugated graphene nanocomposite prepared by a novel acid-less method



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ARTICLE INFO

Article history:

Received 14 October 2015

Received in revised form

18 December 2015

Accepted 8 January 2016

Available online 13 January 2016

Keywords:

Graphene

Polyaniline

Photocatalyst

Photothermal effect

Electrical conductivity

ABSTRACT

Herein, we present a novel acid-less synthetic approach for *in-situ* polymerization of aniline synchronized with reduction of graphene oxide to graphene. This method provides uniform deposition of ordered polyaniline nanotubes over the surface of graphene nanosheets. The synthesized graphene-polyaniline nanocomposite has the ability of complete removal of harmful dyes commonly used in industry: such as methyl orange, methylene blue, and rhoadmine B from the waste water under the exposure to natural sunlight. The system can be used as an efficient solar energy operated photocatalyst due to effective suppression of recombination of the charge carriers. The unique spatial structure of the graphene-polyaniline nanocomposite has high chemical stability, can be recycled after photolysis, and allows using in multiple cycles without reduction in its photocatalytic activity. In addition, the graphene-polyaniline nanocomposite exhibits strong near-infrared (NIR) absorption, good photothermal stability, as well as shows substantial thermal energy generation under exposure to 808 or 980 nm NIR lasers. The electrical conductivity of polyaniline nanotubes is improved as a result of their conjugation with graphene nanosheets in the nanocomposite. Owing to its outstanding photocatalytic activity and chemical stability, the reported graphene-polyaniline nanocomposite has a great potential in purification of industrially generated waste water.

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1. Introduction

In the recent years, lot of research has been devoted to address the issues of energy shortage and environmental pollution. A promising way of overcoming the existing barriers in the field is an efficient utilization of the solar energy [6,7]. In this context several new promising photocatalysts were suggested and tested recently for their catalytic activity [1–5]. Sunlight driven photocatalysis, in general, has a prominent ability in utilization of the solar energy conversion and environmental remediation. Yet now, the overall photocatalytic efficiency of the existing photocatalysts is too low for commercial applications. In addition, current photocatalysts suffer from a slow electron transfer rate and relatively fast charge recombination process. It is highly desired to explore and develop new photocatalysts with a higher quantum yield. Among the so far investigated photocatalytic materials, polyaniline (PANI)

is an important compound owing to its good stability, corrosion protection property and low toxicity [8]. Furthermore, PANI with an extended π -conjugated electron system exhibits great potential in the field due to its high absorption coefficient in the visible range of light and high mobility of charge carriers [9,10]. In addition, PANI is simultaneously a good electron donor and excellent hole acceptor material under photo illumination [11].

However, apart from above mentioned benefits, the catalytic activity of PANI has hindered from fast recombination of charge carriers generated during photolysis. In order to inhibit the recombination of photo-generated electron-hole pairs, various approaches can be considered. Among those, possible conjugation of PANI with graphene (GR) has received special attention due to the superior electron mobility ($2 \times 10^5 \text{ cm}^2/\text{Vs}$) and high specific surface area ($2600 \text{ m}^2/\text{g}$) of the latter [12]. Owing to its high electron mobility, GR quickly accumulates photo-generated electrons from the PANI thus reducing the probability of the electron-hole pair recombination. At the same time, high surface area of GR facilitates better adsorption of pollutants at the surface of the photocatalyst. Moreover, the presence of the GR phase promotes better dispersion

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of PANI in the composite thus increasing its photocatalytic efficiency. It can be identified that the GR acts as an electron acceptor in the nanocomposite because of its two-dimensional π - π conjugation, which reduces the recombination rate of charge carriers and ultimately enhances the performance of the photocatalyst [13]. In consideration of the synergistic effect between GR and PANI Ameen et al. have studied degradation of bengal rose dye using a PANI/GR photocatalyst. They have found that about 56% of the dye has been degraded during three hours of photoillumination [14]. Zhang et al. have prepared the hierarchical nanocomposites of PANI nanorods and graphitic carbon nitride sheets and used them to trigger degradation of methylene blue and methyl orange [10]. As reported the complete degradation of methyl orange occurred within the first 25 min and about 79% of methylene blue has been degraded within 30 min of illumination. So far reported synthetic approaches for preparation of graphene-polyaniline (GR-PANI) nanocomposites required usage of some acids, which is in contradiction with modern “green chemistry” approaches. In our paper, we report on an alternative benign synthetic way for the GR-PANI nanocomposites preparation.

As discussed in previous publications possible means for the enhancement in the photocatalytic activity of GR based composites include: 1 increase of the material's ability for sorption of pollutants, 2 broadening of the light absorption range, and 3 optimization of the trapping and shuttling of the photogenerated electrons [15–20]. In addition, the GR component was reported to possess a strong photothermal effect (PTE), which may also be a key factor in the enhancement of the photocatalytic activity of GR based composites. However, till now this possibility has not been explored.

Recently, the photothermal therapy (PTT) method has been introduced as a valuable and increasingly recognized alternative in medical cancer treatments [21–24]. The method uses near-infrared (NIR) laser light to generate heat and destroy tumor cells *in vivo*. Compared to traditional therapeutic treatments, the PTT shows a minimal invasive nature and improved selectivity since only the lesion that is exposed to the light is treated, while other tissues (which are not exposed to laser radiation) are not affected. In the PTT treatment, the applied photothermal agent should be able to generate a sufficient heat or thermal energy under the laser light exposure in order to destroy cancerous cells and so the success of the treatment depends entirely on the PTE property of the material being used. The GR component of the photocatalyst should be able to generate enough thermal energy for thermal degradation of pollutants in a steady state regime under continuous photo-illumination when the temperature of the reaction mixture remains nearly constant. This effect restricts also recombination of the photogenerated charge carriers and significantly enhances the photocatalytic activity of the catalyst.

In this work, we suggest a novel, acid-less method for the preparation of GR-PANI nanocomposites with enhanced photocatalytic activity. This process provides the route for *in-situ* reduction of graphene oxide (GO) to GR coupled with synchronous polymerization of aniline. The latter process results in a uniform deposition of ordered PANI nanotubes over the surface of GR nanosheets. Thus constructed GR-PANI nanocomposites have been studied using various experimental techniques including testing their electrical, spectroscopic properties, photocatalytic activity, and PTE. The catalytic activity of GR-PANI nanocomposite has been evaluated by the process of degradation of several industrially versatile and harmful dyes *viz.*, methyl orange (MO), methylene blue (MB) and rhodamine B (RhB) by exposing them to a natural sun light. Furthermore, we report on the PTE effect in GR-PANI nanocomposites, which has been explored when aqueous dispersions of the GR-PANI material were exposed to 808 or 980 nm NIR laser light.

2. Experimental

2.1. Materials

All the reagents were purchased from Aldrich and used without further purification unless otherwise noted and aniline was distilled under reduced pressure prior usage. Aqueous solutions were prepared using ultra-pure water obtained from Milli-Q Plus system (Millipore).

2.2. Preparation of GO

GO was prepared from graphite powder according to the Hummers and Offeman method with slight modifications [25]. In a typical procedure, 1g of graphite powder (<20 μ m, Aldrich) was added to 40 mL concentrated H_2SO_4 and stirred for 1 h under ice-cooling condition. Then, 15 mL fuming HNO_3 was slowly added and stirred the mixture for 30 min. To this, 5 g of $KMnO_4$ was gradually added with stirring and cooling and the resulting mixture was stirred at room temperature for 12 h followed by addition of 150 mL DI water. After stirring the mixture for 30 mins, 30 mL of H_2O_2 (30%) was slowly added, which turned the color of the reaction mixture to bright yellow. The resulted mixture was centrifuged and washed with 1:10HCl in water solution in order to remove metal ions. Further, the mixture was washed with DI water until complete removal of the acids and thus obtained dark-yellow colored GO was dried under vacuum at 40 °C for 12 h. The drying process of GO was carried out at lower temperature in order to avoid its deoxygenation.

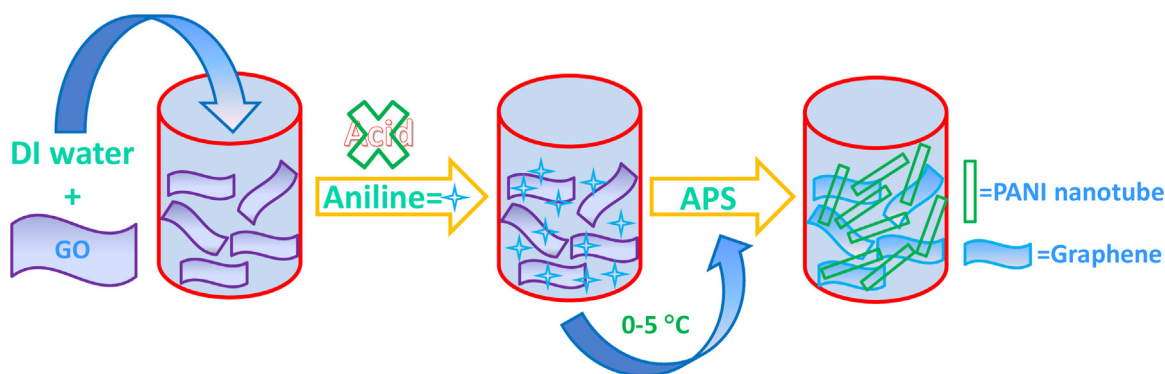


Fig. 1. Schematic illustration of preparation of GR-PANI nanocomposite.

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