Applied Surface Science 376 (2016) 276–285

Contents lists available at ScienceDirect

Applied Surface Science

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

Photocatalytic degradation of organic contaminants under solar light using carbon dot/titanium dioxide nanohybrid, obtained through a facile approach

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ARTICLE INFO

Article history:
Received 6 January 2016
Received in revised form 19 March 2016
Accepted 21 March 2016
Available online 1 April 2016

Keywords:
Carbon dot
Nanohybrid
Carbon dot/titanium dioxide
Photocatalyst
Degradation

ABSTRACT

In the present study, a novel, simple and green method was developed to synthesize highly luminescent nitrogen containing carbon dot (CD) using carbon resources like bio-based citric acid and glycerol in the presence of cost free cow urine. The as-synthesized CD showed exciting wavelength dependent down- and up-conversion flourescence properties. To utilize the advantage of up-conversion flourescence, a nanohybrid (CD@TiO_2) was synthesized from the above carbon resources and titanium butoxide through a facile one pot single step hydrothermal protocol. Nanomaterials like bare TiO_2 and nanohybrid of TiO_2 in presence of CD (CD/TiO_2) were also synthesized for comparison purpose. The optical properties and structural characteristics of the prepared CD, bare TiO_2, CD@TiO_2 and CD/TiO_2 were examined by Fourier transform infrared (FTIR), UV–vis and fluorescence spectroscopic, scanning electron microscopic (SEM), transmission electron microscopic (TEM) and X-ray diffraction (XRD) studies. The elemental compositions of bare CD and CD@TiO_2 nanohybrid were obtained from EDX analyses. The poor crystalline nature and narrow distribution of spherical CD and anatase form of TiO_2 were confirmed from XRD and TEM studies. Amongst the studied nanomaterials, CD@TiO_2 exhibited the most promising photocatalytic degradation of organic pollutants like benzene and phenol as well as an anthrogenic pesticide under sunlight.

1. Introduction

Nanotechnology is an emerging and rapidly growing field because of its wide range of outstanding applications in science and technology. Again, nanomaterials owing to their diversified physico-chemical attributes resulted in an explosion for a broad range of innovative applications [1,2]. Recent times carbon dot (CD) becomes a rising star as a new category of photoluminescent carbon nanomaterial with size below 10 nm due to its benign, abundant and inexpensive nature [3–5]. It is one of the green alternatives for fluorescent semiconductor quantum dots (QDs) and possesses superior properties such as chemical stability, low toxicity, high aqueous solubility, low photobleaching, easy functionalizability, good biocompatibility etc. over inorganic QDs. Because of its distinct advantages it has great potential in the area of photocatalysis, multicolour printing, sensing, bio-imaging, light emitting device and so on [6–12]. In last few years, CD has been synthesized by a variety of approaches namely microwave irradiation [13], laser ablation [14], hydrothermal treatment [8], arc discharge [15], pyrolysis [7] etc. But these approaches involve high energy consume protocol, complex process, high cost, high temperature and/or long time for synthesis. Therefore, green synthesis of CD is a highly attractive research area in recent times which utilizes naturally renewable low cost and nontoxic carbon precursors. There are already a few reports on synthesis of CD from renewable resources like cabbage [3], banana juice [4], hair fibre [6], plant leaves [7], sweet pepper [8], apple juice [16] etc. and also from bio-based commercially available chemicals like starch [17], glucose [18] etc. In most of the cases hydrothermal method were used to synthesize CD. The drawbacks of these reported methods are utilization of expensive and food based bio-precursors, high temperature and organic solvents. These disadvantages hampered the applications of CD in biological, chemical, environmental and life sciences. Till now, there are only a few reports on CD showing both down and up-conversion fluorescences [3,19]. Therefore, it is highly virgin area to investigate an easily available and cheap carbon resource for the synthesis of CD through an environmentally friendly green technique and to obtain excellent up-conversion

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http://dx.doi.org/10.1016/j.apsusc.2016.03.165
0169-4332/

attribute of CD. To explore easily available natural precursors associated with green synthesis of CD, herein, we have synthesized CD through a simple and efficient harmless approach from bio-based precursors like citric acid and glycerol in the presence of cost free cow urine. In this approach other than water, no solvent or medium was used. Thus this approach is not only eco-friendly but it also avoids the additional step for nitrogen doping to enhance the fluorescence behavior of CD as the used cow urine contains nitrogenous compounds like urea, uric acid, ammonia etc. Again, researchers designed nanohybrid of CD with other metal or metal oxide nanoparticles for enhancing their catalytic efficiency by exploiting the up-conversion fluorescence property of the former [19–21]. Metal oxide nanoparticles like TiO_2, ZnO, Cu_2O etc. are extensively used as photocalysts for degradation of organic pollutants. Photocatalysis by metal oxide nanomaterials is gaining significant interest as a green technology. This is because of the fact that it can be widely used for removal of different hazardous organic pollutants and thereby purifying the environment [22–24]. More recently, many efforts have been focused on the preparation of novel hybrids comprising of CD and inorganic nanoparticles of silica, zinc oxide, iron oxide, and titanium dioxide. The resultant hybrids integrated the fluorescence properties of CD with the mechanical, magnetic or optical properties of the metal oxides. Such hybrids act as efficient photocatalysts [21,25–27]. Among different types of metal oxide nanomaterials, TiO_2-based materials are well known as the most effective photocatalysts due to their abundances, cost-effectiveness, physico- chemical stability and nontoxic nature. However bare TiO_2 exhibited photocatalytic activity under UV light only [24,28,29]. As CD possesses up-conversion fluorescence property, so to achieve natural sunlight exposed photocatalytic activity, attempts were made to obtain its nanohybrid with TiO_2, though the reported approaches were tedious. However, most of CD-loaded nanohybrids are prepared by physical blending only without any chemical coupling, which may lead to poor performance [21,30–33]. In the present study, therefore the desired nanohybrid was synthesized by a one pot single step facile and green technique with strong physico-chemical interactions. Again, among different types of organic pollutants, phenol and benzene are highly toxic and carcinogenic compounds, produced from different chemical industries [31]. Therefore synthesized nanohybrids (CD@TiO_2 and CD/TiO_2) were utilized for photocatalytic degradations of these pollutants. Further, amongst different hazardous anthropogenic organic chemicals, pesticides are the most common non-degradable anthropogenic chemical contaminants both in water and soil [34]. Therefore synthesized nanohybrids were also tested for degradation of a representative paraxon pesticide.

Authors, therefore, wish to report a facile one-step green synthetic protocol for synthesis of highly fluorescent CD from bio-based precursors in presence of cost free cow urine and fabrication of CD/TiO_2 nanohybrid. This nanohybrid was used as an efficient photocatalyst for degradation of organic pollutants like benzene and phenol, and a representative pesticide under normal sunlight. The bare CD, TiO_2 and CD/TiO_2 nanomaterials were also synthesized to judge the superiority of in situ synthesized CD@TiO_2 nanohybrid for the same purpose.

2. Experimental

2.1. Materials

All the chemicals were used without further purification. Citric acid (Merck, Germany), glycerol (Merck, Germany), ethanol (Merck, India), titanium butoxide (Sigma Aldrich), phenol (Merck, Mumbai) and benzene (Merck, Mumbai) were used as received. Cow urine was collected from the nearest farm of Tezpur University. Ethyl paraoxon pesticide was used in photocatalytic reaction as it is one of the most common non-degradable anthropogenic chemical contaminants both in water and soil, and used in industry as well as in agriculture. It was obtained from Sigma Aldrich, Germany.

2.2. Synthesis of CD

CD was synthesized from citric acid and glycerol in the presence of cost free cow urine. At first, equal amount (2.5 g) of citric acid and glycerol was dissolved in 15 mL distilled water. To the above mixture 30 mL cow urine was added. The reaction mixture was taken in a 100 mL conical flask plugged with a cotton cork and heated at a constant temperature of 150 °C for 4 h in a muffle furnace. After cooling to room temperature a dark brown product was obtained. This was dissolved in 20 mL of water and the residue was separated by filtration. Then the aqueous filtrate was centrifuged at 3000 rpm for 15 min under ambient conditions. The remaining water was evaporated at 60 °C by heating for 8–9 h to obtain highly fluorescent CD. The yield of the synthesized CD was found to be 70%. CD in absence of cow urine was also synthesized by following the same procedure. To examine the consistency of cow urine, three different samples of cow urine were used to synthesize CD by following the same technique.

2.3. Synthesis of bare titanium dioxide nanoparticle (TiO_2)

Bare TiO_2 nanoparticles were synthesized by a single step hydrothermal process. Firstly, 15 mL of concentrated HCl was mixed with 5 mL of distilled water and 10 mL cow urine and the mixture was stirred for 10 min. Then, 0.8 mL of titanium butoxide was added dropwise to the above mixture. After vigorously stirring for another 10 min, the solution was transferred to a 50 mL Teflon lined stainless steel autoclave which was kept in a muffle furnace at 150 °C for 8 h. The autoclave was cooled down to room temperature. Then the solution was centrifuged at 5000 rpm for 15 min and dried at 50 °C for 7–8 h to obtain the solid residue. This solid product was calcined at 300 °C for 2 h in a muffle furnace.

2.4. Synthesis of nanohybrids of CD and TiO_2

CD and TiO_2 nanohybrids were synthesized by both in situ and ex situ techniques. In in situ technique, at first equal amount (0.668 g) of citric acid and glycerol was mixed with 5 mL water, 10 mL urine and 15 mL concentrated HCl and the mixture was continuously stirred for 10 min. To this above mixture 1.6 mL titanium butoxide was added dropwise and stirred for another 10 min. Then the above mixture was transferred to a 50 mL Teflon lined stainless steel autoclave which was placed in a muffle furnace and heated at 150 °C for 8 h. The autoclave was cooled to room temperature and the suspension obtained after the reaction was centrifuged at 5000 rpm for 15 min and dried at 50 °C for 5–7 h in an oven for further use. The obtained nanohybrid was coded as CD@TiO_2. In this case also three different samples of cow urine were used to synthesize CD@TiO_2 by following the same technique to judge the consistency of cow urine.

In ex situ technique, 0.25 g CD was mixed with 5 mL water, 10 mL cow urine and 15 mL concentrated HCl by continuous stirring for 5 min. Then, 0.8 mL titanium butoxide was added dropwise to the above mixture and stirred the mixture for another 10–15 min. In the same way, as above the mixture was taken in an autoclave and heated at 150 °C for 8 h inside a muffle furnace. The autoclave was cooled down at room temperature. The obtained suspension was centrifuged like CD@TiO_2 and obtained product was dried at 50 °C for 5–7 h. This nanohybrid was coded as CD/TiO_2.