Original Article

Synthesis of magnetically reusable Fe$_3$O$_4$/TiO$_2$-N, P co-doped graphene quantum dot nanocomposites using hexachlorocyclophosphazene; high photoluminescence property and photocatalytic promoter

Hossein Khojasteh$^a$, Mahnaz Amiri$^{b,c}$, Ataollah Sohrabi$^d$, Salah Khanahmadzadeh$^d$, Masoud Salavati-Niasari$^{e,*}$, Hossein Moayedi$^{f,*}$

$^a$ Department of Chemistry, Faculty of Science, Soran University, P. O. Box 624, Soran, Kurdistan Regional Government, Iraq
$^b$ Department of Hematology and Laboratory Sciences, Faculty of Allied medicine, Kerman University of Medical Sciences, Kerman, Iran
$^c$ Cell Therapy and Regenerative Medicine Comprehensive Center, Kerman University of Medical Science, Kerman, Iran
$^d$ Department of Chemistry, Faculty of Science, Mahabad branch, Islamic Azad University, Mahabad, 59135-443, Islamic Republic of Iran
$^e$ Institute of Nano Science and Nano Technology, University of Kashan, Kashan, P. O. Box 87317-51167, Islamic Republic of Iran
$^f$ Institute of Research and Development, Duy Tan University, Da Nang, 550000, Viet Nam

**ARTICLE INFO**

Article history:
Received 26 October 2019
Accepted 24 November 2019
Available online 6 December 2019

Keywords:
Hexachlorocyclophosphazene
Photoluminescence
GQDs
Citric acid
Fe$_3$O$_4$/TiO$_2$/N
P-GQDs nanocomposite

**ABSTRACT**

Hexachlorocyclophosphazene (PNT) was used as new P and N doping source for synthesizing of graphene quantum dots (N,P-GQDs). Hydrothermal process was applied for importing P and N atoms into the GQDs texture. Three different amounts of hexachlorocyclophosphazene were used to obtain optimum sample. All products were characterized using XRD, SEM, PL, FT-IR, EDS, AFM, TEM and Raman spectroscopy. XRD result indicated that the sample with 0.1 g of PNT (sample 2) has sharp peaks with medium wide and intensity and has a more principle in structure in comparison with other samples. So sample 2 was chosen as optimum sample. Also sample 2 showed strongest PL emission under excitation at 396 nm which was an evidence of successful doping of P and N atoms in the GQDs structure during hydrothermal process. The Fe$_3$O$_4$/TiO$_2$/N,P-GQDs nanocomposite was obtained using S2 as N,P-GQDs source showed a high activity in organic dye degradation. The higher catalytic activity of Fe$_3$O$_4$/TiO$_2$/N,P-GQDs versus TiO$_2$ can be attributed to the synergistic effect between TiO$_2$ and N,P-GQDs. The magnetic properties of the catalysts allow fast separation of the catalysts from the reaction media.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

Recently, carbon nanodots (CDSs) and graphene quantum dots (GQDs) have been used extensively in photocatalysts, bioimaging, light-emitting diodes, ion detection, and electrochemical luminescence due to their unique properties [1–5]. Carbon nanodots are amorphous carbon nanoparticles with no structural discipline. But for graphene quantum dots just like graphene, honeycomb structure can be observed. Regular carbonic nanostructures such as graphite, graphene, carbon nanotubes and graphene quantum dots have two specific peaks in their XRD pattern at 2θ≈ 26° and 2θ≈ 43° which are reflected from (002) and (001) plans, respectively [6,7].

Just like graphene, GQDs are made of two dimensional sheet of sp2-hybridized carbon atoms, but they are nanometer-scaled graphene particles with size of less than 30 nm in diameter [8,9]. Since GQDs show a PL emission, most applications of them have been focused on the photoluminescence (PL)-related fields. On the other hand, due to high transparency and high surface area property, GQDs have been proposed for energy and display applications [10]. Also recent researches showed that GQDs have a good hole transporting ability and they can be applied as hole transport layers [11].

The size of GQDs is very small and they can in different solvents according to their surface functional groups. Accordingly, by modifying the surface or inner structure of GQDs, the band gap will changes and different PL colors with different intensity and life time can be achieved. Mass preparation of GQDs is an important challenge for industrial and commercial applications. For that, a simple, cheap, safe and large scale process is needed. In the case of GQDs, such as other nanostructures, there is two main strategies known as top-down and bottom-up [12,13]. In top-down approach, preparation of GQDs involves fragmentation of ordering bulk carbonic materials into smaller particles with nanoscale in diameter. But the main obstacle is that usually strong and corrosive acids are implemented in this process. So process conditions are very acidic, corrosive and eruptive which is very dangerous and unsafe for the operator or researchers and can damage the reactor or vessel reaction.

In contrast, in the bottom-up case, a wide range of organic molecules can be implemented as carbon source. The size control is simpler in this strategy in compare to too-down method and sometimes uniform GQDs with narrow particle size distribution can be achieved without using any stabilizer or capping agent [14]. Carbonization, electrochemical, solvo and hydro-thermal methods are used frequently in bottom-up route for synthesis of GQDs [15–17]. As we know, hydrothermal process is a technique for crystallizing materials at high-temperature and high vapor pressures of water. In case of using a solvent other than water, the process is called solvothermal [18]. This process is safe, cheap, variable, and controllable for large scale production of nanomaterials. Various of organic molecules, including glucose, citric acid, o-phenylenediamine, dicyandiamide [15–19]. However, the photoluminescence emission of the GQDs is rather low if no further modification and/or doping is made. Recently, some studies are made on the doping of heteroatoms such as nitrogen and sulfur into a GQDs structure for improving the quantum yield and PL properties [16,17].

Hexachlorocyclophosphazene (Phosphonitrilic chloride trimer (PNT)) is a nontoxic, inexpensive readily available catalyst for various organic reactions with high yields and high selectivity. PNT is a Lewis acid which make it appropriate for organic transformations [20]. To the best of our knowledge, PNT has never been investigated as a source for P and N doping in GQDs. Here we report a one-step hydrothermal bottom-up synthesis of N-P doped GQDs using hexachlorocyclophosphazene as nitrogen and phosphorus dopant source. We believe that this matter decomposes at high temperatures and N–P atoms will release which they can diffuse into carbonic structure. A mixture of ethanol and water was used to obtain homogeneous system during the process. Final products have promoted PL emission in compare with the sample which no hetero atom doped. The obtained suspension is stable at room temperature for a long time. The products were characterized using XRD, SEM, PL, FT-IR, EDS, AFM and Raman spectroscopy. Our procedure is cheap, quick, scalable, and the products are stable with blue luminescence emission which made them suitable for different applications such as bio imaging, additive for photocatalysts and solar cells.

2. Experimental

2.1. Materials and characterization methods

Citric acid (CA) and absolute ethanol were purchased from Merck Company. Hexachlorocyclophosphazene (Phosphonitrilic chloride trimer) was provided by Sigma-Aldrich. Deionized water was used throughout and all mentioned materials and solvents were used without further purification. To characterization of products, various analytical methods were used. XRD patterns were recorded by a Philips, X-ray diffractometer using Ni-filtered Cu Kα radiation. SEM analysis was performed by using LEO instrument model number 1455 V. Samples were coated with a thin conductive layer of Pt before imaging. FT Infrared (FT-IR) spectra were obtained as potassium bromide pellets in the range of 400–4000 cm–1 with a Nicolet-Impact 400D spectrophotometer. Raman spectra were taken with a confocal Raman microscope (SENTERRA (2009); BRUKER, Germany) with high-energy laser diodes. The power and the wavelength of the laser are 10 mW and 785 nm, respectively. The confocal depth resolution and the objective lens used for the Raman measurements are 2 μm slit and 50×, respectively. The thickness of the products was characterized by an Atomic Force Microscope (AFM) (Digital Instruments NanoScope IV) working in the tapping mode, and a Mica surface. Transmission electron microscope (TEM) images of nanopowders were taken by a JEM-2100 with an accelerating voltage of 100 kV equipped with a high resolution CCD Camera. Photoluminescence spectra (PL) was collected using a Cary Eclipse fluorescence spectrophotometer.

2.2. Synthesis of N,P-GQDs

The GQDs used in the experiment were synthesized by hydrothermal process using CA as the carbon source as well as Hexachlorocyclophosphazene as the nitrogen and phos-
Table 1 – Synthesis conditions of N,P-GQDs samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CA/g</th>
<th>PNT/g</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1</td>
<td>0.05</td>
<td>Low crystalline order</td>
</tr>
<tr>
<td>S2</td>
<td>1</td>
<td>0.1</td>
<td>Good incorporation into the structure- high crystalline</td>
</tr>
<tr>
<td>S3</td>
<td>1</td>
<td>0.2</td>
<td>Low crystalline order</td>
</tr>
</tbody>
</table>

phorous source. Firstly, 1 g CA was added to a 100 ml beaker with a mixture of 50 ml EtOH:H2O (3:1) and stirred for 10 min to obtain a homogeneous system (solution 1). In another 100 ml beaker, 0.05 g Hexachlororocyclohexaphazene was dissolved in 20 ml absolute ethanol and stirred for 15 min (solution 2). Subsequently, the two solutions were mixed in a Teflon lined autoclave and the reactor was sealed. Hydrothermal process was carried out in an oven and the temperature increased to 180 °C and kept for 12 h. Finally, the reactor was cooled down to room temperature and the product was centrifuged at 4000 RPM to remove any heavy solid particles (schematic of synthesis process is illustrated in Scheme 1). Three samples with different PNT concentrations was prepared in this way. Table 1 sets out the experimental parameters.

2.3. Synthesis of Fe3O4/TiO2/P, N-GQDs

In the following, for more investigation about the potential and quality of the products, Fe3O4/TiO2/N, P-GQDs nanocomposite was prepared. In a beaker, 0.441 g of FeCl3, 4H2O and 1.79 g of FeCl3,6H2O was dissolved in deionized water and stirred for 30 min. A reflux system was designed and two mixtures were added to the conical flask, which is connected to the condenser, then inert gas was flowing into the solution. 0.3 g NaOH was added to the system and the reflux process was continued for 3 h at 70 °C under continues stirring. Finally, the black product was collected and washed using a centrifuge and dried at 60 °C overnight. In the next step, 0.3 g of Fe3O4 nanoparticles was dispersed in 80 ml of Merck ethanol and sonicated for 20 min. After that 2 ml PEG 400 was added to the mixture. In a second vessel, 3 ml tetranoormal-butylitanate was added to 20 ml of Merck ethanol and 0.5 ml acetylacetone and stirred using a magnetic stirrer for 10 min. The contents of the second vessel were added slowly to the above mixture while gently shaking using a mechanical stirrer. After 20 min, 2 ml deionized water was added and the final mixture stirred at 70 °C for 12 h. The obtained gray products were separated using an external magnet and washed thoroughly with ethanol and deionized water before drying at 60 °C. Subsequently, the powder was calcined at 400 °C under an inert atmosphere for 1 h to improve the crystalline properties of the obtained nanocomposite. Finally, for obtaining the Fe3O4/TiO2/N,P-GQDs nanocomposite, 1 g of the previous composite (Fe3O4/TiO2) was dispersed in 20 mL ethanol and sonicated for 15 min. Then 0.06 g of sample2 was added into the mixture and sonicated for 20 min. The system was refluxed for 1 h at 80 °C. Finally the solids were separated from the solution using a magnet. The color of the product was darker after interaction with S2.

2.4. Photocatalitic activity

To investigate the catalytic activity of photocatalysts, degradation of rhodamine B as a water pollutant was studied. The photocatalytic efficiency of the catalysts was investigated using a 100 ml quartz tube. 0.03 g of photocatalyst nanoparticles were mixed with 50 ml of rhodamine B solution (initial concentration of about 10 ppm). Finally, 1 ml HNO3 65% was added to the vessels. The resulting suspensions were stirred to obtain the maximum absorption of organic pollutant molecules on the photocatalyst surface and to make oxygen available for the reaction and to obtain the highest level of homogeneity in the mixture. The reaction was carried out under the UV lamp irradiation and the mixture was placed inside the photoreactor in which the vessel was 40 cm away from the UV source of 400 W Mercury lamp. After each 10 min or 15 min period, sampling was performed and the samples were juxtaposed to a magnet to separate the solid particles, which were subsequently analyzed using the UV–vis spectrometer.

3. Results and discussion

The crystalline structure of the obtained products was characterized by using XRD technique. As we know, ordered carbon structures has a a specific peak at 2θ ≈ 25 ° corresponding to the well-organized layer structure along the (002) orientation [21]. The sharper peak shows higher order in structure. Also, wide peak shows smaller structure. As shown in Fig.1, all samples have two specific peaks at 2θ ≈ 25° and 2θ ≈ 44° relates to carboxylic structures. As shown it is deduced that sample 2 has more principle in structure in compare with two other samples. Sharp peaks with medium wide and intensity for sample
indicated identified graphene for PES, under dehydration the sample surface that the process, introducing nanoparticles using N,P-GQDs, of bands of Fig. 2 makes it suitable to introduce it as optimized sample. These data show that CA molecules are compacted to produce larger structure during the hydrothermal reaction.

The proposed theory for the formation of the N,P-GQDs says that at the initial stage the CA molecules assemble into a sheet structure through intermolecular H-bonding. Then under high temperature and pressure in hydrothermal process, carboxyl and hydroxyl groups of the molecules react to dehydration and nanosheet structures will produce [15,22]. During the process, the PNT decomposes and free N and P groups reacts with carboxyl or hydroxyl groups of the graphene nanoparticles to form N–P doped GQDs [16].

The surface functional groups present on N,P-GQDs were identified using FT-IR spectra (Fig. 2). For all samples the broad absorption bands at 3000–3700 cm⁻¹ are assigned to stretching vibrations of O–H and N–H. The high intensity of this region indicate that there is a lot of amino and hydroxyl groups on the surface of N,P-GQDs, which leads to having good hydrophilic properties and high water dispersibility for products. Also for sample 2 bending vibrations due to O–H band has been appeared at 1383 cm⁻¹. All samples have C=O band of carboxyl and carboxyl group vibrates in narrower bands at about 1620 cm⁻¹. Epoxy or ether functional groups have been identified by vibrating band at 1094 cm⁻¹. All samples have vibration peaks at 2921 cm⁻¹ and 2850 cm⁻¹ caused by symmetric and anti-symmetric stretching vibrations of CH₂ groups [23]. As we know, P–C and i N–P have P–O–C stretch bond has a medium-weak vibration at 750–630 in IR which all samples have this property [24]. Also Out-of-phase P–O–C stretch shows a strong vibration at 1088–920 cm⁻¹ which this band is more specified for sample 2 at 1070 cm⁻¹ which proves that P and N atoms was better doped in the structure.

As a result, it is necessary to understand the morphology and element distribution of products. So SEM analysis has been employed to characterize the morphology and approximate size of our nano products. For that, 5 ml of N,P-GQDs solution was heated to evaporate its solvent. Heating was performed slowly and in three steps. First step 80 °C for 5 h, second step 200 °C for 2 h and final step 300 °C for 1 h. Higher temperature may distort or combustion the carboxic structures. Fig. 3 proves that small particles have aggregated after solvent removing. So exact particle size cannot be estimated using the obtained SEM images.

More investigations were performed about the thermal effect on the optimized sample. For that, sample 2 was heated up to 800 °C under inert atmosphere (Argon gas). The temperature was increased 10 °C/min and hold for 60 min. Finally a black powder with low density was obtained and characterized. SEM analysis showed that N,P-GQDs at high temperature agglomerate together and make a sheet like structures (Fig. 4). We think that by using this strategy graphene structure can be produced. Since the N,P-GQDs particles are very small, they have high surface energy and high temperature give them more energy to aggregate and produce condensed sheet like structure with lower surface energy.

To obtain the exact particle size of the products, we had to use a more powerful analysis, such as atomic force microscopy (AFM). For sample preparation, drops of a dilute aqueous solution of the N,P-GQDs (sample 2) were deposited on a freshly cleaved mica surface. A layer of small particles was formed via spin-coating deposition at a spin speed of 2500 rpm for 20 s. According to Fig. 5, the AFM images show that the height or thickness of the N,P-GQDs is approximately 1.5–1.6 nm (about 1–2 graphene layers). The height of N,P-GQDs is mostly distributed in the range of 1.5 nm and this amount approximately is average height.

A more and closer examination about the real size of the particles was done by using transmission electron microscopy (TEM). According to Fig. 6, the mean size of the product of S7 product was estimated about 11 nm. TEM images with different magnitudes indicated very small diameter for N,P-GQDs (sample 2) (Fig. 6a and 6b). Since the thickness of N,P-GQDs is so thin, the electron beam can be passed through the sample. Another result that can be indicated according to Fig. 6, is good stability of the product under high-energy electron beam. Very thin layer is well visible in the TEM image.

To investigate the product surface structure and element distribution and to prove effective entry of P and N atoms into the structure, X-Ray energy dispersive spectroscopy (EDS)
Fig. 3 – SEM images of Sample 2 before calcination.

Fig. 4 – SEM images of Sample 2 after calcination at 800 °C.

Fig. 5 – AFM image of N,P-GQDs (sample 2).
analysis was employed. Fig. 7 shows the EDS spectrum of the GQDs indicates that final product includes C, N, O and P. This is a sufficient evidence which demonstrates that hetero atoms were successfully doped into the GQDs structures by the present method.

For studying physical properties of graphene like structures such as edge strain and defects, Raman spectroscopy is an appropriate analyze [25–28]. Raman is very sensitive to geometric structure and bonding within molecules [29]. The spectra of graphene exhibit a simple structure characterized by two specified so-called D and G bands. The G band is a vibrational mode involving the sp² hybridized carbon atoms in the structure of the graphene sheet. As the layer thickness decreases, the G band position shifts to higher energy. In addition, the intensity of the G band can be used to determine graphene thickness. There is a linear decrease in G band intensity as the number of graphene layers decreases. The D band is known as the disorder or defect band and it represents a ring adjacent to a graphene edge or a defect. The D band will also be disappearing or decreasing in large graphene sheets with no defects [30,31].

Fig. 8 shows the Raman spectra of the natural graphite and Sample 2. Two main peaks of the D band and G band has been emerged in all of the Raman spectra. Results indicate that the position of G in N-P-GQDs sample band has been shifted to higher frequencies. This observation prove that after reduction and interaction in hydrothermal process, the number of produced layers is very low. There is another point in the spectrum that relates to the intensity of the bonds. As seen, the intensity of D and G for sample 2 is very low in compare to graphite sample, indicating the production of low layer N-P-GQDs. The disorder degree of products Generally was investigated by considering the intensity ratio of D band to G band (I_D/I_G) [32]. This ratio is very higher for sample 2 compar-
ing to graphite sample indicating excessive amounts of carbon atoms with sp$^3$ hybridization on the edge [33].

As shown in Fig. 9, the as-synthesized GO-dots show the maximum excitation at wavelength of 383 nm assigned to the $\pi-\pi^*$ transition of aromatic sp$^2$ domains. Two peaks at 310 and 396 nm related to two types of electron transitions, indicating that there are at least two kinds of excitation energy trapped on the surface of GQDs [34-45]. Fig.10 depicts the UV-vis and PL excitation spectra of N,P-GQDs. The as-prepared N,P-GQDs solution shows yellow color under visible light and blue color under UV light (insets of Fig. 10). The results clearly prove that sample 2 has strongest PL emission under excitation at 396 nm. This observation indicates that enough P and N atoms have been doped in the GQDs structure during the hydrothermal process. Guest atoms should not be more of the structural capacity. More guest atoms leads to destruction of order in structure and low atoms leads to lower PL emission.

Ultraviolet light irradiation was used as an energy source for photodegradation of rhodamine B by Fe$_3$O$_4$/TiO$_2$/N,P-GQDs nanocomposite. At the next step, the changes in dye color were followed by UV absorption spectroscopy. The well-known equation of DP(t) was used for The degradation of rhodamine B over time t (DP(t)) as follows:

$$\text{DP}(t) = \left( \frac{A_0 - A_t}{A_0} \right) \times 100$$

(1)

In this equation $A_0$ and $A_t$ are the absorbance of the sample at 0 and t min, respectively. We mixed all components and stirred them in dark conditions to confirm that self-degradation is infinitesimally. However, after 50 min mixing in dark conditions, dye degradation was not observed in the absence of UV irradiation or photocatalysts. All of these results indicate that the contribution of self-degradation can be ignored.

The change in the concentration of rhodamine B after 50 min under UV irradiation was monitored and recorded and displayed as a figure in Fig.11. Usually the most value of dye degradation occurs in the initial minutes because of the existence of the pollutant molecules around the nanopowder photocatalyst and at time passes, the degradation rate decreases. Calculations of the photocatalytic activity were performed according to Eq. (1). The rhodamine B degradation after 50 min by Fe$_3$O$_4$/TiO$_2$/N,P-GQDs catalyst was obtained at 92%, while it was about 84% for TiO$_2$ nanoparticles. All of the reaction conditions for all samples were kept the same, so the higher catalytic activity of Fe$_3$O$_4$/TiO$_2$/N,P-GQDs versus TiO$_2$ can be attributed to the synergistic effect between TiO$_2$ and N,P-GQDs. The magnetic properties of the catalysts allow fast separation of the catalysts from the reaction media and simplify the catalyst separation and reuse of them in successive reactions which is an important issue from economical points of view.

4. Conclusion

Hexachlorocyclophosphazene (Phosphonitrilic chloride trimer (PNT)) was used for a one-step hydrothermal bottom-
up synthesis of N–P doped GQDs as nitrogen and phosphorus dopant source. High temperature in a hydrothermal process leads to the decomposing of PNT and releasing N–P atoms. The products were characterized using XRD, SEM, PL, FT-IR, EDS, AFM, TEM and Raman spectroscopy. Final products have promoted PL emission in comparison with the sample which no hetero atom doped. The product which had 0.1 g of PNT presented the most PL emission. All suspensions were stable at room temperature for a long period time. This procedure is cheap, quick, scalable, and gives products with blue luminescence emission. The Fe3O4/TiO2/N,P-GQDs nanocomposite which was obtained using S2 as N,P-GQDs source showed a high activity in organic dye degradation. The higher catalytic activity of Fe3O4/TiO2/N,P-GQDs versus TiO2 can be attributed to the synergistic effect between TiO2 and N,P-GQDs. The magnetic properties of the catalysts allow fast separation of the catalysts from the reaction media.

Conflict of interest

The authors declare no conflicts of interest.

Acknowledgment

Authors are grateful to the council of Iran National Science Foundation; INSF (97017837) and University of Kashan for supporting this work by Grant No. (159271/81190).

REFERENCES


