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Carboxyl and nitrite functionalized graphene quantum dots as a highly active reagent and catalyst for rapid diazotization reaction and synthesis of azo-dyes under solvent-free conditions



PIĞMĔNTS

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1. Introduction

Due to their diverse application in various fields of organic dye chemistry, azo-dyes and pigments are among the most important classes of organic colorants [1,2]. About three thousand azo dyes are known and are currently in use worldwide. Most of these compounds are monoazo compounds, which have the common structure unit of -N=N-, linking two aromatic systems. Despite the toxicity of some azo dyes, dozens of additional monoazo dyes are applied in drugs and cosmetics [3]. Compounds containing an arylazo group have been known as pharmaceutically important materials in the literature [4,5]. Azo-dyes are active in biological systems via their oxidation-reduction behavior [6], and many investigations have been reported on the synthesis, spectroscopic properties and dyeing performance of these compounds [7–10]. The synthesis of azo-dyes is usually carried out at low temperature in two steps: diazotization of the arylamine with sodium nitrite in hydrochloric or sulfuric acid followed by reaction with active aromatic compounds under alkaline conditions. Recently, new versions of this chemistry have been employed for the preparation of

ABSTRACT

Carboxyl and nitrite functionalized graphene quantum dots was prepared from carboxyl and hydroxyl functionalized graphene quantum dots using NaNO₂ in the absence of mineral acids. This functional group conversion was confirmed by FT-IR spectroscopy, photoluminescence and X-ray diffraction. The carboxyl and nitrite functionalized graphene quantum dots was used as an effective nitrosonium ion source and reusable catalyst for the efficient diazotization of a variety of arylamines without using any additional acid. Subsequent azo-coupling of these freshly prepared diazonium salts with a range of active aromatic compounds led to the requisite azo-dyes in excellent yields in very short reaction times with a simple experimental procedure.

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these compounds [11–13]. Although each of these methods have specific merits, they suffer from various drawbacks including long reaction times and the use of concentrated acids such as hydrochloric or sulfuric acid. There is therefore considerable interest in developing simple methods that require low manufacturing cost while minimizing environmental pollution. Aromatic diazonium salts are important intermediates for the synthesis of azo dyes which are prepared via diazotization of arylamines using nitrite salts and strong protic acids as a nitrosonium ion source instead of nitrous acid. Organic nitrite esters have also been used as alternative sources of nitrosonium ion in the presence of protic solvents in organic solvents [14,15]. Recently, we reported the synthesis of azodyes using nitrite ionic liquid (IL-ONO) and its immobilized form on silica as an affective nitrosonium sources [16,17]. Zarei et al. reported the synthesis of diazonium salts using supported reagents at room temperature [18]. Synthesis of 1-naphthol derived azo-dyes in the presence of SiO₂/HIO₄ under solvent-free conditions has also been reported [19].

Graphene has received much attention in physics, chemistry, and in material science due to its unique properties, including high surface area, electronic conductivity, and mechanical stability [20]. There is strong current interest in graphene quantum dots (GQDs) which are graphene sheets smaller than 100 nm [21]. QDs have been modified chemically to modulate their chemical and optical



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Scheme 1. GQDs-ONO as an effective nitrosonium source and highly active catalyst for the synthesis of azo-dyes.

properties [22]. Zhang et al. have successfully prepared watersoluble, uniform sized GQDs with strong yellow emission by electro-chemical exfoliation of graphite followed by room temperature reduction with hydrazine [23]. Carboxyl- and hydroxylfunctionalized graphene quantum dots (CHGQDs) were synthesized by Pan et al. [24]. In this report we prepared carboxyl- and nitrite-functionalized graphene quantum dots (CNGQDs) by conversion of HO-functionalized group of CHGQDs to -ONO by using NaNO₂ in the absence of any additional acid. This functional group conversion was confirmed by comparison of the FT-IR and photoluminescence of CHGQDs with CNGQDs.

Our interest in employing ionic liquids (ILs), water, or solventfree systems as green methods for organic transformations [25–27] provided the impetus to employ CNGODs as an effective nitrosonium source and active catalyst for facile diazotization of anilines and subsequent synthesis of azo-dyes by reaction with reactive aromatic compounds under solvent-free conditions at room temperature (Scheme 1).

2. Experimental

2.1. Chemicals

All reagents were purchased from Merck and used without further purification. Infrared spectra were recorded with KBr on a Perkin Elmer FT-IR spectrometer. ¹H and ¹³C NMR spectra were recorded on a Bruker Avance AC-400 MHz using CDCl₃ as solvent and TMS as an internal standard. Melting points are uncorrected and were measured in open glass-capillaries using Stuart melting point apparatus. CNGQDs structure was characterized by X-ray diffractometry (XRD; Bruker AXS model D8 Advance). TEM image was recorded with Philips CM-10 (Eindhoven, The Netherlands). Fluorescence spectra and intensity measurements were carried out using an FP-6200 spectrofluorometer (JASCO Corporation, Tokyo, Japan) with a wavelength range of 220–730 nm (with 1 nm intervals).

2.2. Synthesis of carboxyl and nitrite functionalized graphene quantum dots (CNGQDs)

Freshly prepared GQDs (25 g) was dissolved in water (100 mL). Then a concentrated solution of sodium nitrite in water (18 mL) was added dropwise to the GQDs solution at 0 °C in 30 min. While cold, NaCl saturated aqueous solution (25 mL) was added to the reaction mixture and the modified GQDs were extracted with ethyl acetate (3×25 mL). The solvent was evaporated and the residue was dried under vacuum at room temperature for 4 h to produce carboxyl-and nitrite-functionalized graphene quantum dots (CNGQDs; 19.5 g) (Scheme 2).

2.3. General procedure for the synthesis of azo dyes 6a-q

The mixture of aniline derivative (30 mmol) and CNGQDs (0.3 gr) was thoroughly ground at room temperature for 15 min. The diazonium salt product was assayed by well-known azo-coupling reaction with either a phenol or an aniline derivative. For the coupling reaction with phenolic compounds or anilines, the mixture was continuously added to the phenol or aniline (30 mmol) which had been moistened with water moistened with water (0.5 mL). Then water (30 mL) was added to the mixture and stirred to dissolve the GQDs. After that the participated dyes were filtered and washed three times with cold water to afford the crude azo-dyes which were purified by re-crystallization from EtOH/water. Saturated solution of sodium chloride was added to the filtrate containing GQDs while stirring, then the GQDs was extracted with ethyl acetate 3×15 mL and evaporation of ethyl acetate led to the GQDs.

2.4. Selected spectroscopic data (see Table 2 for physical data and comparison with literature data)

2.4.1. 1-(4-Nitrophenylazo)-2-naphthol (6a)

 $C_{16}H_{11}N_3O_3$: FT-IR (KBr, cm⁻¹): 3401 (bs), 1660, 1619. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 12.06 (broad, OH); 8.48 (1H, dd, *J* = 8.12



Scheme 2. Preparation of GQD-ONO from GQD-OH by using NaNO2.



Fig. 1. A) TEM image of the synthesized GQDs; B) XRD patterns of CHGQDs and CNGQDs.

and 2.04 Hz); 7.87 (2H, d, J = 7.98 Hz); 7.61 (2H, d, J = 7.98); 7.57 (1H, d, J = 7.25 Hz); 7.49 (1H, d, J = 7.25 Hz); 7.48 (1H, dd, J = 7.96 and 2.02 Hz); 7.44 (1H, dt, J = 7.65 and 1.98 Hz); 7.42 (1H, dt, J = 7.75 and 1.96 Hz); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 142.33, 137.38, 134.08, 130.25, 128.57, 127.28, 124.82, 121.83, 120.28, 119.45, 119.18, 117.11, 115.61, 112.38.

2.4.2. 1-Phenylazo-2-naphthol (6b)

C₁₆H₁₂N₂O: FT-IR (KBr, cm⁻¹): 3410 (bs), 1668, 1615. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 12.08 (broad, OH); 8.05 (1H, dd, *J* = 7.37 and 2.13 Hz); 7.68 (2H, m); 7.55 (1H, d, *J* = 7.82 Hz); 7.48 (1H, dd, *J* = 7.22 and 2.11 Hz); 7.46 (1H, dt, *J* = 7.74 and 2.04 Hz); 7.45 (1H, d, *J* = 7.82 Hz); 7.42 (1H, dt, *J* = 7.55 and 1.89 Hz); 7.17 (3H, m); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 140.00, 138.25, 135.45, 128.86, 128.41, 127.58, 124.57, 121.41, 120.38, 120.16, 119.22, 117.27, 116.19, 110.21.

2.4.3. 1-(4-Hydroxyphenylazo)-2-naphthol (6c)

C₁₆H₁₂N₂O₂: FT-IR (KBr, cm⁻¹): 3412, 3390, 1661, 1615. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 12.11 (2H, OH); 7.69 (1H, d, *J* = 7.58 Hz); 7.63 (1H, d, *J* = 7.58 Hz); 7.55 (1H, dd, *J* = 7.45 and 2.13 Hz); 7.49 (1H, dt, *J* = 7.61 and 2.08 Hz); 7.43 (1H, dt, *J* = 7.59 and 2.14 Hz); 8.26 (1H, dd, *J* = 7.54 and 2.20 Hz); 7.59 (2H, d, *J* = 7.51); 7.51 (2H, d, *J* = 7.51); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 159.55, 138.95, 135.44, 129.33, 128.56, 127.18, 123.53, 122.31, 122.30, 121.59, 120.42, 116.89, 115.91, 111.33.

2.4.4. 2-(2-Carboxylphenylazo)-1H-indole-3-carbaldehyde (6g)

C₁₆H₁₁N₃O₃: FT-IR (KBr, cm⁻¹): 3402, 3099, 1660, 1527, 1340; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 11.93 (1H, s, NH); 11.15 (1H, s, COOH); 9.85 (1H, s, CHO); 8.17 (2H, d, J = 7.61 Hz); 7.91 (2H, d, J = 7.46 Hz); 7.79 (2H, m); 7.45 (2H, m); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 163.15, 160.13, 134.42, 131.28, 130.93, 128.87, 127.94, 126.73, 125.64, 124.59, 124.16, 123.39, 122.52, 120.11, 117.89, 115.22.

2.4.5. 2-Phenylazo-1H-indole-3-carbaldehyde (6i)

C₁₅H₁₁N₃O₁: FT-IR (KBr, cm⁻¹): 1782, 1614, 1543, 1132; ¹H NMR (400 MHz, CDCl₃) δ (ppm): 11.81 (1H, s, NH); 9.92 (1H, s, CHO); 8.12 (1H, dd, *J* = 7.56 and 2.11 Hz); 7.41 (1H, dd, *J* = 7.49 and 2.04 Hz); 7.85 (2H, m); 7.41 (2H, m); 7.23 (3H, m); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 163.54, 131.43, 130.92, 125.76, 124.55, 123.11, 122.74, 122.33, 121.55, 121.12, 118.42, 116.15, 113.84.

2.4.6. 4-(4-Nitrophenylazo) resorcinol (6j)

C₁₂H₉N₃O₄: FT-IR (KBr, cm⁻¹): 3450 (bs), 3385, 1624, 1616. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 12.03 (s, OH); 8.92 (s, OH); 7.85 (d, 2H, *J* = 8.20 Hz); 7.83 (2H, d, *J* = 8.20 Hz); 7.74 (1H, d, *J* = 8.15 Hz); 6.62 (1H, dd, *J* = 8.15 and 2.41 Hz); 6.32 (1H, d, *J* = 2.41 Hz). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 156.24, 149.73, 148.14, 146.16, 130.91, 128.35, 127.33, 120.91, 110.64, 105.88.

2.4.7. 4-(4-Nitrophenylazo) N,N-dimethylaniline (6n)

 $C_{14}H_{14}N_4O_2$: FT-IR (KBr, cm⁻¹): 1613, 1512, 1479, 1536, 1335. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.74 (2H, d, *J* = 8.02 Hz); 7.71 (2H,



Fig. 2. A) FT-IR spectrum of CHGQDs and CNGQDs; B) Fluorescence microscopy spectra of CHGQDs and CNGQDs.

 Table 1

 Diazotization of anilines using CNGQDs and synthesis of azo dyes.



(continued on next page)

Table 1 (continued)
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d, *J* = 8.02); 7.66 (2H, d, *J* = 7.95 Hz); 6.65 (2H, d, *J* = 7.95 Hz); 3.61 (6H, s, NMe₂); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 135.52, 128.83, 126.53, 125.54, 123.33, 120.17, 117.84, 115.11, 35.12.

2.4.8. 2-Hydroxy-5-(4-nitrophenylazo) benzaldehyde (6p)

C₁₃H₉N₃O₄: FT-IR (KBr, cm⁻¹): 3412, 3113, 1648, 1606, 1522, 1479, 1332, 1285. ¹H NMR (400 MHz, CDCl₃) δ (ppm): 11.48 (1H, s); 10.06 (1H, s); 8.37 (2H, d, *J* = 7.26 Hz); 8.28 (1H, d, *J* = 2.21 Hz); 8.25 (1H, dd, *J* = 7.21, 2.21 Hz); 8.07 (2H, d, 7.26 Hz); 7.19 (1H, d, *J* = 7.21 Hz). ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 160.19, 135.83, 134.18, 130.21, 129.34, 128.62, 121.51, 117.67, 112.16, 110.99.

3. Result and discussion

3.1. Preparation and structural features of CHGQDs

Carboxyl- and hydroxyl-functionalized graphene quantum dots (CHGQDs) was prepared according to the literature procedure [25]. Fig. 1A shows the TEM image of the synthesized GQDs [28]. It can be seen that nano-size sheets of CHGQDs are dispersed in the solution. CHGQDs were converted to carboxyl- and nitrite-functionalized graphene quantum dots (CNGQDs). The typical XRD patterns of CHGQDs and CNGQDs are shown in Fig. 1B. The wide-angle peaks belong to the (002) planes of GQDs according to previous reports

[24,29]. The (002) interlayer spacing of CHGQDs and CNGQDs are 3.82 Å and 3.77 Å respectively (Fig. 1B), which are larger than that of bulk graphite (3.34 Å). During the modification process in which –OH groups were converted to –ONO groups on the GQDs, the interlayer spacing did not changed noticeably.

The FT-IR and photoluminescence of two CHGQDs and CNGQDs are shown in Fig. 2. The data are consistent with conversion of CHGQDs to CNGQDs. As it can be seen from Fig. 2A the signal at 1375 cm⁻¹ in FT-IR spectrum of CNGQDs is related to N=O bond. Fig. 2B shows the photoluminescence of CHGQDs and CNGQDs on excitation at 388 nm. The strong photoluminescence peaks at 503 nm in the case of CHGQDs and CNGQDs originate from free zigzag sites with a carbene-like triplet ground state [30]. The maintenance and heightening of the photoluminescence of the CNGQDs shows the success of GQDs modification process, and the potential of CNGQDs in fluorescence sensing and imaging applications.

3.2. Reactions

The reaction of p-nitroaniline (1 mmol) with NaNO₂ in aqueous HOAc at 0-5 °C and subsequent azo-coupling with sodium β naphthoxide was used as model. This gave product **6a** in 25% yield after 2 h (based on p-nitroaniline). By comparison, the reaction rate improved noticeably when carboxyl-functionalized CHGQDs was used instead of HOAc. The model reaction proceeded smoothly to give a 95% yield of 6a in only 15 min at 0-5 °C under these conditions. We then transformed the hydroxyl groups of CHGQDs to nitrite in order to examine its dual role as catalyst and nirosonium source. A very fast reaction was observed at 0 °C with almost complete conversion in less than 15 min in the absence of any added acid when the CNGQDs were employed. We also examined the reaction by addition of β -naphthol instead of its anion and found that the reaction was completed in less than 20 min and the expected azo dye 6b was isolated in 96% yield (entry 2). Solventfree conditions at room temperature were also evaluated for this procedure and no difference was observed in comparison with the reaction in water. The generality of this promising reaction was evaluated by employing a variety of aniline derivatives, and different coupling reagents (Table 1).

Isolated yields of the products via this method were compared with the reported values in the literature (Table 2). With all

 Table 2

 Melting points of the products and comparison of their yields with the reported values.

Entry Product		Time (min)		M.P (°C)		Yield ^a (%)	
	number	Diazonium salts	Azo dyes	Found	Reported [Ref.]	Found	Reporetd [Ref.]
1	6a	5	10	249-250	248-252 [31]	98%	92% [18]
2	6b	10	10	130-131	131–132 [32]	96%	87% [17]
3	6c	10	10	191-193	192-193 [33]	94%	88% [18]
4	6d	5	15	125-126	127-128 [34]	89%	78% [34]
5	6e	10	15	194-197	194-197 [18]	89%	81% [18]
6	6f	10	15	160-163	162-163 [18]	93%	82% [18]
7	6g	5	10	192-195	190-195 [18]	94%	84% [18]
8	6h	5	10	205-207	207 [17]	96%	64% [36]
9	6i	5	15	191-194	190-195 [18]	91%	77% [18]
10	6j	5	10	183-185	185 [33]	95%	90% [18]
11	6k	5	15	131-135	130-135 [18]	89%	74% [18]
12	61	5	10	201-202	199-202 [35]	91%	90% [17]
13	6m	5	15	110-112	108-112 [35]	90%	81% [19]
14	6n	5	10	223-226	225-228 [19]	94%	74% [35]
15	60	5	10	143-145	145 [17]	95%	85% [17]
16	6р	5	15	183-185	184–186 [36]	93%	85% [34]
17	6q	5	10	188-190	188-190 [35]	95%	88% [17]

^a Isolated yield.

substrates examined, the reactions were completed within 15–25 min under solvent-free conditions. Moreover, faster reactions and generally higher yields of azo-dyes were observed as compared to our previously reported reaction using task-specific nitrite ionic liquids [11,37,38]. We examined this procedure on a 50 mmol scale and found that they underwent a smooth trans-formation to the related derivative of azo-dyes in good yields, suggesting that the present procedure is amenable to scale-up. Upon completion, the CHGQDs was extracted with ethyl acetate and the extracted CHGQDs could be recovered with high recovery >96% in each cycle. In representative cases the azo-coupling reaction was repeated 3 times by using recovered CHGQDs and the corresponding azo-dye was isolated in 89–90% yield, showing that CHGQDs can be recycled with minimal loss of activity.

In summary, we have introduced carboxyl- and nitritefunctionalized graphene quantum dots, CNGQDs as an effective nitrosonium source and active catalyst for solvent and acid-free diazotization reaction and synthesis of azo-dyes in excellent yields and with short reaction times. The present acid and base free protocol is applicable to the synthesis of a variety of azo dyes.

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