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Efficient Synthesis of α-Oximinoketones using Carboxyl and Nitrite Functionalized Graphene Quantum Dots: Dual role of Nanostructure as a Catalyst and Reagent

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ABSTRACT

Carboxyl and nitrite functionalized graphene quantum dots (CNGQDs) was used for the efficient synthesis of α-oximinoketones under free mineral acid conditions at room temperature. CNGQDs was prepared via o-nitrozation of carboxyl and hydroxyl graphene quantum dots (CHGQDs) and used as a nitrosonium source and also as an efficient acidic catalyst for the synthesis of α-oximinoketones. The structure of the catalyst was characterized by FT-IR, XRD, TGA and photoluminescence techniques. The structures of the synthesized products were confirmed by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopic techniques. Stability and recyclability of the prepared homogeneous catalyst was studied in details. Reaction times and yields of the products were compared with previous reported methods resulting high yields and also shorter reaction times.

Keywords

Carboxyl and nitrite functionalized graphene quantum dots; α-Oximinoketones; Nitrosation

Academic Discipline And Sub-Disciplines

Chemistry

SUBJECT CLASSIFICATION

Organic Chemistry

TYPE (METHOD/APPROACH)

NanoCatalyst

INTRODUCTION

α-Oximinoketones are important organic compounds and organic chemists have great interest for the synthesis of these compounds. Significance of these compounds are because of applications of some oximinoketones derivatives in agricultural fields as a herbicides[1-3]. Also α-oximinoketones attached to heterocyclic compounds were used as useful pharmaceuticals[4-6]. Some α-oximinoketones derivatives are key intermediates for the synthesis of important compounds like amino acids[7], α-diketones[8], nylon[9], nitrosopyrazoles[10]. α-Oximinoketones are commonly synthesized via the reaction of carbonyl compounds with hydroxylamine hydrochloride in the presence of sodium nitrite and a mineral acid[11] as a nitrosonium source[12] and used of solid support such as silica gel in the presence of a base[13]. CaO was used as an efficient catalyst for the preparation of oximes at 130℃ under mild conditions[14]. Recently, we reported TSIL-ONO as a heterogeneous catalyst and effective nitrosonium source for the synthesis of oximinoketones[15]. Although various synthetic methods have been reported for the synthesis of these compounds, however in most of these methods one environmentally harmful mineral acid was used as a catalyst.

Recently graphene quantum dots (GQDs) have received intensive research interest among the chemists because they have important features such as good semiconductivity, high aqueous solubility, biocompatibility, low toxicity, strong photoluminescence and easy functionalization[16-23]. In recent study, we synthesized carboxyl functionalized graphene quantum dots as an acidic nano-catalyst under microwave irradiation for the synthesis of xanthene derivatives[24]. Herein, considering the importance of the α-oximinoketones, we reported the use of CNGQDs as an efficient reagent and catalyst for the synthesis of α-oximinoketones via the reaction of ketones and diketones under mineral acid free mild and green conditions (Scheme 1). In comparison with reported methods, it was found that the reactions were performed in shorter reaction times with higher yields of products under mild conditions.

Scheme 1: CNGQDs as a highly effective reagent and nanocatalyst for synthesis of α-oximinoketones.

RESULTS AND DISCUSSION

Preparation and structural features of CNGQDs

CHGQDs was synthesized according to the literature[24]. The morphology of this compound was studied by TEM image (Figure 1, part A). According to this image uniform distribution (30-50 nm) of nano-sheets could be seen. CNGQDs was synthesized from freshly prepared CHGQDs according to our recently published paper[25]. The XRD patterns and TGA diagram of CHGQDs and CNGQDs were shown in Figure 1 (part B and C). Interlayer spaces were determined from the XRD patterns as 3.82 Å and 3.77 Å for CHGQDs and CNGQDs respectively. Interlayer spacing for to bulk graphite is 3.34 Å[26]. Increasing of the interlayer spaces for CHGQDs and CNGQDs in comparison with bulk graphite confirmed the expected modification. Also, comparison of TGA diagrams of CHGQDs and CNGQDs confirmed the interchange of functional group in these compounds. The conversion of OH groups in CHGQDs to ONO groups in CNGQDs could decrease the hydrogen bond formation between interlayers in CNGQDs causing decomposition of this compound at low temperatures in comparison with CHGQDs.

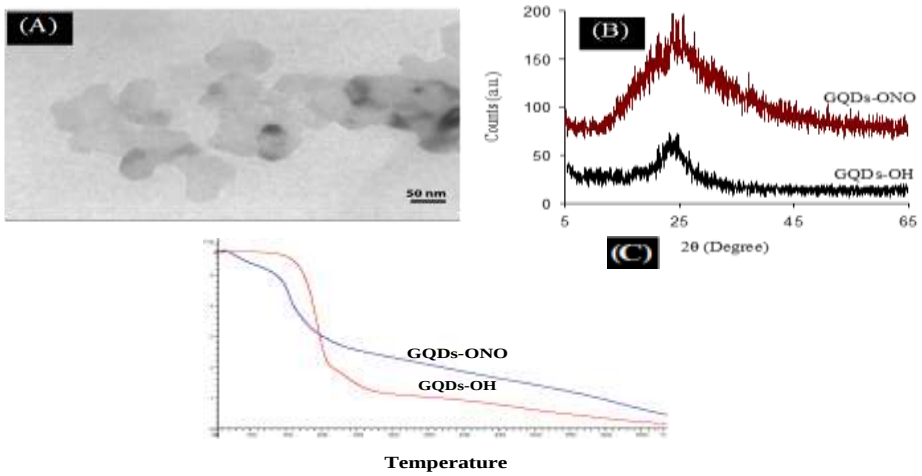


Fig 1: A) TEM image of CNGQDs; B) XRD patterns of CHGQDs and CNGQDs; C) TGA diagram of CHGQDs and CNGQDs.

FT-IR and photoluminescence spectra of CHGQDs and CNGQDs are shown in Figure 2. Absorptions at 1375 cm^{-1} in CNGQDs spectrum corresponding to N=O bond that confirmed modification (Figure 2, part A). The strong photoluminescence peaks at 503 nm are originated from free zigzag sites with a carbene-like triplet ground state[27]. The fluorescence intensity of CNGQDs is remarkably increased in comparison with CHGQDs approving the successful interconversion of functional groups (Figure 2 B).

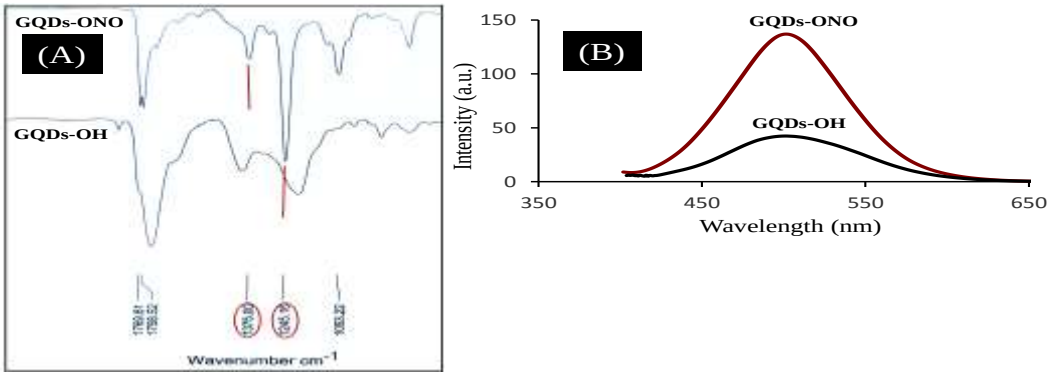


Fig 2: A) FT-IR spectra of CHGQDs and CNGQDs; B) Fluorescence spectra of CHGQDs and CNGQDs.

Reactions

Malonamide as an activated methylene compound was chosen as a typical carbonyl compound for the oximation reaction in water in the presence of CNGQDs as a nitrosonium source and an acidic catalyst at room temperature. At first, malonamide-2-one-2-oxime (2k) was prepared from the reaction of malonamide (10 mmol) with CNGQDs (0.2 g) in 50 min and 65% yield. For optimization, the reaction was studied with different amounts of catalyst. It was found that the optimum value of catalyst in this reaction is 0.4 g and 90% yield of product was achieved under these conditions. The increase of CNGQDs amount had no effect on the reaction efficiency. The participated crude oximinoketone were isolated by filtration under vacuum and then dried at room temperature. For further purification, crude products were recrystallized by water/ethanol. Efficiency of this reagent was compared with reported reagents for the synthesis of oximinoketones under optimized conditions. The results were shown in Table 2. As it can be seen from Table 2, CNGQDs has higher efficiency in comparison. Thus, it can be introduced as an effective catalyst and reagent for the synthesis of oximinoketones from active methylene compounds in the absence of any mineral acid.

Table 1. Synthesis of oximinoketones using nitrite functional graphene quantum dots (CNGQDs).

Entry	Ketone / Diketone	Reactant number	Product	Product number
1		**1a**		**2a**
2		**1b**		**2b**
3		**1c**		**2c**
4		**1d**		**2d**
5		**1e**		**2e**
6		**1f**		**2f**

7		**1g**		**2g**
8		**1h**		**2h**
9		**1i**		**2i**
10		**1j**		**2j**

Table 1. (continued)

Entry	Ketone / Diketone	Reactant number	Product	Product number
11		**1k**		**2k**
12		**1l**		**2l**
13		**1m**		**2m**
14		**1n**		**2n**
15		**1o**		**2o**
16		**1p**		**2p**
17		**1q**		**2q**

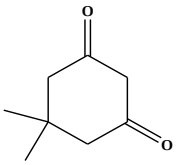
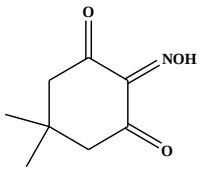
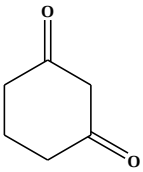
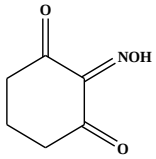
18		**1r**		**2r**
19		**1s**		**2s**
20		**1t**		**2t**

Table 2. Comparison of the yields of products with reported values.

Entry	Product number	Time (min)	M.P (C)		Yield[a] (%)	
			Found	Reported [Ref.]	Found	Reported [Ref.]
1	**2a**	25	128-129	128-130 [28]	90	90 [28]
2	**2b**	30	-	-	80	65 [15]
3	**2c**	30	149-150	148-150 [28]	98	93 [28]
4	**2d**	25	140-141	141-143 [28]	98	93 [28]
5	**2e**	30	162-163	162-163 [29]	92	87 [29]
6	**2f**	30	125-126	126-127 [29]	89	68 [29]
7	**2g**	20	115-116	114-115[29]	86	77 [29]
8	**2h**	25	-	-	95	83 [30]
9	**2i**	20	145-146	145-149 [15]	90	75 [12]
10	**2j**	20	130-131	129-131 [15]	89	86 [12]
11	**2k**	30	167-168	168-170 [15]	98	95 [15]
12	**2l**	30	129-130	129-132 [15]	98	94 [15]
13	**2m**	30	-	-	90	85 [15]
14	**2n**	30	-	-	91	89 [15]
15	**2o**	25	-	-	85	85 [15]
16	**2p**	30	-	-	96	84 [12]
17	**2q**	25	-	-	82	61 [30]
18	**2r**	25	-	-	87	75 [15]
19	**2s**	30	-	-	81	60 [30]
20	**2t**	30	-	-	89	70 [30]

[a]**Isolated yield.**

CONCLUSION

In summary, we introduced a new efficient reagent with dual role (as nitrosonium source and acid catalyst) for the oximination of active methylene compounds. Mild reaction conditions in water as a green solvent and simple workup procedure are the advantages of this method. Excellent yields of the products were obtained in shorter reaction times.

EXPERIMENTAL

Materials and instrumentation

All reagents were purchased from Merck Company and used without further purification. Infrared spectra were recorded with KBr on a Perkin-Elmer FT-IR spectrometer. Melting points were determined in open glass-capillaries using a Stuart melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker Avance AC-400MHz using DMSO-d_6 as the deuterated solvents and TMS as an internal standard. Elemental analysis was determined by CHNSO; Euro EA; model EA3000. CNGQDs structure was characterized by X-ray diffraction (XRD) (Bruker AXS model D8 Advance). Transmission-electron microscopy (TEM) was recorded on a Philips CM-10 (Eindhoven, The Netherlands). Fluorescence spectra and intensity measurements were carried out using an FP-6200 spectrofluorometer (JASCO Corporation, Tokyo, Japan). Thermal gravimetric analysis (TGA) was determined using Mettler Toledo TGA-DTA STAR SW.8.10.

Synthesis of CNGQDs

CNGQDs was synthesized from carboxyl and hydroxyl functionalized graphene quantum dots (CHGQDs) according to the reported method in our recently published work[25]. The solution of sodium nitrite in water (18 mL) was added slowly to the freshly prepared CHGQDs aqueous solution (25 g CHGQDs was dissolved in water 100 mL) at 0-5 ˚C in 30 min. After saturating the prepared solution by NaCl (10 g), the modified GQDs were extracted with ethyl acetate (3×25 mL). The ethyl acetate was removed under reduced pressure at 40 ºC and the residue was dried under vacuum at room temperature to produce CNGQDs (19.5 g) (Scheme 2).

Scheme 2: Preparation of CNGQDs from CHGQDs.

General procedure for the synthesis of α-oximinoketones (2a-t)

Diketone or ketone (10 mmol) were dissolved in water or mixed water - alcohol (12 mL) and was stirred at room temperature. Then, CNGQDs (0.4 g) was added slowly while stirring in 20 min. The progress of the reaction was monitored by thin layer chromatography (TLC) until the products were appeared as precipitated. In order to separate catalyst and unreacted ingredients from products, the precipitated were filtered and washed three times with cold water. The precipitated crude products were further purified by recrystallization (water/ethanol) to afford the pure products (2a-t) in high yields (Table 2). In order to isolate the catalyst, the separated aqueous solution was extracted by ethyl acetate in three times. Finally, the catalyst was revived from aqueous solution using vacuum and temperature (rotary evaporator). Recyclability of the catalyst was proved by repeating the sample reaction 5 times and the results was represented in Figure 3. Regardless decrease of yields proves appropriate recyclability of the catalyst in sample reaction.

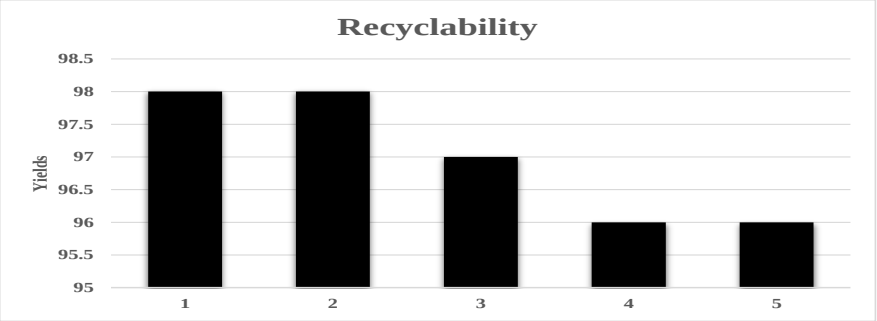


Fig 3: Recyclability study diagram of separated catalyst.

Selected spectroscopic data

1-Phenyl-1,2-ethanedione-2-oxime (2a)

Yield 90%; mp 128-129 °C (literature[24] 128-130 °C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 7.73-7.77 (m, 2H, ph-H), 7.81-7.85 (m, 3H, ph-H), 8.12 (s, 1H, =CH), 12.75 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 112.32, 117.65, 125.63,

128.45, 148.63, 161.54. IR (KBr) υ_{max}: 3421 (br, OH), 1688, 1685, 1614, 1450, 1318 cm^{-1}. Anal. Calcd. for $C_8H_7NO_2$ (%): C, 64.42; H, 4.73; N, 9.39. Found: C, 64.87; H, 4.71; N, 9.35.

1-(2-Hydroxyphenyl)-1,2-ethanedione-2-oxime (2b)

Yield 80%;[13] ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 6.35 (br, 1H, OH), 7.41-7.44 (m, 1H, Ph-H), 7.60-7.65 (m, 1H, ph-H), 7.75-7.78 (m, 2H, ph-H), 8.19 (s, 1H, =CH), 12.82 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 114.32, 117.56, 119.75, 121.32, 122.52, 122.98, 149.96, 165.85. IR (KBr) υ_{max}: 3449 (br, OH), 1684, 1531, 1384 cm^{-1}. Anal. Calcd. for $C_8H_7NO_3$ (%): C, 58.18; H, 4.27; N, 8.48. Found: C, 59.08; H, 4.26; N, 8.46.

1,3-Diphenyl-1,2,3,-propanetrione-2-oxime (2i)

Yield %; mp 145-146 °C (literature[13] 145-149 °C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 7.61-7.68 (m, 4H, ph-H), 7.75-7.79 (m, 2H, ph-H), 7.81-7.85 (m, 4H, ph-H), 12.87 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 109.78, 112.25, 127.12, 144.80, 158.14, 160.21. IR (KBr) υ_{max}: 3383 (br, OH), 1701, 1685, 1590, 1458, 1370 cm^{-1}. Anal. Calcd. for $C_{15}H_{11}NO_3$ (%): C, 71.14; H, 4.38; N, 5.53. Found: C, 71.23; H, 4.39; N, 5.52.

1-Phenyl-1,2,3,-butanetrione-2-oxime (2j)

Yield 89%; mp 130-131 °C (literature[13] 129-131 °C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.51 (s, 3H, Me), 7.56-7.60 (m, 2H, Ph-H), 7.71-7.75 (m, 1H, ph-H), 7.77-7.80 (m, 2H, ph-H), 13.04 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 19.73, 114.05, 124.16, 128.74, 130.00, 141.10, 154.87, 162.36. IR (KBr) υ_{max}: 3379 (br, OH), 1689, 1579, 1451, 1372 cm^{-1}. Anal. Calcd. for $C_{10}H_9NO_3$ (%): C, 62.82; H, 4.74; N, 7.33. Found: C, 63.02; H, 4.75; N, 7.31.

Malonamide-2-one-2-oxime (2k)

Yield 98%; mp 167-168 °C (literature[13] 168-170 °C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 7.73-7.79 (br, 2H, NH_2), 7.32-7.36 (br, 2H, NH_2), 12.04 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, MHz) δ: 138.63, 159.32, 162.52. IR (KBr) υ_{max}: 3431 (br, OH), 3310 (N-H), 3211 (N-H), 1680, 1675, 1437, 1261 cm^{-1}. Anal. Calcd. for $C_3H_5N_3O_3$ (%): C, 27.49; H, 3.84; N, 32.05. Found: C, 28.14; H, 3.85; N, 31.58.

Methyl 4-methoxy-2,3-dione-2-oxime butanoate (2l)

Yield 98%; mp 129-132 °C (literature[13] 129-132 °C); ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 3.25 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 12.68 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 59.65, 60.25, 135.25, 161.87, 163.45. IR (KBr) υ_{max}: 3330 (br, OH), 1743, 1691, 1627, 1437, 1388 cm^{-1}. Anal. Calcd. for $C_6H_9NO_5$ (%): C, 41.15; H, 5.18; N, 8.00. Found: C, 42.10; H, 5.16; N, 7.98.

Benzyl 2,3-dione-2-oxime butanoate (2m)

Yield 90%;[13] ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.50 (s, 3H, Me), 3.95 (s, 2H, OCH_2), 7.52-7.58 (m, 2H, ph-H), 7.67-7.72 (m, 1H, ph-H), 7.75-7.78 (m, 2H, ph-H), 13.08 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 36.78, 71.41, 113.63, 117.87, 119.56, 122.36, 149.79, 160.52, 163.53. IR (KBr) υ_{max}: 3331 (br, OH), 1746, 1698, 1627, 1498, 1379 cm^{-1}. Anal. Calcd. for $C_{11}H_{11}NO_4$ (%): C, 59.73; H, 5.01; N, 6.33. Found: C, 60.23; H, 4.99; N, 6.32.

Methyl 2,3-dione-2-oxime butanoate (2n)

Yield 85%;[13] ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.35 (s, 3H, CH_3), 3.78 (s, 3H, OCH_3), 13.34 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 31.25, 62.53, 147.69, 161.53, 165.82. IR (KBr) υ_{max}: 3448 (br, OH), 1751, 1654, 1452, 1373 cm^{-1}. Anal. Calcd. for $C_5H_7NO_4$ (%): C, 41.38; H, 4.86; N, 9.65. Found: C, 41.42; H, 4.88; N, 9.63.

Methyl 2,3-dione-2-oxime hexanoate (2o)

Yield 91%;[13] ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.02-1.09 (t, 3H, CH_3), 1.15-1.17 (m, 2H, CH_2), 2.61-2.66 (t, 2H, CH_2), 3.65 (s, 3H, OCH_3), 12.89 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 15.52, 18.45, 23.36, 62.52, 145.56, 158.89, 164.75. IR (KBr) υ_{max}: 3354 (br, OH), 1726, 1694, 1627, 1458, 1374 cm^{-1}. Anal. Calcd. for $C_7H_{11}NO_4$ (%): C, 48.55; H, 6.40; N, 8.09. Found: C, 48.74; H, 6.43; N, 8.08.

2,4-Dione-3-oxime pentane (2q)

Yield 82%;[26] ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 2.15 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 13.04 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 31.25, 29.81, 137.79, 159.51, 161.72. IR (KBr) υ_{max}: 3437 (br, OH), 1747, 1634, 1425, 1351 cm^{-1}. Anal. Calcd. for $C_5H_7NO_3$ (%): C, 46.51; H, 5.46; N 10.85. Found: C, 46.53; H, 5.47; N, 10.83.

3,5-Dione-4-oxime heptane (2r)

Yield 87%;[15] ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 1.24 (t, 3H, CH_3), 1.14 (t, 3H, CH_3), 2.24 (m, 2H, CH_2), 2.18 (m, 2H, CH_2), 13.02 (s, 1H, OH). ^{13}C NMR (DMSO-d_6, 150 MHz) δ: 18.28, 19.72, 30.16, 32.42, 136.70, 159.43, 160.63. IR (KBr) υ_{max}: 3435 (br, OH), 1748, 1641, 1430, 1356 cm^{-1}. Anal. Calcd. for $C_5H_{11}NO_3$ (%): C, 53.49; H, 7.05; N, 8.91. Found: C, 53.50; H, 7.06; N, 8.89.

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