



# 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



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## ABSTRACT

Carboxyl and nitrite functionalized graphene quantum dots was prepared from carboxyl and hydroxyl functionalized graphene quantum dots using  $\text{NaNO}_2$  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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## 1. Introduction

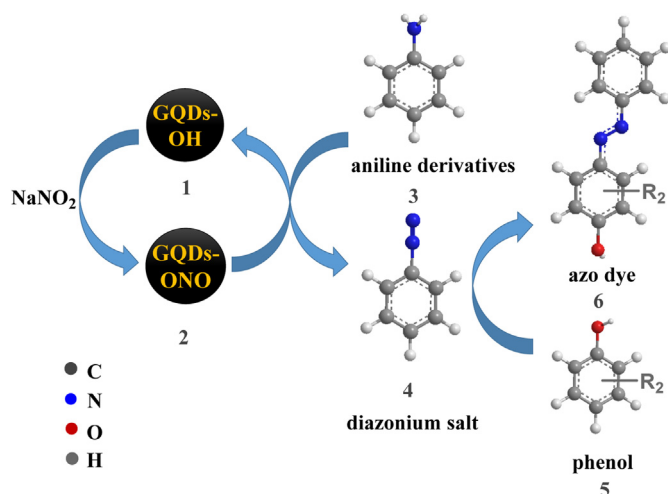
Due to their diverse application in various fields of organic dye chemistry, azo-dyes and pigments are among the most important classes of organic colorants [1,2]. About three thousand azo dyes are known and are currently in use worldwide. Most of these compounds are monoazo compounds, which have the common structure unit of  $-\text{N}=\text{N}-$ , 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

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 azo-dyes 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  $\text{SiO}_2/\text{HIO}_4$  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 water-soluble, uniform sized GQDs with strong yellow emission by electro-chemical exfoliation of graphite followed by room temperature reduction with hydrazine [23]. Carboxyl- and hydroxyl-functionalized 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  $\text{NaNO}_2$  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 solvent-free systems as green methods for organic transformations [25–27] provided the impetus to employ CNGQDs 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.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance AC-400 MHz using  $\text{CDCl}_3$  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  $0^\circ\text{C}$  in 30 min. While cold,  $\text{NaCl}$  saturated aqueous solution (25 mL) was added to the reaction mixture and the modified GQDs were extracted with ethyl acetate ( $3 \times 25$  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).

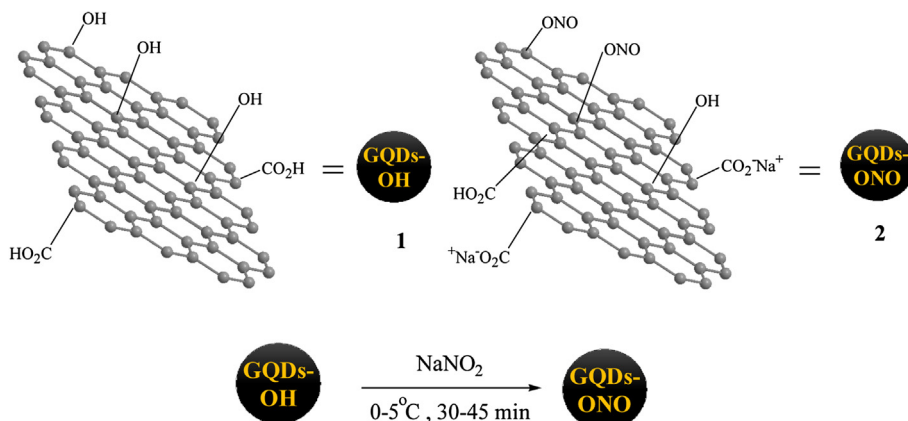
### 2.3. General procedure for the synthesis of azo dyes 6a–q

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 (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  $3 \times 15$  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)

$\text{C}_{16}\text{H}_{11}\text{N}_3\text{O}_3$ : FT-IR (KBr,  $\text{cm}^{-1}$ ): 3401 (bs), 1660, 1619.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  (ppm): 12.06 (broad, OH); 8.48 (1H, dd,  $J = 8.12$



**Scheme 2.** Preparation of GQD-ONO from GQD-OH by using  $\text{NaNO}_2$ .

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