



# Synthesis of potential antioxidants by synergy of ultrasound and acidic graphene nanosheets as catalyst in water



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## ABSTRACT

Efficient synthesis of a set of bisphenolic compounds, resulting from the incorporation of 2,4-dialkylphenols and aromatic or aliphatic aldehydes, allowed the discovery of new bisphenols with relative modest to good antioxidant activity. Bisphenolic compounds were prepared via easy and simple approach under ultrasound irradiation in water. Sulfonated graphene nanosheets were employed as a catalyst for the synthesis of bisphenolic compounds. These compounds were obtained in high to excellent yields (88–98%) and relatively short reaction times (4–20 min). Moreover, some of the synthetic compounds were investigated and revealed outstanding antioxidant activity, when examined by a 1,1-diphenyl-2-picrylhydrazyl radical (DPPH) decolorization assay system. The proposed method has a novel viewpoint in the preparation of potential antioxidant compounds.

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## 1. Introduction

Oxidation process is a chemical reaction involving an increase in oxidation state or the loss of electrons [1]. Free radicals can be produced via oxidation reactions and these intermediates, especially reactive oxygen species have strongly disruptive effect on body and industry products e.g. rubbers, plastics and oil. Nitric oxides (NO<sup>•</sup>), alkoxy (RO<sup>•</sup>), peroxy (ROO<sup>•</sup>), superoxides (O<sub>2</sub><sup>•-</sup>) and hydroxyls (OH<sup>•</sup>) are different form of reactive oxygen species [2]. These radicals can potentially cause oxidation in industry products through several degradation reactions both on heating and on long term storage [3]. The retardation and prevention of these oxidation processes are very important for all food and industrial producers. Different methods such as prevention of oxygen access, use of lower temperatures, reduction of oxygen pressure and the use of suitable packaging can be used to inhibit oxidation process [4]. Another method for protection against oxidation is the use of specific additives, which inhibit or delay the chain reaction.

Phenolic compounds can act as antioxidants and radical scavengers, e.g., vitamin E [5], flavonoids [6], catechins [7], resveratrol [8], and vanillin [9]. Polyphenolic antioxidants are one of the antioxidants including a polyphenolic or natural phenol substructure. Phenolic antioxidants especially bisphenolic antioxidants are

frequently added to the industry products as stabilizer additives in polymers e.g., plastics, rubbers, and hydroxyl terminated polybutadiene (HTPB). Double bonds in their main chains of polymers (for example polybutadiene) are especially susceptible to the oxidation process. Polymers can be protected by bisphenolic antioxidant such as AO-2246 in HTPB [10,11].

There are several methods for the evaluation of antioxidant capacity of pure compounds such as oxygen radical absorbance capacity (ORAC), cupric reducing antioxidant capacity (CUPRAC), ferric reducing antioxidant power (FRAP), the 2,2-azinobis(3-ethylbenzothiazoline-6-sulfonate) radical cation (ABTS<sup>•+</sup>) assay and the 2,2-diphenyl-1-picrylhydrazyl radical (DPPH<sup>•</sup>) assay [12–16]. The DPPH assay is a well-known method to evaluate the ability of compounds to act as free radical scavengers or hydrogen donors. The radical of DPPH<sup>•</sup> is a long-lived organic nitrogen radical with a deep purple color. When an antioxidant or a reducing compound is mixed with a solution of DPPH<sup>•</sup> radical, its purple color turns to yellow corresponding hydrazine (Fig. 1). The reducing ability of antioxidants towards DPPH<sup>•</sup> can be evaluated by monitoring the decrease of its absorbance at 515–528 nm as the formed corresponding hydrazine DPPH<sub>2</sub> yields a yellow solution [17].

Nowadays, phenolic antioxidants are synthesized by several research groups. Many Lewis and Brønsted acid catalysts have been successfully applied in the synthesis of phenolic antioxidants [18–30]. Liquid acids such as homogeneous catalytic systems are not suitable for the synthesis of phenolic antioxidants. They are corrosive, non-recoverable, toxic, and non-reusable catalyst.

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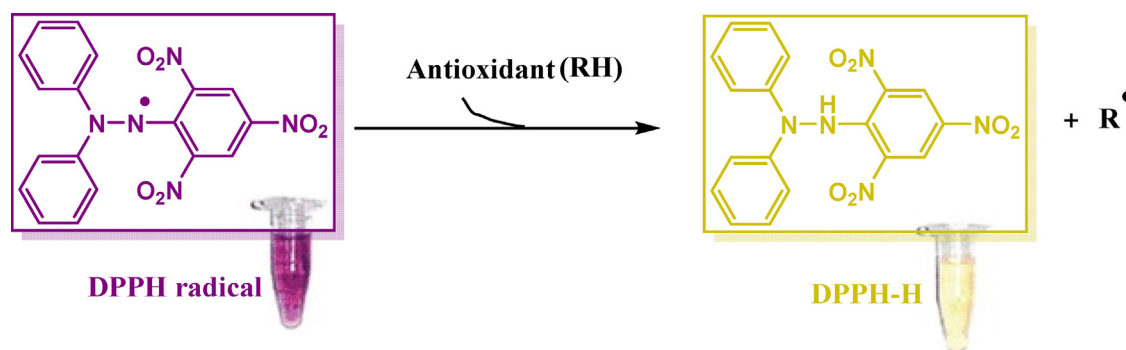
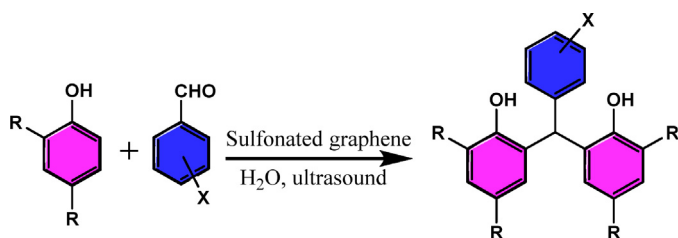


Fig. 1. Chemical structure of DPPH• radical and its reaction with antioxidant.



Scheme 1. Synthesis of antioxidant active compounds under ultrasound irradiation.

Therefore, heterogeneous catalytic systems were designed and applied in the synthesis of phenolic antioxidants. Meanwhile, long reaction times, low yields, use of organic solvents and high temperatures, and tedious work-up were some of the disadvantages of these mentioned methods. Accordingly, attempts for developing catalysts have gained increasing attentions as catalysts are recyclable and capable of performing the reaction under novel conditions.

In continuation of our interest in ultrasound sonochemistry [31–33], we hope to synthesize phenolic antioxidants by treatment of 2,4-dialkylphenol with different aromatic or aliphatic aldehydes using sulfonated graphene in water under ultrasound irradiation (Scheme 1).

## 2. Experimental

### 2.1. Materials and apparatus

The chemicals were purchased from Merck, Fluka, and Sigma–Aldrich chemical companies and used without purification. The DPPH was purchased from Sigma–Aldrich (USA). Also, butylated hydroxytoluene was purchased from E. Merck (India). The <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded in dimethylsulfoxide (DMSO-d<sub>6</sub>) solvent on a Bruker DRX-400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard. The IR spectra were recorded as KBr pellets in the range of 400–4000 cm<sup>-1</sup> on a Perkin-Elmer 781 spectrophotometer. The crystallographic structure of sulfonated graphene was investigated on a Philips instrument with 1.54 Å wavelengths of X-ray beam and Cu anode material, at a scanning speed of 2° min<sup>-1</sup> from 10° to 80° (2θ). The elemental analyses (C, H, N) were obtained from a Carlo ERBA Model EA 1108 analyzer. The BANDELIN ultrasonic HD 3200 with probe model KE 76, 6 mm diameter, was used to produce ultrasonic irradiation and homogenizing the reaction mixture. Thermogravimetric analysis (TGA) was performed on a mettler TA4000 system TG-50 at a heating rate of 10 K min<sup>-1</sup> under N<sub>2</sub> atmosphere. The Raman spectrum was recorded with an Almega Thermo Nicolet Dispersive Raman spectrometer excited at 532 nm. The morphology of

catalyst was characterized by FESEM Hitachi S4160 instrument. The TEM images were recorded by a Zeiss-EM10C with an acceleration voltage of 80 kV. The AFM image of GO nanosheets and sulfonated graphene nanosheets were measured using a scanning probe microscope (SPM-9600, Shimadzu). Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. The purity determination of the substrates and reaction monitoring were accomplished by TLC on silica-gel polygram SILG/UV 254 plates (from Merck Company).

### 2.2. Synthesis of graphene oxide and graphene

GO nanosheets were provided from raw graphite powder (Merck Company) by the modified Hummer's method [34]. First, sodium nitrate (NaNO<sub>3</sub>) (2.5 g) and natural graphite powder (5.0 g) were mixed with H<sub>2</sub>SO<sub>4</sub> (98%) (115 mL) in a 1000 mL round-bottom flask equipped with a magnetic stirrer and condenser place in an ice won at 0–5 °C. The mixture was stirred and potassium permanganate (KMnO<sub>4</sub>) (15.0 g) was slowly added during 1 h, and the stirring of mixture was followed for 2 h. The mixture was transferred to water won (35 °C) and stirred for 30 min. Then, distilled water (230 mL) was slowly added into the mixture and the temperature of mixture was about 98 °C and stirred for 15 min. Then, distilled water (700 mL) and hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) (30%) (50 mL) were sequentially added to the mixture until the reaction was concluded. The final materials were filtered and eluted exhaustively with hydrogen chloride (5%) and distilled water for several times. The solution was filtered under reduced pressure by vacuum pump upon sinter-glass (G4). The graphite oxide powder was obtained after drying in vacuum oven at 60 °C for 12 h. The graphite oxide was dispersed in distilled water to make concentration of 0.5 mg mL<sup>-1</sup>, and exfoliated by ultrasound (40 W) for 30 min, followed by centrifugation at 3500 rpm for 30 min to delete unexfoliated graphite oxide. After preparation of GO nanosheets, the graphene was obtained by chemical reduction of GO using sodium borohydride (NaBH<sub>4</sub>) as a reducing agent. In a 1000 mL round-bottom flask, the GO (1.0 g) was added into distilled water (700 mL). Then, the mixture was sonicated using ultrasound device (40 W) for 15 min. After that, NaBH<sub>4</sub> (2.4 g) was added into the round-bottom flask, and heated at about 100 °C for 24 h. Afterward, the obtained materials were washed with distilled water several times and filtered by vacuum pump over sinter-glass (G4) and then centrifuged at 3500 rpm for 15 min in order to obtain graphene.

### 2.3. Preparation of sulfonated graphene

Sulfonated graphene was obtained from hydrothermal process using H<sub>2</sub>SO<sub>4</sub> (100%) at 180 °C. In order to synthesize the catalyst, graphene (1.0 g) was added into H<sub>2</sub>SO<sub>4</sub> (50 mL). The mixture was sonicated using ultrasound device (40 W) for 15 min. Then, the

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