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Review

# State of the art and recent advances in the ultrasound-assisted synthesis, exfoliation and functionalization of graphene derivatives

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ABSTRACT

Sonochemistry, an almost a century old technique was predominantly employed in the cleaning and extraction processes but this tool has now slowly gained tremendous attention in the synthesis of nanoparticles (NPs) where particles of sub-micron have been produced with great stability. Following this, ultrasonication techniques have been largely employed in graphene synthesis and its dispersion in various solvents which would conventionally take days and offers poor yield. Ultrasonic irradiation allows the production of thin-layered graphene oxide (GO) and reduced graphene oxide (RGO) of up to 1 nm thickness and can be produced in single layers. With ultrasonic treatment, reactions were made easy whereby graphite can be directly exfoliated to graphene layers. Oxidation to GO can also be carried out within minutes and reduction to RGO is possible without the use of any reducing agents. In addition, various geometry of graphene can be produced such as scrolled graphene, sponge or foam graphene, smooth as well as those with rough edges, each serving its own unique purpose in various applications such as supercapacitor, catalysis, biomedical, etc. In ultrasonic-assisted reaction, deposition of metal NPs on graphene was more homogeneous with custom-made patterns such as core-shell formation, discs, clusters and specific deposition at the edges of graphene sheets. Graphene derivatives with the aid of ultrasonication are the perfect catalyst for various organic reactions as well as an excellent adsorbent. Reactions which used to take hours and days were significantly reduced to minutes with exceedingly high yields. In a more recent approach, sonophotocatalysis was employed for the combined effect of sonication and photocatalysis of metal deposited graphene. The system was highly efficient in organic dye adsorption. This review provides detailed fundamental concepts of ultrasonochemistry for the synthesis of graphene, its dispersion, exfoliation as well as its functionalization, with great emphasis only based on recent publications. Necessary parameters of sonication such as frequency, power input, sonication time, type of sonication as well as temperature and dual-frequency sonication are discussed in great length to provide an overview of the resultant graphene products.

## 1. Introduction

Sonochemistry has gained vast attention in the synthesis and development of nanoparticles and graphitic materials. Since sonochemistry intervention, chemical syntheses were made easy by the elimination of high temperature, pressure and long reaction time as well as laborious reaction steps. Among the various applications of ultrasonication such as extraction, dispersion, catalysis and nanoparticle syntheses, ultrasonic irradiation has also been closely used in the production of graphene. Exfoliation of the layered-graphitic materials was made possible as well as its oxidation, reduction, dispersion and modification with various chemical functional groups. Even covalent functionalization can be carried out within minutes of ultrasonication.

Fundamentally, during ultrasound irradiation sound waves propagate through the liquid and at the same time microbubbles are created from the existing impurities such as $O_2$, $N_2$ or Ar dissolved gasses. These microbubbles gain energy and undergo rapid inertial overgrowth until they implode inward catastrophically through a series of stages collectively referred as cavitation [1,2,3]. The cavitation bubble collapse occurs rapidly (less than a microsecond) creating local 'hot spots'. High local temperatures (10,000 K) and pressures (up to 10,000 atm) are generated, which fuel the homolysis of water forming highly reactive H· and OH· radicals as well as homolysis of any other surfactants that are present [4,5]. In addition, excited state species or

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**List of abbreviations**

| | |
|---|---|
| 1D | one-dimensional |
| 4-AP | 4-aminophenol |
| 6-AIND | 6-aminoindazole (6-AIND) |
| $CCI_4$ | carbon tetrachloride |
| $CH_3CN$ | acetonitrile |
| -COCI | acyl chloride |
| CTAB | cetyl trimethyl ammonium bromide |
| DBS | dodecylbenzenesulfonate |
| DMA | *N*,*N*-dimethylacetamide |
| DMEU | 1,3-dimethyl-2-imidazolidinone |
| DMF | *N*,*N*-dimethylformamide |
| DMSO | dimethyl sulfoxide |
| DPA | 2-dipyridylamine |
| DSPE-mPEG | 1,2-distearoyl-sn-glycero-3-phosphoethanolamine-*N*-[methoxy(polyethyleneglycol)-5000 |
| EDC | 1-Ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC) |
| GBL | γ-butyrolactone |
| GO | graphene oxide |
| GNRs | graphene nanoribbons |
| HMPA | hexamethylphosphoramide |
| HOPG | highly-oriented pyrolytic graphite |
| IA | isatoic anhydride |
| LOD | limit of detection |
| MO | methyl orange |
| $MoS_2$ | molybdenum disulphide |
| NHS | *N*-Hydroxysuccinimide |
| NMP | *N*-methylpyrrolidone |
| NO | nitric oxide |
| NVOC | non-volatile organic compounds |
| ODA | octadecylamine |
| $PCI_5$ | phosphorus pentachloride |
| PDDA | polydiallyldimethylammonium chloride |
| PEG | poly(ethylene glycol) |
| PIL | poly(1-vinyl-3-ethyl-imidazolium bromide) |
| PmPV | poly(*m*-phenylenevinylene-co-2,5-dioctoxy-*p*-phenylene-vinylene) |
| PSS | poly(sodium 4-styrenesulfonate) |
| PTSC | 2-pyridinecarboxaldehyde thiosemicarbazone |
| PVP | polyvinylpyrrolidone |
| RT | room temperature |
| SC | sodium chloride |
| SDS | sodium dodecylsulfate |
| SERS | surface enhanced Raman spectroscopy |
| TBA | tetrabutylammonium hydroxide |
| TCNQ | 7,7,8,8-tetracyanoquinodimethane |
| THF | tetrahydrofuran |
| TTIP | titanium tetraisopropoxide |
| USP | ultrasonic spray pyrolysis |

even meta-stable molecular ions are also produced [5,6].

For a heterogeneous system containing solid materials such as graphene, a slightly different mechanism is accounted. Similar cavitation bubbles were created upon ultrasound irradiation, however the cavitation which takes place near the solid surface of graphene will generate nonspherical bubbles that results in high-speed liquid jets that drive into the graphene's surface. The liquid jets which can reach velocities of up to hundreds of meters per second create shockwave damage to the graphene's surface, which weakens van der Waals interactions between the graphene sheets and cause increased interlayer spacing [5,7]. Consequently, aggregation of the graphene sheets is restricted and the multi-layered or stacked graphene sheets are now exfoliated to single or few-layer sheets [8]. In addition to cavitation, ultrasound also causes vibration which is transferred to an elastic environment by spreading into longitudinal or transverse waves. Since these waves cannot propagate through liquid, they are transformed into stationary waves instead. These stationary waves can vibrate through lamellar particles such as graphene, overcoming the graphene sheets' van der Waals forces and gradually peeling off the stacked graphene to liberate individual sheets [9].

In addition, fragmentation of the solid also takes place due to the concentrated high-energy and shockwaves. This allows the breaking of continuous graphene sheets into smaller fragments forming homogeneously sized graphene materials [7]. Besides, ultrasound irradiation in a heterogeneous system also induces enhanced mass transport due to acoustic streaming and turbulent mixing. Subsequently, this generates high-velocity interparticle collision in the bulk solution [5], which aids in various catalysis reactions involving graphene or during functionalization of graphene. Collectively, these phenomena make graphene dispersion in various solutions more effective and chemical functionalization much faster and easier. It is worth mentioning that ultrasonication helps in dispersion of graphitic materials, however prolonged stabilization of the graphitic material in various solvents mainly depends on the surface charge of the graphene (predominantly negative charge) [10] as well as the presence of surfactants or polymers (detailed explanation provided in Section 3).

The type of sonication employed also affects the stability of the graphene dispersion. In an attempt to determine the stability of the hydrothermally produced reduced graphene oxide (RGO), three types of sonication were tested: bath (200 W, 35 kHz), horn (750 W 20 kHz) and high-power microtip sonication (1000 W, 20 kHz) [11]. Interestingly, horn sonication produced the most stable RGO dispersion for up to 2 years, supplying the optimum power intensity for RGO dispersion. Whereas, the microtip horn sonication which produced even higher power intensity failed to yield a stable RGO dispersion due to the energy supplied which was beyond the needed optimum energy, hence lead to unstable dispersion.

Sonication is also a useful tool for the production of RGO, which is mainly produced from the reduction of graphene oxide (GO). Theoretically, if the bulk solution contains high molecular weight compounds such as liquid polymers, the large shear force and strain gradient generated by the rapid streaming of the solvent molecules in the vicinity of the bubbles and its collapse will emanate intense shock waves that may result in bond cleavage or degradation to smaller radicals [5,6,12]. Consequently, these organic radicals initiate the reduction of GO to RGO (detailed description in Section 5). This phenomenon coupled with the cavitation bubbles' extraordinary rapid cooling drive numerous high-energy chemical reactions [5,12]. Various catalysis reactions can be carried out using graphene due to the supply of high energy that activates the hydroxyl and carboxyl functional groups on graphene. Generally the specific shock waves conditions depend on the frequency and power of the sound wave, the dissolved gases as well as the solutes present in the medium [3–5,12,13].

### 1.1. Parameters of ultrasonication for graphene related reactions

There are various parameters involved in the production of graphene materials using ultrasonication techniques. One of the essential factors is the starting material which determines the type of resultant graphitic material. For example, to produce graphene sheets there is a choice of either exfoliating graphite or graphite oxide/graphene oxide (GO). The selection of starting material will then determine the size, the thickness as well as the number of layers formed due to various lateral dimensions and crystallinity of the precursor. For instance, artificial graphite which has small lateral dimension and low crystallinity will produce graphene sheets which are predominantly single layers