Copper/Graphene Based Materials Nanocomposites and Their Antibacterial Study: A Mini Review

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ABSTRACT

Due to their biocidal activity properties, graphene based materials have been widely studied especially in biomedical, agriculture and water treatment process which focus on mitigating the microbial resistance problem. However, the antibacterial performance of these materials alone are relatively weak and need to be improved in order to enhance their biological activity. Copper nanoparticles is a low cost metal also has the antibacterial properties which is almost similar with the silver and gold nanoparticles. The combination of these two materials had produced to a new potential material as another alternative for the antibacterial agents. Therefore, in this work, a brief review of copper/graphene based material nanocomposites and their antibacterial study was discussed.

Keywords: Copper nanoparticles, graphene based materials, nanocomposites, antibacterial

1. Introduction

The emergence of nanotechnology nowadays has open a new pathway for the researchers to find an alternative to solve the problems arise in most of the industries around the world such as agriculture, water treatment and medical industries. One of the common problems faced by these kind of industries is the growth of microbial resistance species that could harm the human health and also ecological system [1-4]. Due to that, nanomaterials were introduced in order to mitigate this problem as these materials have unique properties to be explored. Since then, an extensive amount of studies had been done during the last decade and it also has been widely expand to be utilized into multidiscipline applications [5-7]. Nanocomposite is one of the classifications in nanomaterials where
it could be defined as a materials that have at least one of them in a dimension of less than 100 nm scale [8]. A few nanocomposites that commonly explored are polymer nanocomposites [9], graphene based nanocomposites [10] and metal-metal oxide nanocomposites [11]. Usually nanoparticles that have size between 1 to 100 nm such as metal nanoparticles and metal oxide nanoparticles are used to produce the nanocomposite as it could enhance the application activities in the form of nanocomposite. In this paper, a short review on the production of copper/graphene based material nanocomposites is discussed including their antibacterial activity study.

2. Graphene Based Metal/Metal Oxide Nanocomposites

An extraordinary characteristic of graphene based materials related to their unique structure have attract researchers to investigate on their potential features for diverse applications. Generally, graphene based materials could be divided into three most common types which are known as graphene, graphene oxide (GO) and reduce graphene oxide (RGO). Graphene is known as an excellent support material because of its high surface area (~2600 m^2 g^-1), high thermal/electrical conductivity, good mechanical strength and flexibility [12, 13]. Besides, due to the thick layer of carbon atoms bonded together by sp^2 hybridization which arrange in a hexagonal array structure of graphene, it lead to its other special properties such as high density and very high hydrophobicity. The difference structure of GO and RGO with graphene is the presence of oxygen functional groups attach to the layer of the sheet. Hence, that make them differ with the graphene as well as their properties which also change because of their structure. GO consists of an exogenous oxygen – containing group on its surface while RGO has less oxygen functional groups attach compare to GO.

GO could be produced by the oxidation of graphite through several methods such as Staudenmaier’s method, Brodie’s method and Hummer’s method [14]. Hummer’s method and its modification have been used extensively nowadays to produce GO as it is less hazardous route and could produce high level of oxidation [15]. Chemical exfoliation of graphite to graphite oxide was pioneered by William S. Hummers and Richard E. Offeman in the year 1958 [16]. Shahriary and Athawale studied on the production of GO by using Hummer’s method and they found that this method was an efficient method to produce the GO [17]. By the present of the various oxygenated functional groups on the GO layer such as hydroxyl, carbonyl and epoxy, it leads for a better dispersion of metal nanoparticles as they could act as nucleation sites for the nanoparticles. RGO normally obtained through the reduction of GO and it could be done through the chemical reduction [18], green synthesis [19], thermal [14] and photochemical method [20]. Usually, the negative charge of functional groups such as -COOH, -OH and C=O of the GO were used as the precursor to produce the RGO. It leads to an easy dispersion of the material in aqueous solution and enable for this material to also acts as an effective anchor sites for nanoparticles immobilization [21].

GO and RGO are widely used in metal/metal oxide nanocomposites since these materials consist the oxygen-functional groups that could interact with the metal ions for the nucleation and growth to produce nanocomposites. Yin et al., reported that several routes to synthesis GO loaded with the nanoparticles were through chemical reduction process, hydrothermal, electrochemical and ex-situ (loading the premade nanoparticles to the graphene surface) [22]. Jayabalan et al., produced nickel oxide/reduce graphene oxide (NiO/RGO) and cobalt oxide/reduce graphene oxide (Co_3O_4/RGO) as catalyst in microbial electrolysis cell through ex-situ preparation. The nanocomposites were characterized using XRD, Raman spectra, SEM and EDX analysis. They found that the performance of NiO/RGO and Co_3O_4/RGO gave a better result as catalyst when combining with the RGO [23]. Pang et al., studied on producing zinc oxide/reduce graphene oxide (ZnO/RGO) nanocomposites for photo catalysis and they mentioned that ZnO alone had a weak activity as catalyst due to low surface
area. RGO was introduced to enhance the catalytic properties as it could minimize the recombination rate and produced high surface area with less aggregation for the photocatalytic study. Simplified impregnation method was used and the particle size ranging from 50 to 100 nm where the RGO acted as template to control the size of nanoparticles [24].

3. Copper/Graphene Based Materials Nanocomposites

Copper is a transition metal which has several oxidation states that make it special in term of its properties depending on its state. The surface plasmon resonance (SPR) of copper nanoparticles (Cu-NPs) also could help in improving the optical materials and devices due to its non-linear optical properties. It also has a high surface area to volume and low cost production compared to the noble metal such silver and gold [13]. Cu-NPs also known as a potential antibacterial agent as it has been used for centuries to disinfect microbial. However, the difficulties that need to be faced in producing Cu-NPs are (i) stabilization of particles against agglomeration, (ii) the achievement of monodisperse size distribution and (iii) easily oxidized when in contact with oxygen which could affect their potential application activity [25]. Cu-NPs is favourable in widespread of implementation including catalyst [26], sensor [27], anticancer [28] and antibacterial study [29].

In order to produce copper/graphene based material nanocomposites, the interaction of copper ions and graphene based materials occur through physisorption, cation-π interaction and electrostatic force interaction [30, 31]. Rios et al., produced copper/reduce graphene oxide nanocomposites (Cu/RGO-NCs) as catalyst for ammonium perchlorate decomposition by in situ reduction and they also studied the interaction between the materials using ab initio calculation to reveal the important role of the functional groups in stabilizing metal nanoparticles [32]. Fahiminia et al., reported a green synthesis of Cu/RGO-NCs using Euphorbia cheiradenia Boiss extract and it was used for reduction of organic dyes and 4-nitrophenol. The presence of phenolic compounds in the plant extract such as quercetin, kaemferol and rutin with sugar moieties acts as bio-reducer for the nanostructure formation. The size of the Cu-NPs synthesized was in the average size of 30 nm and spherical shape dispersed on the reduce graphene oxide sheet layer [12]. Some previous works of copper/graphene based material nanocomposites and their applications are shown as in Table 1.

| Copper/graphene based nanocomposites | Methodology          | Size and Structure/Shape | Application         | Reference |
|-------------------------------------|----------------------|--------------------------|---------------------|-----------|
| Copper oxide-graphene nanocomposites | Wet chemical method  | Less than 10 nm; spherical shape | Photocatalytic application | [33]      |
| Copper oxide/graphene oxide nanocomposites | Ex-situ method       | Less than 100 nm; cluster structure | Anticancer and catalytic application | [34]      |
| Copper oxide/graphene oxide nanocomposites | Hydrothermal method  | ~ 10 nm; not stated             | Catalytic application | [35]      |
| Copper-functionalize/reduce graphene oxide nanocomposites | Chemical reduction    | < 100 nm; not stated              | Sensor application study | [36]      |
Copper/reduced graphene oxide nanocomposites

i. Ball milling
ii. Electroless deposition method
Size not stated; porous structure
Tribological properties study [37]

Copper /reduce graphene oxide nanocomposites

i. cyclic voltammetry
ii. amperometry technique
< 100 nm; irregular shape
Sensor application study [38]

Copper oxide/graphene oxide

Hydrothermal method
26 nm; irregular shape
Antibacterial and anticancer study [39]

Copper/graphene oxide nanocomposites

In situ reduction method
~30 nm; not stated
Bone regeneration study [40]

Table 2. A few previous literatures of the copper/graphene based materials nanocomposites for the antibacterial application.

| Nanomaterials                        | Methodology                          | Type of Bacteria                  | Size and Structure/Shape | Reference |
|--------------------------------------|---------------------------------------|-----------------------------------|--------------------------|-----------|
| Reduce graphene oxide/copper (I) oxide nanocomposites | Chemical reduction (toluene) | P. aeruginosa¹, B. subtilis² and E. coli³ | 70-90 nm; cubic structure | [51]      |
| Reduce graphene oxide/copper (I) oxide nanocomposites | Thermal chemical vapour deposition method | E. coli³ | 5-40 nm; crystal structure | [52]      |

4. Antibacterial Applications of Copper/Graphene Based Nanocomposites

The growth of microbial resistance because of the bacteria that withstand to multiple antibiotics have been remain as a part of source for the morbidity, mortality and socioeconomic loss worldwide [41]. Due to the excellent antibacterial activity of copper, the US Environmental Protection Agency had registered about 300 copper-containing products as antibacterial agent back in 2008 and they were studied for biomedical application [42], crop disease control [43] and waste water treatment [44]. Cu-NPs has been a cheap and efficient antibacterial agent for centuries where it was discovered to exhibit broad antibacterial properties by oxidizing their proteins and lipids [45]. GO and RGO are toxic to both gram positive and gram negative bacteria [46]. However, the weak ability of the graphene based material to act as antibacterial agent leads to the aim in enhancing the antibacterial activity by hybridizing it with the Cu-NPs. Lately, green synthesis of graphene based materials attached with metal nanoparticles are favoured to utilize as biological agent since it is biocompatible and less hazardous [47]. Several factors are important for the nanocomposite to be used as biological agent such as size, shape, surface functionalization, stability and size distribution [48].
Reduce graphene oxide/copper nanocomposites  
In situ chemical reduction  
E. coli²  
15–50 nm; cluster structure  
[53]

Graphene oxide/copper oxide nanocomposites  
Chemical reduction  
S. aureus⁴ and E. coli³  
3–10 nm; spherical shape  
[54]

Graphene oxide/copper oxide nanocomposites  
Thermal chemical reaction  
E. coli² and S. typhimurium⁵  
190 ± 2.84 nm; not stated  
[55]

Graphene oxide/copper oxide nanocomposites  
Chemical reduction  
Pseudomonas syringae pathovar tomato  
21.28 nm; cluster structure  
[56]

¹P. aeruginosa: Pseudomonas aeruginosa; ²B. subtilis: Bacillus subtilis; ³E. coli: Escherichia coli; ⁴S. aureus: Staphylococcus aureus; ⁵S. typhimurium: Salmonella typhimurium

Tu et al., reported that antibacterial activity for copper/reduce graphene oxide (Cu/RGO-NCs) exhibit better antibacterial activity compared to the Cu-NPs alone [30]. Normally, the possible mechanism for copper/graphene based material nanocomposites is by the interaction of the positive charge of copper ions on RGO with the negatively charge surface of both gram positive and gram negative bacterial cells. The negative charge of gram positive bacteria is due to the presence of the teichoic acid with high amount of phospholipid groups that extend from the cell wall of the bacterial strain [49]. However, according to the Alayande et al., the antibacterial activity of the nanocomposite was not related with the copper ion released nor the generation of reactive oxygen species but due to the electron transfer mechanism [50]. Table 2 shows a few previous literatures related to the copper/graphene based materials nanocomposites for the antibacterial application.

5. Conclusions

In conclusion, the usage of graphene based materials as supporting materials for metal nanoparticles including copper could lead to the enhancement of the nanomaterial properties and activities. Hence, copper/graphene based material has a good potential for the antibacterial agent which could be one of the options to combat the microbial resistance.

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