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Historical perspective

Magnetic graphene–carbon nanotube iron nanocomposites as adsorbents and antibacterial agents for water purification

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ABSTRACT

One of the biggest challenges of the 21st century is to provide clean and affordable water through protecting source and purifying polluted waters. This review presents advances made in the synthesis of carbon- and iron-based nanomaterials, graphene–carbon nanotubes–iron oxides, which can remove pollutants and inactivate virus and bacteria efficiently in water. The three-dimensional graphene and graphene oxide based nanostructures exhibit large surface area and sorption sites that provide higher adsorption capacity to remove pollutants than two-dimensional graphene-based adsorbents and other conventional adsorbents. Examples are presented to demonstrate removal of metals (e.g., Cu, Pb, Cr(VI), and As) and organics (e.g., dyes and oil) by grapheme-based nanostructures. Inactivation of Gram-positive and Gram-negative bacterial species (e.g., *Escherichia coli* and *Staphylococcus aureus*) is also shown. A mechanism involving the interaction of adsorbents and pollutants is briefly discussed. Magnetic graphene-based nanomaterials can easily be separated from the treated water using an external magnet; however, there are challenges in implementing the graphene-based nanotechnology in treating real water.

Contents

1. Introduction

Reliable access to purified water devoid of toxins and microorganisms is one of the major global health issues of the 21st century. The current water supply systems in developing counties and industrialized nations face enormous pressure to provide access to clean drinking water sources [1–3]. Human activities contaminate natural source waters and consequently create water scarcity [4]. Rapid increase in global population, increasingly stringent water quality standards, and negative climate change effects on distribution of fresh water and supply as well as emerging contaminants in water put additional burden on water suppliers, and consequently lead to use of unconventional water sources such as brackish water and storm water [5]. More significantly, currently applied water and wastewater treatment technologies are not able to sustain the water quality and demand to meet requirements of

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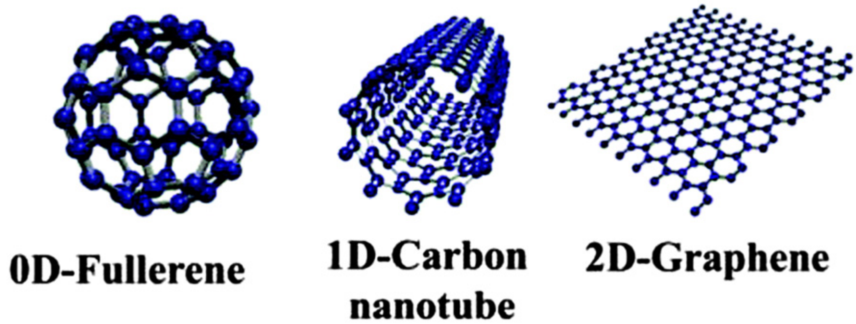

Fig. 1. Schematic illustration of the 0D (fullerene), 1D (carbon nanotube) and 2D (graphene) nanostructure of carbon based materials.
Adapted from [170] with the permission of Royal Society of Chemistry.

environment and human health [6,7]. This paper presents adsorptive nanotechnology solution to fulfill next-generation demand of clean water supply.

Adsorption is usually applied to remove contaminants (inorganic and organic) in treatment of water and wastewater [8–11]. However, removal efficiency of adsorbents is limited by their surface area, active sites, non-selectivity, and slow adsorption kinetics. For example, activated carbon, which is applied commonly as adsorbent to treat polluted water is not able to remove pollutants to parts per billion (ppb) level [12]. The smart adsorbents are thus needed which can have excellent adsorption capacity to remove pollutants to the ppb level. Nanomaterials, which are normally defined as materials smaller than 100 nm, possess high specific surface area and strong sorption [13]. Nano-adsorbents can thus address shortcomings of conventional adsorbents [8,14–16]. Carbon-based nano-adsorbents with their high specific surface area and associated sorption sites and fast kinetics can enable technological innovation in advancing treatment efficiency of polluted water to provide clean and affordable water [5,17–20].

This review first presents current status of magnetic carbon-based nanomaterials and a progress made in their synthesis, followed by recent examples of applications of such nanostructures in removing metals and organics and in inactivating bacteria in water and wastewater.

2. Carbon-based nanomaterials

Carbon nanomaterials comprise of different allotropic forms of carbon that include fullerene, carbon nanotube (CNT), and graphene, which are zero-, one- and two-dimensional structures (Fig. 1). Graphene has two-dimensional (2D) structure material with atomic thickness having sp^2-bonded carbon atoms with honeycomb rings [21–25]. Graphene has a high surface-to-volume ratio because of its unique morphology and is ideal for many applications such as high performance electromagnetic interference, superior thermal conductivity, robustness, and a large theoretical specific surface area [26–33]. Graphene is thus a good candidate to be an effective adsorbent for removing contaminants in water [21, 22,34–45]. However, it encounters difficulties in recycling because it is not easily separable from the treated water. This problem can be circumvented by combining graphene with iron materials to make nanohybrid and to subsequently carry out magnetic separation. Iron oxides of varying valence states can promote the magnetic separation after the adsorption of pollutants from water [46–51].

Iron oxide nanoparticles are frequently used in removing metals in water [52–58]. However, removal efficiency of these nanoparticles is not high because of agglomeration. Other difficulty is the recycling of the nanoparticles having small sizes, particularly in a continuous flowing system. Embedded iron oxide nanoparticles on carbon-based nanomaterials which cost less and have high surface area is an attractive alternative. Examples include growth of iron oxide nanomaterials on graphene sheets [59]. The deposition of iron oxides onto graphene results in reduction on sorption sites on carbon surfaces; hence additional surfaces are required to increase sorption of pollutants on adsorbents. Unfortunately, the synthesized three-dimensional (3D) nanomaterial using this approach has low value because tubular metallic shapes on graphene reduce the specific surface area [60]. One approach of having smart carbon nanomaterial (SCNM) is the growth of 1D CNT on graphene and then subsequently decorated with iron oxide(s) to obtain 3-D nanostructures, which provide larger surface area. Fig. 2 shows such SCNM, which can have iron nanoparticles on surfaces of both graphene and CNTs [61]. Importantly, smart magnetic graphene (SMG) can be magnetic-separated easily after the water treatment.

2.1. Synthesis

The initial step to obtain SMG first involves the synthesis of graphene independently [26,62,63]. Graphene is also termed as reduced graphene oxide (RGO); its synthesis is usually from the reduction of graphene oxide (GO). Most of the workers applied Hummers' method to synthesize GO (HGO) from graphite [64]. In recent years, an improved method to synthesize GO (IGO) has also been proposed [65]. Fig. 3 summarizes both methods in which graphite were oxidized by a mixture of $KMnO_4$, H_2SO_4, and either $NaNO_3$ or H_3PO_4. In the modified HGO (HGO^+), larger amount of oxidant is applied; 6 M $KMnO_4$ is used in HGO^+ while 3 M $KMnO_4$ in HGO. The use of $NaNO_3$ in the Hummers' method generated toxic NO_2, therefore the IGO method using H_3PO_4 is relatively safer. Other important finding of IGO was the increased efficiency; indicated by the production of the very small amount of under-oxidized material after the synthesis. For example, 0.7 g of under-oxidized material was obtained from 3.0 g graphite in IGO

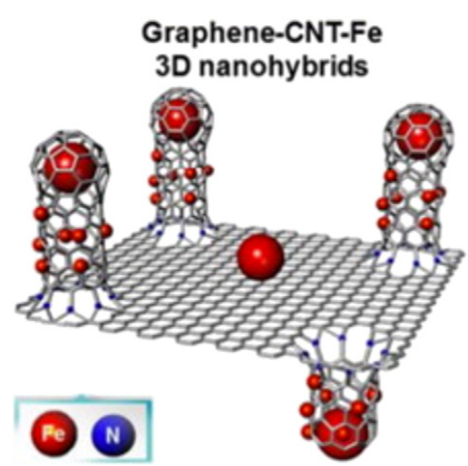

Fig. 2. Growth of carbon nanotubes and iron oxide nanoparticles on graphene surfaces.
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