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Short communication

Slow-release fertilizer encapsulated by graphene oxide films

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HIGHLIGHTS

- KNO_3 pellets were encapsulated in graphene oxide (GO) films.
- Separated GO sheets fuse together to form a shell on KNO_3.
- GO-coated KNO_3 pellets exhibited slow-release behavior.

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ABSTRACT

A slow-release fertilizer was developed by encapsulating KNO_3 pellets with graphene oxide (GO) films. The material was then subjected to heat treatment, where adjacent GO sheets were soldered and reduced to reduced graphene oxide (re-GO) sheets by potassium. After the re-GO shell formed on KNO_3 pellets, the slow-release characteristics of the fertilizer dramatically improved. The process of releasing fertilizer was prolonged to 8 h in water. We believe that this new coating technology could hold great promise for the development of environmentally-benign controlled-release fertilizer for crop production.

1. Introduction

In order to sustain crop yields, fertilizers have to be applied to soils to provide plants with essential nutrients. Conservative estimates show that 30–50% of crop yields are attributed to natural or synthetic commercial fertilizers [1]. As modern agriculture relies increasingly on non-renewable fertilizer resources, future related minerals are likely to yield lower quality at higher prices [2,3]. Part of nutrients in those non-renewable fertilizers are not absorbed by plants and therefore, leach into groundwater or surface water, lead to eutrophication, and impose great risk to the ecosystem [4–8]. To improve fertilizer quality and protect the environment and the ecosystem, there has been increasing research towards developing new technologies for delivering plant nutrients in a slow- or controlled-manner in the water or soil.

Past efforts for developing slow- or controlled-released fertilizers focused on employing polymers that were already used in coating various fertilizers [9–12]. For instance, Jarosiewicz et al. reported that coating fertilizer nutrients with polymers, such as polysulfone, polyacrylonitrile, and cellulose acetate tends to decrease the nutrient release rate [9]. Jia et al. found that a polydopamine film coated on double copper potassium pyrophosphate trihydrate undergoes spontaneous oxidative polymerization of dopamine when reacted with the three essential nutrients (Cu, K, and P); the resulting coated fertilizers had good slow-release properties when incubated in either water or soil [10]. However, all of these coating techniques require either organic solvents or toxic polymerization initiators or hazardous monomers, which not only increase the costs of production, but also lead to environmental and health issues [13,14].

Graphene is an ultra-thin carbon material with high mechanical strength, excellent conductivity, and high surface area is being utilized for various applications, including field effect transistors, sensors, transparent electrodes, batteries, supercapacitors, and composited materials [15–22]. Although there are also concerns over potential environmental impact of large scale production of graphene or graphene oxide (GO) through the traditional oxidization and reduction methods, recent advances in technologies make it possible to prepare them with green methods, requiring no toxic starting materials or oxidization/reduction agents. For example, it has been demonstrated that graphene oxides can be produce in

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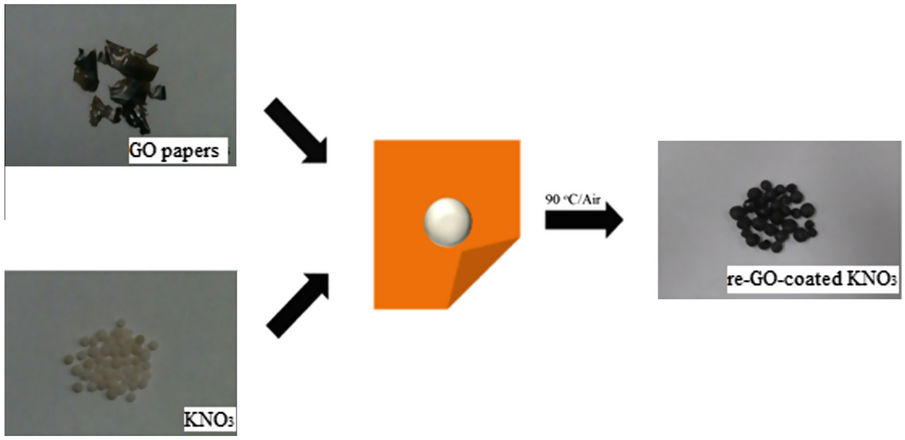

Fig. 1. Schematic illustration of preparation of re-GO-coated KNO_3.

large scale via electrochemical exfoliation of pencil cores in aqueous electrolytes without a requirement for toxic chemical agents [23]. In addition, Guo et al. reported a facile approach that can produce high quality graphene nanosheets in large scale through electrochemical reduction of exfoliated graphite oxide precursor at catholic potentials [24]. Because of its unique morphological structure and related properties, graphene has been reported to be an effective carrier for various chemical compounds, thus holding potential opportunities for developing new controlled release delivery systems [25–28]. For example, Yang et al. developed a simple, effective, and scalable method to chemically deposit Fe_3O_4 nanoparticles onto GO. This hybrid can be loaded with the anti-cancer drug DXR with a high loading capacity [27]. However, besides those medical applications, little research has been done to explore graphene-based slow- and controlled release systems for agricultural applications such as fertilizers, pesticides and so forth.

More recently, a simple and cost effective approach for producing graphene composites was developed, by reducing GO sheets [29–33]. During a heating process, a variety of metal cations with different valences can not only serve as catalyst reduce GO, but also cross-link adjacent GO sheets to form reduced GO (re-GO) films [34–36]. This ion-mediated thermal reduction method provides a potential new route for coating the fertilizer without organic solvents and toxic initiators.

Herein, we tested a simple procedure to prepare re-GO-coated KNO_3 fertilizer by encapsulating of KNO_3 pellets with GO film and then baking GO-coated KNO_3 pellets at 90 °C in an oven for 6 h. According to the analysis from TEM images, XPS and Raman spectra, potassium ions are not only able to act as a "glue", soldering adjacent graphene sheets but also reduce GO to re-GO. This procedure allows GO films to form a shell around KNO_3 pellets and prevents KNO_3 from fast release. This new method is different from the conventional polymer coating methods which need organic solvents and toxic initiators. The as-prepared re-GO-coated KNO_3 pellets took on improved slow-release properties. Because of its simplicity, feasibility and environmental friendliness, we believe this new method will have great potential for developing controlled-release fertilizers that provide plants with nutrients and ensure soil quality and crop productivity.

2. Materials and methods

2.1. Materials

Graphene oxide (GO) and potassium nitrate (KNO_3) were obtained from ACS Material and Fisher Scientific, respectively. All the chemicals are analytical grade and their solutions were prepared using deionized water (18.2 MΩ) (Nanopure water, Barnstead).

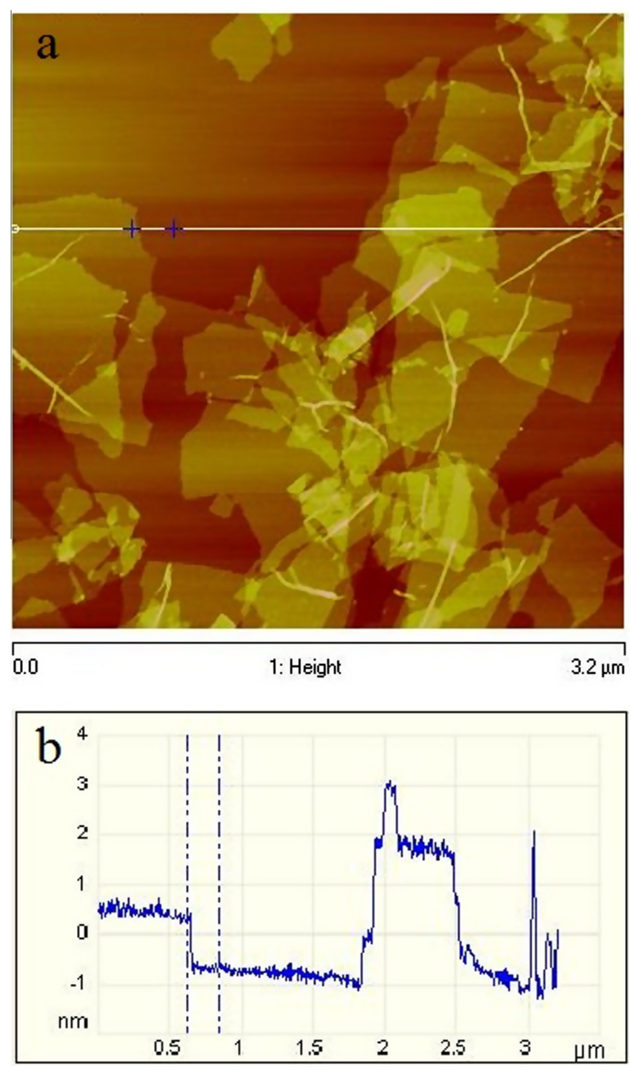

Fig. 2. AFM analysis of GO sheets on a mica substrate: (a) AFM image and (b) sectional analysis of the AFM image along the white line (AFM channel). The cross in the figure helps to show the height of the graphene sheet.