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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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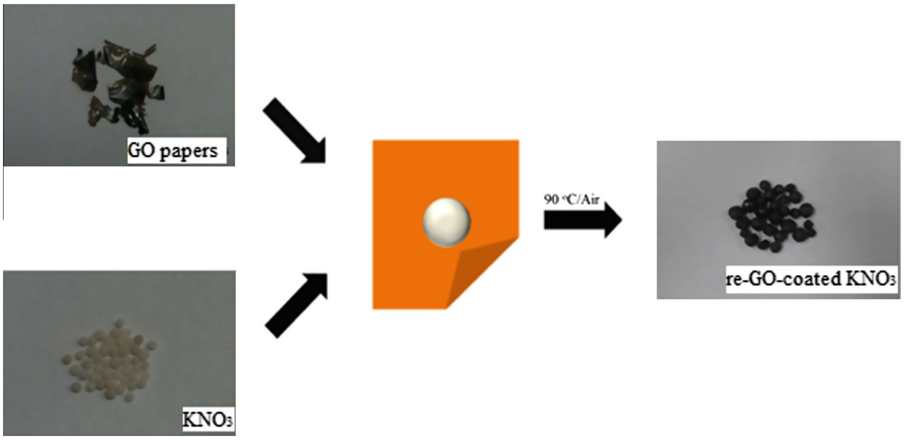

Fig. 1. Schematic illustration of preparation of re-GO-coated KNO_3.

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).

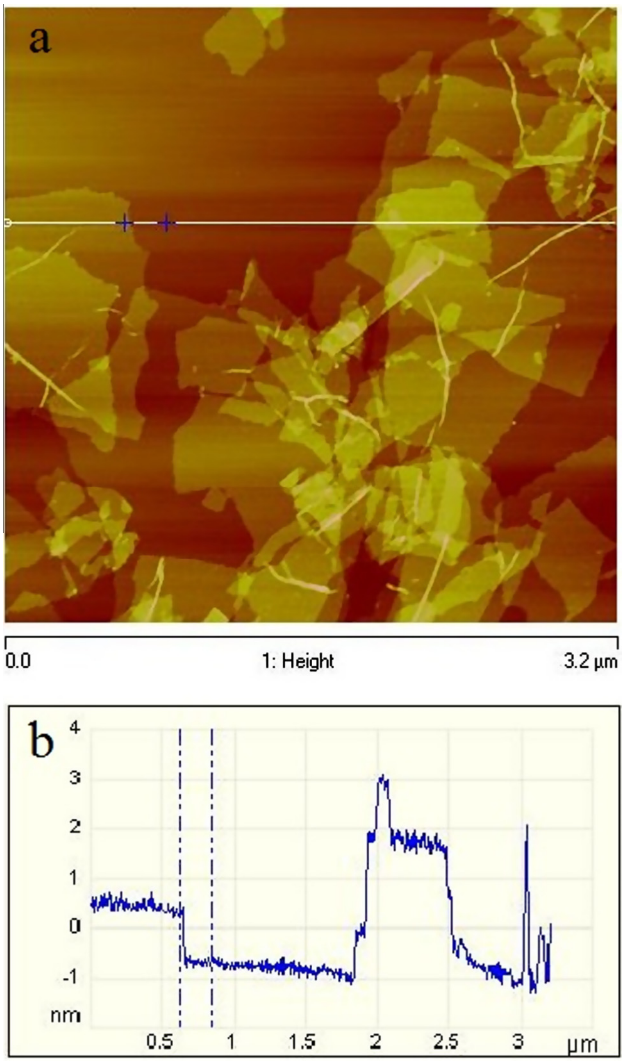

Fig. 2. AFM analysis of GO sheets on a mica substrate: (a) AFM image and (b) sectional analysis of the AFM image along the white line (AFM channel). The cross in the figure helps to show the height of the graphene sheet.

2.2. Preparation of GO-coated KNO_3 pellets

GO solutions at the concentration of 2 mg/mL were prepared via 2 h of ultrasound in 20 ml batches. To produce GO film, 10 mL of the resulting GO solutions was filtered through an Anodisc membrane filter (47 mm in diameter, 0.2 μm pore size; Whatman), air dried, and lastly peeled from the filter. The resulted GO film was mechanically coated on KNO_3 pellets surfaces with little amount of water. The GO-coated KNO_3 pellets were then baked at 90 °C in an oven for 6 h (Fig. 1). Because KNO_3 decomposes at 400 °C and above, the coated fertilizer is stable during the heating process. Slow-release behavior of the as-prepared GO-coated KNO_3 pellets was characterized after being cooled to room temperature.

2.3. Characterizations

The microscopic features of GO-coated KNO_3 pellets were characterized with a field emission gun scanning electron microscopy (FEG-SEM, JEOL 6335F), transmission electron microscopy (JEOL 200CX TEM), and atomic force microscopy (SPM/AFM Dimension 3100). X-ray photoelectron spectra (XPS) of the samples were obtained with a Perkin Elmer 5100 XPS System. Raman spectra were recorded using a Renishaw Invia Bio Raman with excitation from a 785 nm diode laser.

2.4. Slow-release behavior of re-GO-coated KNO_3 pellets

To study the slow-release behavior of re-GO-coated KNO_3 pellets, the following experiment was carried out: 0.2 g samples were added into conical bottles containing 100 mL of distilled water. Then, the bottles were kept at 25 °C in an incubator for the duration of the experiment. At certain time intervals (0.5 or 1 h), 2 mL of solution were sampled for potassium determination and an additional 2 mL of water was carefully injected into the bottles to maintain a constant amount of solvent. Only the potassium concentration was monitored during the experiment because the molar ratio between the dissolved K and NO_3 is 1:1 in the solution. The potassium concentrations in the solution were analyzed by using an inductively coupled plasma atomic emission spectroscopy (ICP-AES). The release experiments were carried out in triplicate, and the average value was taken as the result.

3. Results and discussion

3.1. Preparation of re-GO-coated KNO_3 pellets

Fig. 1 gives the schematic illustration of the method developed to encapsulate KNO_3 pellets with GO films, where the color of GO film is matte brown, the resultant re-GO-coated KNO_3 pellets is metallic gray. After the heat treatment, the color of the films changed from matte brown (GO color) to metallic gray, indicating the formation of re-GO films. Previous studies have suggested that GO can be hydrothermally reduced in the presence of the catalyst cations (e.g., K) due to the recovery of π-conjugated system from GO sheets [29,34,35]. Furthermore, GO's exposure to cations may lead to ring-opening of the epoxide [33], which can further reduce GO. Atomic force microscopy (AFM) analysis of the dispersal state

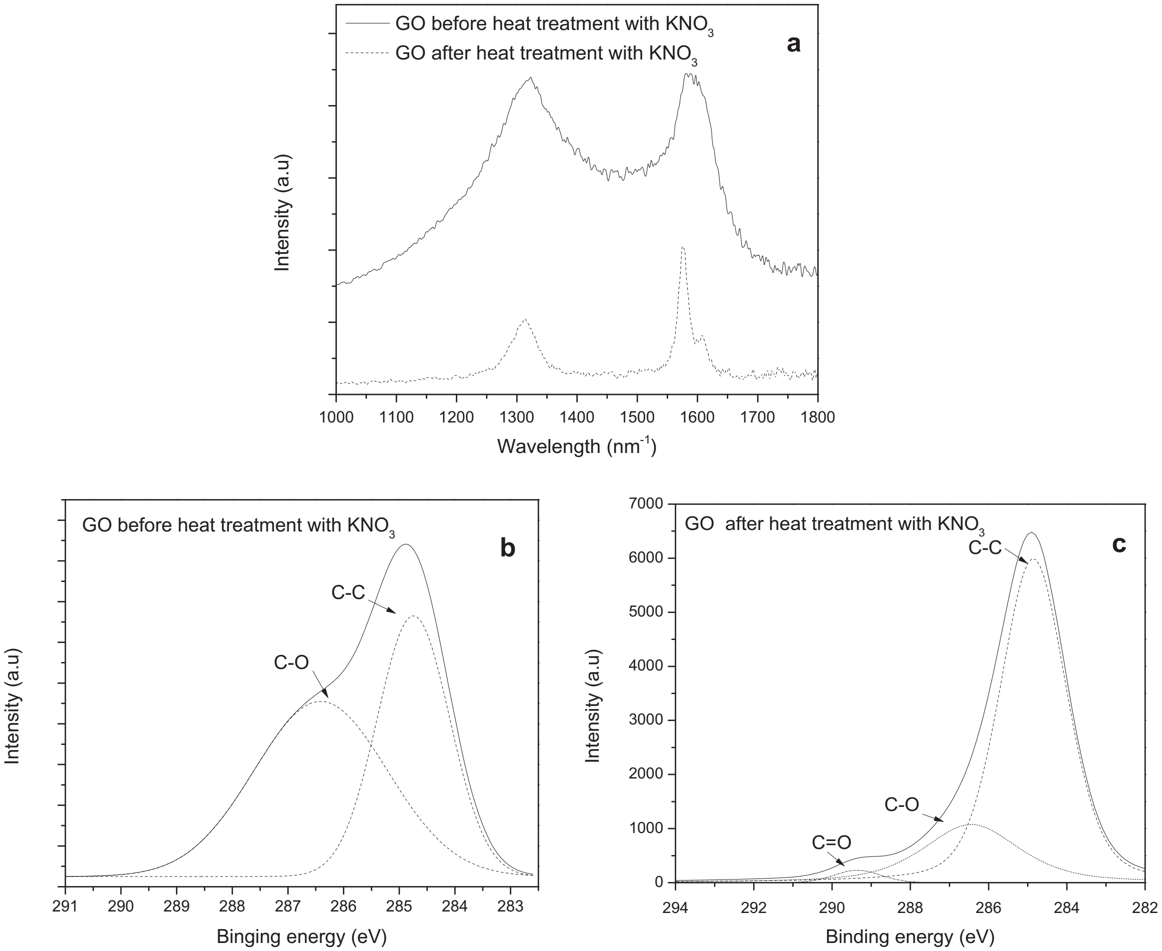

Fig. 3. (a) Raman spectra of GO before and after heat treatment with KNO_3; C1s XPS spectra of (b) GO before heat treatment with KNO_3; and (c) GO after heat treatment with KNO_3.

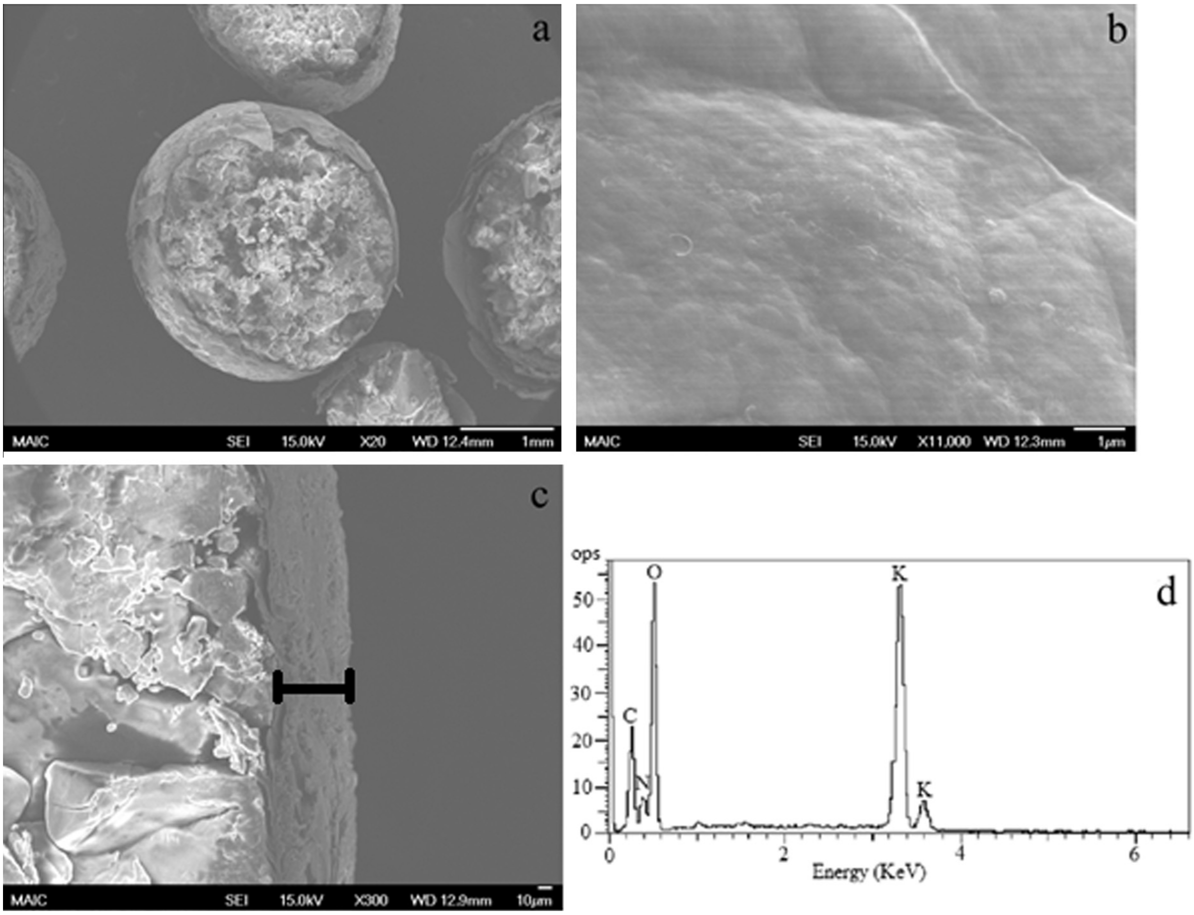

Fig. 4. SEM-EDX analysis of: (a) re-GO-coated KNO_3; (b and c) observation of shell section; and (d) EDX spectrum.

of GO individuals showed the presence of GO sheets on the mica surface and that the size of GO patches was in the micrometer range (Fig. 2). Although a graphene sheet is thin, the AFM could easily characterize the morphological feature of the graphene patches. Cross-sectional images of the AFM revealed that the thickness of a single-layer graphene on the mica surface ranged from 0.5 to 0.9 nm with an average of 0.7 ± 0.2 nm (Fig. 2b), which is in agreement with the typical thickness (<1 nm) observed elsewhere for monolayer graphene sheets [37].

3.2. Characterizations of re-GO-coated KNO_3 pellets

Raman spectroscopy was used to characterize GO on the surface of KNO_3 after heat treatment. The typical features of the G band at 1585 cm and the D band at 1335 cm are shown in the Raman spectra (Fig. 3a), which agrees well with the literatures by direct exfoliation approaches [37]. The G band is usually assigned to the E_{2g} phonon of C sp atoms, while the D band is a breathing mode of κ-point phonons of A_{1g} symmetry. The A_{1g} mode is attributed to

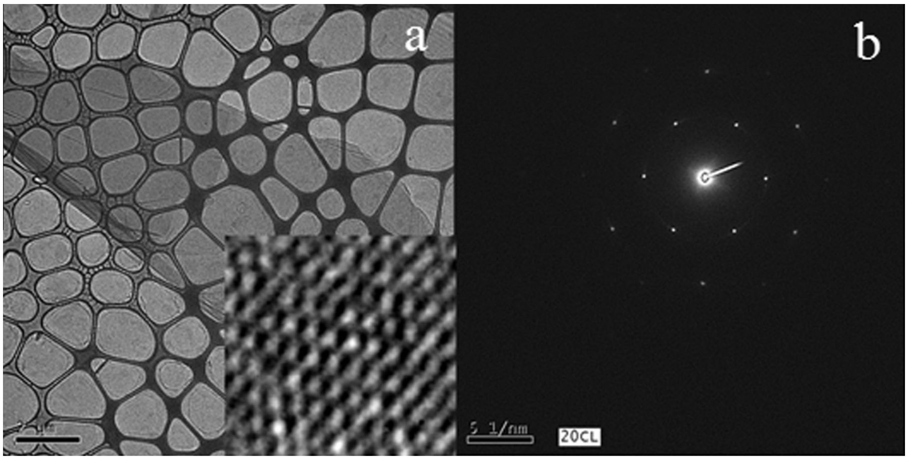

Fig. 5. (a) TEM image of a re-GO sheet taken from re-GO-coated KNO_3; and (b) a selected area electron diffraction (SAED) pattern of the re-GO sheet. The insert in (a) is HR-lattice image of re-GO.

particle-size effects due to the existence of specific vibrations at the edges of graphene sheets. The appearance of a prominent D band in the spectrum is also an indication of disorder in graphene originating from the defects associated with vacancies and grain boundaries. It has been well documented that the size of the defect-free sp cluster regions is the inverse of the ratio of the D and the G band integrated intensities (I_D/I_G). This correlation has been used to determine the size of sp domains in various carbon materials including graphene. Comparisons of the Raman spectra of GO before and after coated on GO-coated KNO_3 by thermal treatment showed a significant decrease of ratios of D and G band intensity from 1.00 to 0.51 (Fig. 3a), suggesting the simple approach successfully reduced the initial GO to re-GO with much less defects [38]. C1s XPS spectra of GO and the GO coating on re-GO-coated KNO_3 were used to further determine the quality of GO and identified the presence of three functional groups, the non-oxygenated C-ring (C–C and C–H, at a binding energy of 284.6 eV), the C in the C–O bond (C–OH, 286.2 eV), and the carbonyl C (C=O, 289.0 eV), for both samples (Fig. 3b and 3c). The sp C–C component of the GO film from re-GO-coated KNO_3 sample (71.8%), however, was much higher than that of the GO film (58.6%), indicating the removal of oxygen-containing groups from GO and improved quality of GO sheets after being heated with KNO_3. The results further confirmed that the metal cations can efficiently reduce the GO by thermal treatment, which is consistent with the results of Raman analysis.

The analysis of cross-sectional re-GO-coated KNO_3 pellets by SEM shows the presence of both re-GO shell and KNO_3 core (Fig. 4a). High magnification SEM imaging of the surface on re-GO-coated KNO_3 pellet revealed that it had a dense re-GO shell without apparent apertures outside (Fig. 4b). With a closer look at cross-sectional re-GO shell, it showed that the thickness of the shell was about 20–30 μm (Fig. 4c). The energy-disperse X-ray (EDX) analysis confirmed that those pellets were made of carbon,

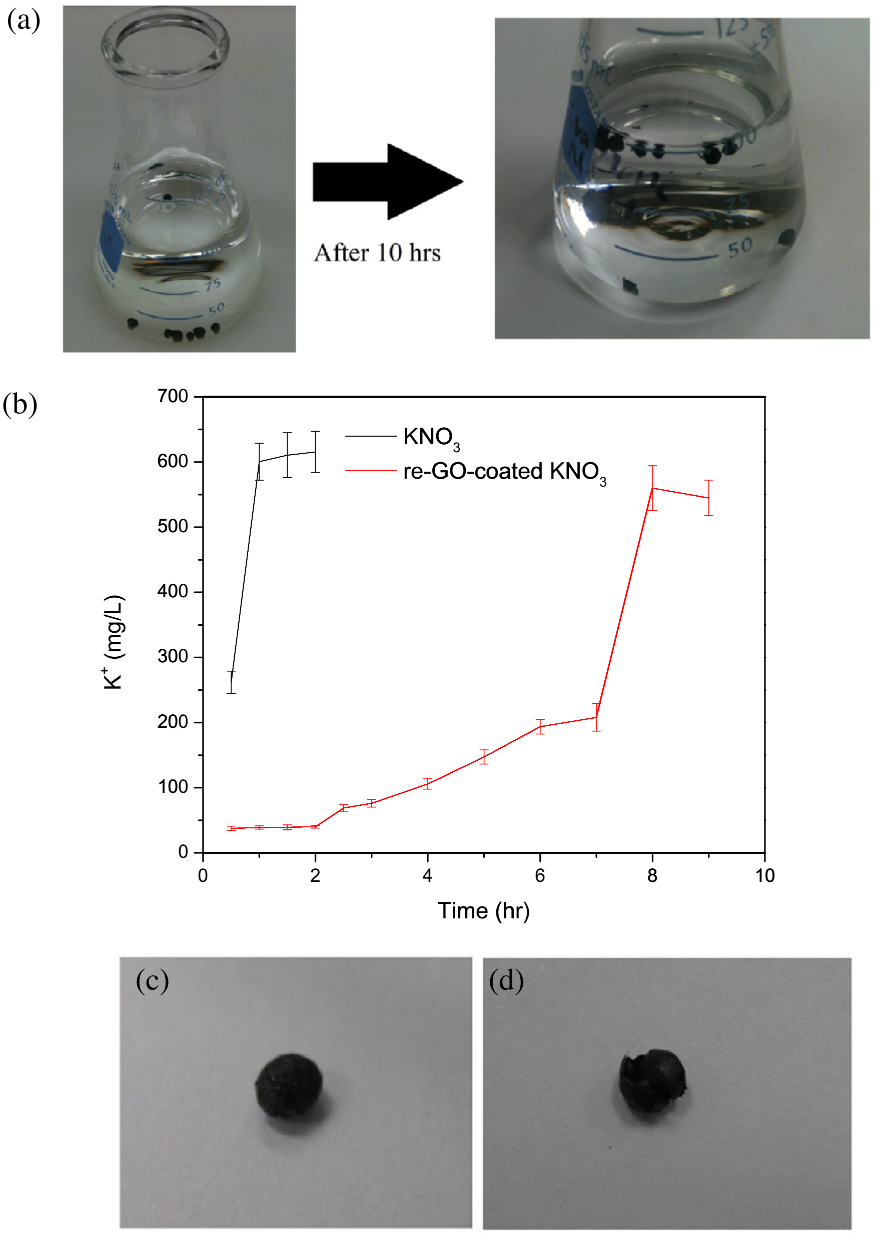

Fig. 6. (a) Photograph of re-GO-coated KNO_3 pellets soaking in water; (b) slow release of potassium ions from re-GO-coated KNO_3 and pure KNO_3 and (c and d) photograph of immersion of single re-GO-coated KNO_3 pellet in water before and after 8 h.

oxygen, potassium and nitrate, a chemical composition that agreed well with re-GO-coated KNO_3.

Fig. 5a shows TEM images of re-GO film of re-GO-coated KNO_3, which clearly depict wrinkles and folding that indicates formation of a thin re-GO film. The TEM images also showed large pieces of re-GO sheets with size of at least 10 μm. As reported by the manufacturer (ACS materials), the sizes of the original GO sheets should be around 1–5 μm, which is confirmed by the AFM analysis. In addition, high-resolution TEM image of the graphene sheets showed that the carbon atoms were densely packed in a honeycomb crystal lattice (Fig. 5a, insert) The corresponding selected area electron diffraction (SAED) pattern of the graphene film is shown in Fig. 5b, where the ring patterns along with point patterns of hexagonal symmetry are clearly seen. The ring patterns indicate various orientations of re-GO sheets due to wrinkling and folding of a re-GO layer or overlapping with different re-GO layers, while the point patterns reflect the presence of a main single crystalline domain composed of sp-hybridized carbons arranged in a hexagonal lattice [39]. The SAED results confirm that well-reduced GO films formed on KNO_3 could be few- or multi-layer graphene sheets.

3.3. Slow-release behavior of re-GO-coated KNO_3 pellets

The slow-release behavior of as-produced re-GO-coated KNO_3 was examined to demonstrate its potential application as an agent for fertilizer delivery. The release characteristics of both the re-GO-coated KNO_3 and the pure KNO_3 were investigated. As shown in Fig. 6a, after soaking for 10 h, the re-GO-coated KNO_3 pellets still kept as good of shape as it was at the beginning and that some pellets drift on the solution without structural collapse. These observations indicate that, after thermal treatment, the GO film is capable of coating KNO_3 pellets. The concentrations of potassium that are released over time from the samples are shown in Fig. 6b, where C_{K+} denotes the concentration of potassium ions in the elutriant. It shows that the release rate of potassium took place in different stages when re-GO sheets are used as coating for delaying the whole release process. In the initial stage from the 0 to the 7 h, the release rate is relatively slow compared with other stages. During this stage, only about 34.5% of potassium ions were released in the water. This could be attributed to the slow diffusion of water through the shell and into the core of re-GO-coated KNO_3 to establish 'channels' for the release of the potassium ions encapsulated in GO sheets. The burst release of potassium ions takes place in the stage from 7 to 8 h, after that about 93.8% of potassium ions were released from the fertilizers. As shown in Fig. 6c and d, the re-GO film on the KNO_3 pellet cracked after immersed in water for 8 h. The cracks on the film leaded to the burst release of potassium ions. After that, the release is restored to a slow rate, similar to that of the first 2 h. The data also reveal that the release of potassium out of the re-GO shell to water reaches its equilibrium after about 8 h, indicating that the shell has excellent controlled-release ability. On the other hand, the release of potassium from the uncoated KNO_3 was rapid and reached equilibrium after only 1 h. The results clearly demonstrate the reduction of GO films on the fertilizers can provide a promising coating technique for the slow release characteristic.

4. Conclusions

We have demonstrated a new and simple method for developing fertilizer (KNO_3) in a slow-release manner. The fertilizer was developed by encapsulating KNO_3 pellets with graphene oxide (GO) films at 90 °C for 6 h in air. Our results show that with the aid of potassium ions, separated GO sheets were not only fused together to form a shell on KNO_3, but also reduced to re-GO sheets during the heat treatment. The as-prepared re-GO-coated KNO_3 pellets exhibited slow-release behavior. Because of the unique characteristics of graphene, this newly developed method could be used for developing fertilizers that have controlled-release manner, providing plants with nutrients, enhancing plant productivity, and minimizing nutrient loss, particularly when the graphene/GO can be produced in large scale with green methods at relatively low cost.

Acknowledgments

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