



# Fabrication of graphene oxide/polymer latex composite film coated on $\text{KNO}_3$ fertilizer to extend its release duration

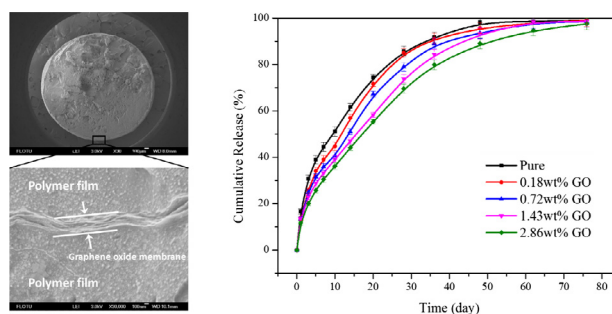
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## HIGHLIGHTS

- Composite film was coated on  $\text{KNO}_3$  fertilizer via spray coating in a fluidized bed.
- GO membrane formed from GO sheets coated each  $\text{KNO}_3$  granule completely.
- Composition of GO membrane in polymer film extended release duration of coated  $\text{KNO}_3$ .
- Long diffusion path & slow diffusion rate for  $\text{K}^+$  &  $\text{NO}_3^-$  give long release duration.

## GRAPHICAL ABSTRACT



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## ABSTRACT

The application of a polymer film coated fertilizer can increase nutrient utilization efficiency and reduce environmental pollution, and polymer latex is an environmental friendly coating material with a promising future. However, because of the hydrophilicity of the film formed from polymer latex, it is difficult to achieve film coated fertilizer with a long release duration and a low consumption of the coating materials. Through spray coating in a fluidized bed, the sandwich structure of a composite film, i.e., polymer film/graphene oxide membrane/polymer film, was coated on  $\text{KNO}_3$  granules. Because of the longer diffusion path for the hydrated  $\text{K}^+$  and  $\text{NO}_3^-$  diffusing within the graphene oxide membrane and the slower diffusion rate caused by cation- $\pi$  interactions between the hydrated  $\text{K}^+$  and graphene oxide, the release duration of the film coated  $\text{KNO}_3$  fertilizer was extended. For the pure polymer film coated  $\text{KNO}_3$  granules, the release duration was 24 days, while the release durations of the composite film coated  $\text{KNO}_3$  granules were extended to 26, 29, 34 and 38 days when the amounts of graphene oxide in the coating were 0.18%, 0.72%, 1.43% and 2.86% of the film, respectively. It is shown that graphene oxide has great potential in applications in the field of controlled release fertilizers.

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## 1. Introduction

The application of polymer film coated fertilizer can increase the nutrient utilization efficiency and reduce environmental pollution [1–4]. The polymer film coated on the fertilizer granules acts as a physical barrier to slow down the release rate of the nutrients

to reduce the loss of the fertilizer nutrient in the environment. The release duration, i.e., the time the coated fertilizer takes to release a specified percentage of nutrient (e.g., 80%), is an important index for evaluating the slow release property [5,6]. Generally, for a film coated fertilizer with a certain amount of coating material, a longer release duration indicates a better slow release property of the coated fertilizer.

Currently, there are mainly three types of polymer materials for producing film coated fertilizer: (1) Organic solvent-based

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polymers used as a coating material. The film coated fertilizer using this type of coating material usually has a long release duration. Shaviv et al. [7] measured the release behavior of polyolefin coated urea in water at 30 °C. The time for the coated fertilizer with a 35 µm film thickness to release 80% of the nutrients was approximately 30 days. However, the coating process with an organic solvent-based polymer involves hazardous organic solvents that not only cause the additional cost of solvent recovery but also bring risks to the environment and human health [8]. (2) Materials consisting of two or more components to react to form a thermosetting polymer film, such as a polyurethane film and an alkyl resin film. The release duration of the film coated fertilizer using this type of coating material is also long. Li et al. [9] prepared polyurethane-coated urea and measured the release property by immersing them in water. The time for the coated urea with a 10–15 µm film thickness to release 60% of the nutrients was approximately 28 days. (3) A polymer latex in which the continuous phase is water. As the coating process is free from toxic organic solvents and is easy to control, it is an environmentally friendly and promising material for producing film coated fertilizer [10,11]. However, because the film formed from the polymer latex has hydrophilic characteristics, the as-prepared coated fertilizer usually has a relatively short release duration. Tzika et al. [12] prepared a film coated compound fertilizer using aqueous latex of a vinyl-idene-chloride-based copolymer as the coating material. The time for the coated fertilizer with a 55–60 µm film thickness to release 80% of the nutrients was only approximately 13 days in a water environment. Thermal post-treatments for a polymer latex coated fertilizer at a high temperature can enhance the cross-linking of the polymer film. The polymer film becomes denser, so the release duration can be extended significantly [13,14]. Yang et al. [13] coated urea using a styrene-butyl acrylate copolymer latex and thermally treated them at 120 °C for 30 min. The time for the coated urea with an approximately 40 µm thick film to release 80% of the nutrients was approximately 30 days in a water environment at 25 °C. However, the release duration of the polymer latex coated fertilizer after the thermal post-treatment is still not long enough. To extend the release duration, a thicker polymer latex film coating is needed, leading to an increase in production costs and a decrease of the nutrient contents in the coated fertilizer.

Graphene oxide (GO) is a type of two-dimensional nanomaterial with a single-atom thickness. There are large amounts of oxygen-containing functional groups, including carboxyl, hydroxyl, epoxy and carbonyl, on GO sheets [15,16]. By stacking GO sheets layer by layer, a freestanding GO membrane (GOM) was obtained [17], and it showed an excellent barrier property for different molecules and ions [18]. Guo et al. [19] deposited a 10 nm thick GOM on a polyethylene film by the drop cast method. The mercury vapor permeability through the composite film was reduced by 60% as the diffusion path of the mercury molecules was extended. Joshi et al. [20] studied the penetration properties of ions of different sizes through a GOM. Because of the size exclusion from the inter-layer space of the GOM, ions with a hydrated radius of >4.5 Å were sieved out by the GOM, while the species with a hydrated radius of <4.5 Å could permeate through. Sun et al. [21] studied the penetration properties of Cu<sup>2+</sup> and rhodamine B molecules in a solution through a GOM. Neither Cu<sup>2+</sup> nor rhodamine B permeation through the GOM was detected. In recent years, with the development of the production method of GO, the large-scale preparation of GO with a high efficiency and a relatively low cost has been achieved [22]. By composing a GOM in a polymer latex film, the release duration of a coated fertilizer is expected to be extended by utilizing the barrier property of the GOM.

In this work, a styrene-butyl acrylate-methyl methacrylate copolymer latex was used as the coating material, and by compos-

ing a GOM in the polymer latex film, composite film coated KNO<sub>3</sub> granular fertilizers were prepared. The release property of composite film coated KNO<sub>3</sub> granules with different GOM coating amounts were measured, and the diffusion mechanism of KNO<sub>3</sub> through the composite film was analyzed.

## 2. Experimental

### 2.1. Materials

The spherical-like potassium nitrate granular fertilizer used (Weifang Changsheng Nitrate Co., Ltd., China) had a size of 1–2 mm and a purity of 99.9%. The styrene-butyl acrylate-methyl methacrylate copolymer latex had 40% solid content, and the latex microspheres had an average diameter of 80 nm, which were used as the coating material. The latex was synthesized via a semi-continuous emulsion copolymerization in the Department of Chemical Engineering, Tsinghua University. Natural flake graphite (325 mesh, Qingdao Jinrilai Graphite Co., Ltd., China), which had a purity of 99.99%, was used to produce graphene in this work. The chemical reagents used include KMnO<sub>4</sub> and concentrated HCl (36–38%) (Beijing Chemical Works, China), concentrated H<sub>2</sub>SO<sub>4</sub> (95–98%) and an H<sub>2</sub>O<sub>2</sub> solution (30%) (Modern Oriental (Beijing) Technology Development Co., Ltd., China), which were all analytical reagent (A.R.) grade. The water used in the experiment was deionized water.

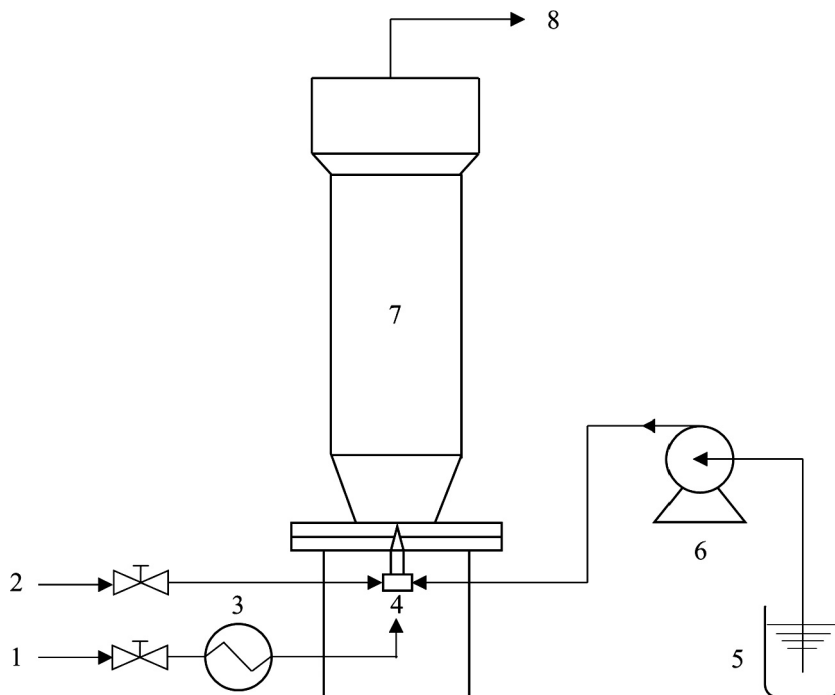
### 2.2. Synthesis of GO

GO was prepared by a modified Hummers method [23]. Concentrated H<sub>2</sub>SO<sub>4</sub> (70 mL) was added to an 800-mL beaker under mechanical stirring in an ice-water bath, and then, 9 g of KMnO<sub>4</sub> was added slowly into the beaker to keep the suspension at a low temperature. After fully mixing, 3 g of natural flake graphite was slowly added to the mixture, and the stirring was continued for 1 h at the low temperature. Successively, the reaction system was transferred to a 40 °C water bath and stirred for 1 h. Then, 140 mL of deionized water was added slowly, and the solution was stirred for another 15 min at 98 °C. An additional 450 mL of deionized water was added, followed by the dropwise addition of 20 mL H<sub>2</sub>O<sub>2</sub>. The mixture was filtered and washed with 500 mL of a 1:10 HCl aqueous solution to remove the metal ions, and it was then washed with 500 mL of deionized water to remove the acid. The obtained filter cake was redispersed in 600 mL of deionized water. Then, the solution was further purified to remove the remaining ions using a dialysis tube with a molecular weight cutoff of 8000–14,000 g/mol (Sinopharm Chemical Reagent Co., Ltd., China) for 10 days. Finally, the solution was stirred for approximately 10 h and sonicated for 30 min to obtain a stable GO aqueous solution.

### 2.3. Preparation of film coated KNO<sub>3</sub> granules

A fluidized bed apparatus used for the coating of KNO<sub>3</sub> granules is shown in Fig. 1.

For preparing the pure polymer film coated KNO<sub>3</sub> granules, the operation procedure is as follows: the fluidization gas was heated to 50 °C and then supplied to the fluidized bed from the bottom, and 1 kg of KNO<sub>3</sub> granules was put into the fluidized bed and fully fluidized by the gas. The polymer latex diluted to a solid content of 30% was pumped into a nozzle by a peristaltic pump at a flow rate of 10 mL/min. The latex was atomized into droplets by the atomization gas through the nozzle. The droplets were sprayed and coated the surface of the KNO<sub>3</sub> granules in the fluidized bed. Then, the droplets spread out on the surface and were dehydrated



**Fig. 1.** Fluidized bed apparatus for the film coating of  $\text{KNO}_3$  granules. 1- fluidization gas; 2- atomization gas; 3- heater; 4- nozzle; 5- polymer latex or GO solution; 6- peristaltic pump; 7- fluidized bed; 8- vent gas.

by the heated fluidization gas, forming a dense polymer film after repeatedly coating. After 133.3 mL of polymer latex was sprayed, pure polymer film coated  $\text{KNO}_3$  granules were obtained. The mass of the polymer film coated on 1 kg of granules was 40 g, namely, the coating amount of the polymer film in the coated  $\text{KNO}_3$  granules was 4%. After coating, the coated  $\text{KNO}_3$  granules were thermally post-treated in the fluidized bed at a temperature of 120 °C for 30 min to enhance the cross-linking of the polymer. Then, the coated  $\text{KNO}_3$  granules were removed from the fluidized bed for the subsequent measurement of the release property. The specific experimental conditions in the coating process are listed in Table 1.

For preparing the polymer/GOM composite film coated  $\text{KNO}_3$  granules, the operation procedure is as follows: first, 66.7 mL of polymer latex diluted to a solid content of 30% was coated on 1 kg of  $\text{KNO}_3$  granules in the fluidized bed. Successively, a GO aqueous solution was pumped by the peristaltic pump at a flow rate of 10 mL/min and sprayed on the surface of the granules. For different coating amounts of GOM, the concentration and volume of the GO aqueous solution were adjusted to ensure a uniform coating on the  $\text{KNO}_3$  granules. The parameters for the GO coating are listed in Table 2. After the GO solution was sprayed, a small amount of granules was sampled from the fluidized bed for observing the mor-

**Table 1**

Experimental conditions in the film coating process of  $\text{KNO}_3$  granules.

Polymer film coating amount <sup>a</sup> , %	4
Flow rate of the fluidization gas, m <sup>3</sup> /h	135
Temperature of the fluidization gas, °C	50
Flow rate of the atomization gas, m <sup>3</sup> /h	3.5
Pressure of the atomization gas, MPa	0.3
Spray rate of the coating material, mL/min	10
Thermal post-treatment temperature, °C	120
Thermal post-treatment time, min	30

<sup>a</sup> Mass fraction of the polymer film to the  $\text{KNO}_3$  granules.

**Table 2**

Operation parameters for different GOM coating amounts.

GOM coating amount <sup>a</sup> , %	Mass of GOM, mg	GO solution volume, mL	GO solution concentration, mg/mL
0.22	87.5	50	1.75
0.88	350	100	3.50
1.75	700	100	7.00
3.50	1400	200	7.00

<sup>a</sup> Mass fraction of the GOM sprayed to the composite film.

phology of the granule surface. Finally, the other 66.7 mL of polymer latex diluted to a solid content of 30% was coated on the granules. The total mass of the polymer film was 40 g for each experiment. After the thermal post-treatment, the composite film coated  $\text{KNO}_3$  granules were taken out to measure their release property. The experimental conditions were the same as those for preparing the pure polymer film coated  $\text{KNO}_3$  granules, as listed in Table 1.

The actual amount of polymer film coated on granules was determined as follows: the pure film coated  $\text{KNO}_3$  granules sample of 4.006 g were weighed precisely. Then, the granule was cut into two parts and put into the deionized water to dissolve the  $\text{KNO}_3$ . After the  $\text{KNO}_3$  was dissolved completely, the polymer films were collected and washed by water to remove  $\text{KNO}_3$  completely. Then the whole films collected were dried in an oven at 80 °C for 2 h to remove the water completely and weighed the mass as M. The actual mass fraction of the polymer film to the coated  $\text{KNO}_3$  granules was calculated by  $\phi = M/4.006 \times 100\%$ . As the amount of GO coated on granules was too little to be weighed, the actual coating amount was estimated from the thickness of GOM in the composite film.

#### 2.4. Measurement of the release property of the film coated $\text{KNO}_3$ granules

The measurement of the release property was carried out according to the National Standard of China (GB/T 23348-2009)

as follows: 10.0 g of coated  $\text{KNO}_3$  granules were weighed accurately and put into a mesh bag of nylon. Then, they were put in a sealed flask containing 200 mL of deionized water, and the flask was then placed in an incubator at 25 °C. The concentration of  $\text{NO}_3^-$  was measured to calculate the cumulative release percentage of  $\text{KNO}_3$ . The whole solution was taken out to measure the concentration, and then, 200 mL of fresh deionized water was added to the flask. The sampling times were set for the 1st, 3rd, 5th, 7th, 10th, 14th, 20th, 28th, 36th, 48th, 62nd and 76th days. The cumulative release percentage of the coated  $\text{KNO}_3$  granules was calculated by the release amount divided by the amount of  $\text{KNO}_3$  core. The release duration was determined as the time for the film coated  $\text{KNO}_3$  granules to release 80% of the  $\text{KNO}_3$ .

### 2.5. Characterization

The X-ray photoelectron spectroscopy (XPS) analysis was conducted using an ESCALAB 250 photoelectron spectrometer (Thermo-Fisher Scientific, UK) with  $\text{Al K}\alpha$  as the X-ray source at 150 W. The Raman spectroscopy analysis was conducted using a LabRAM HR800 spectrometer (Horiba Jobin Yvon, France) with an excitation laser beam wavelength of 532 nm. The X-ray diffraction (XRD) analysis was conducted using a D8 Advance X-ray diffractometer (Bruker, Germany) with  $\text{Cu K}\alpha$  radiation. The morphology of the granules whose outermost surface was coated by a GOM and the cross-section morphology of the film coated  $\text{KNO}_3$  granules were examined using a high-resolution scanning electron microscope (SEM, JSM7401, JEOL, Japan). The concentration of  $\text{NO}_3^-$  released in the solution was determined using a TU-1900 UV-vis spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., China) by measuring the absorbance of the released solution at a wavelength of 210 nm [24].

## 3. Results and discussion

### 3.1. The effect of the thermal post-treatment on GO

The thermal post-treatment of the film coated  $\text{KNO}_3$  granules can enhance the cross-linking of the polymer film and extend the release duration significantly [13,14]. For the composite film coated  $\text{KNO}_3$  granules, a thermal post-treatment at a temperature of 120 °C for 30 min also affected the properties of GO in the composite film. Fig. 2 illustrates the C 1s XPS spectra of GO before and after the thermal post-treatment. The peaks at binding energies of 284.8, 286.9, 288.4 and 289.0 eV correspond to the carbon atoms of  $\text{C}=\text{C}/\text{C}-\text{C}$  in aromatic rings,  $\text{C}-\text{O}$  (epoxy and alkoxy),  $\text{C}=\text{O}$  (carbonyl) and  $\text{COOH}$  (carboxyl), respectively [25,26]. As shown in Fig. 2, the intensity of the  $\text{C}-\text{O}$  peak decreased slightly after the thermal post-treatment, and the ratio of carbon to oxygen (C/O) from the XPS measurements accordingly increased from 2.97 to 3.23.

Fig. 3 presents the Raman spectra of GO before and after the thermal post-treatment. The intensity ratio of the D band at  $1333.4\text{ cm}^{-1}$  to the G band at  $1597.7\text{ cm}^{-1}$ , i.e.,  $I_D/I_G$ , increased slightly from 1.22 to 1.32 after the thermal post-treatment, indicating that more  $\text{sp}^2$  regions were formed [27]. Fig. 4 shows the XRD patterns of GO before and after the thermal post-treatment. The peak position for GO before the thermal post-treatment was  $2\theta = 12.5^\circ$ , corresponding to an interlayer spacing of 7.09 Å, while the peak for GO after the thermal post-treatment showed a shift to a higher  $2\theta$  angle of  $13.4^\circ$ , corresponding to an interlayer spacing of 6.60 Å. The decrease in the interlayer spacing of GO after the thermal post-treatment was attributed to the partial removal of oxygen-containing functional groups from the GO sheets. The above results indicated that GO was reduced to some extent after

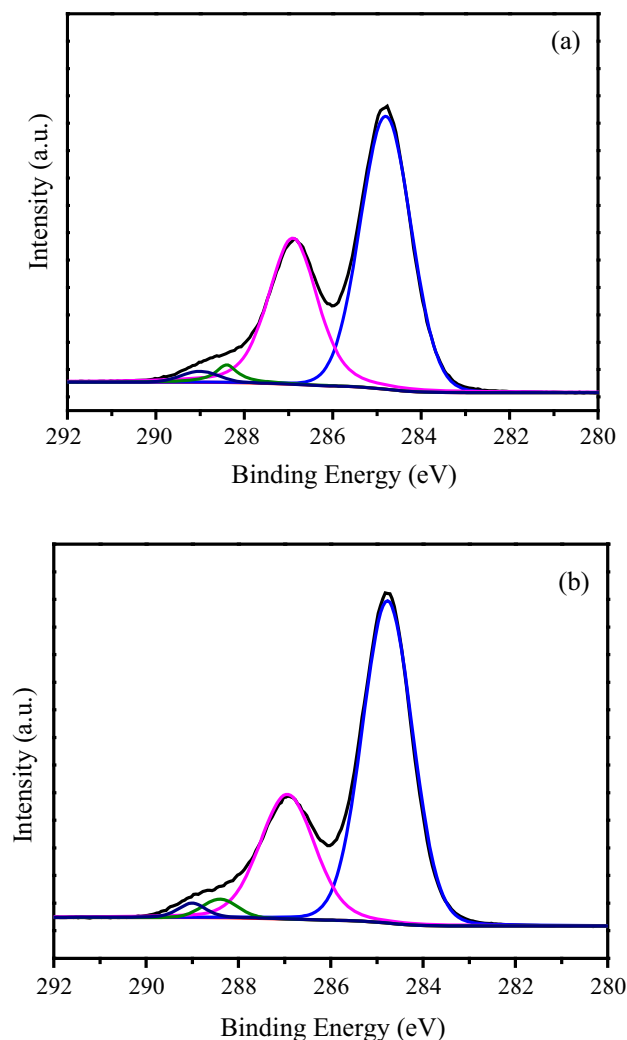


Fig. 2. XPS spectra of GO: (a) before the thermal post-treatment; (b) after the thermal post-treatment.

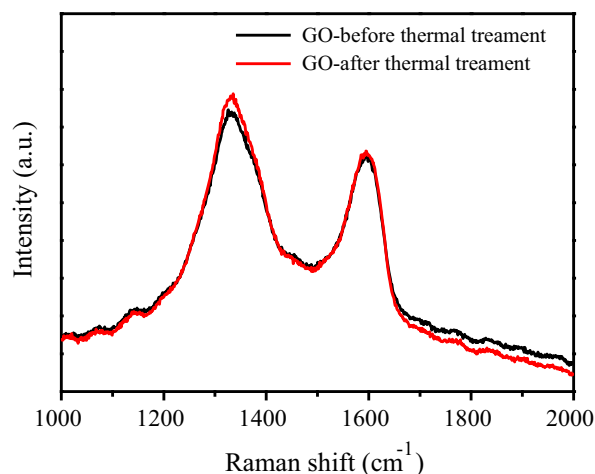


Fig. 3. Raman spectra of GO before and after the thermal treatment.

the thermal post-treatment, in agreement with the results reported by Mei et al. [28]. However, because the temperature of the thermal post-treatment in this work was lower and the treatment time was substantially shorter than those in the literature

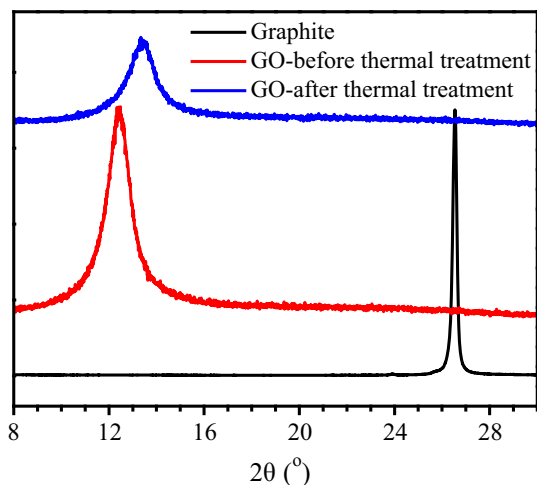


Fig. 4. XRD patterns of GO before and after the thermal post-treatment.

report [28], the degree of reduction of GO in this work was significantly lower.

### 3.2. The structure of film coated $\text{KNO}_3$ granules

The cross-sectional morphologies of the pure polymer film coated  $\text{KNO}_3$  granules and the polymer/GOM/polymer composite film coated  $\text{KNO}_3$  granules are shown in Fig. 5. The two types of films were continuous and dense and had nearly the same thickness of 20–25  $\mu\text{m}$ , in which the coating amount of the polymer film was both 4%. For the preparation process of the composite film coated  $\text{KNO}_3$  granules, a layer of polymer film was first coated on the  $\text{KNO}_3$  granules. This layer of polymer film not only reduced the release rate of  $\text{KNO}_3$  but also played an important role as a water barrier for the GO coating process, in case the  $\text{KNO}_3$  granules were dissolved in the high humidity environment of the fluidized

bed caused by the spraying of the dilute GO solution in the subsequent process. Then, in the process of coating the GOM, the GO solution was atomized into droplets containing GO sheets, and the droplets were sprayed and coated on the surface of the granules. The water in the droplets on the surface of the  $\text{KNO}_3$  granules evaporated rapidly in the heated fluidization gas, leaving the GO sheets stacked layer by layer and forming the GOM. By observing the morphology of the GOM on the surface of the granules, it was found that the GOM was flat and continuously coated the entire granule completely, as shown in Fig. 6. Finally, the other layer of polymer film was coated on the granules. This outermost layer of polymer film not only reduced the release rate of the nutrients but also protected the GOM from being worn away because of the impact and friction between granules. Finally, the composite film with the sandwich structure, i.e., polymer/GOM/polymer film, was coated on the granules. The cross-sectional morphology of the composite film peeled from the granule showed that the GO sheets forming the GOM were well packed, and for the composite film in which the GOM coating amount was 1.75% of the film, the thickness of the GOM was approximately 350 nm, as shown in Fig. 7.

The actual amount of polymer film in 4.006 g of the pure film coated  $\text{KNO}_3$  granules was measured to be  $M = 0.1507$  g, which indicated the actual coating amount of the polymer film to the coated  $\text{KNO}_3$  granules was  $\varphi = M/4.006 \times 100\% = 3.76\%$ . Therefore, for the experiment with 1000 g  $\text{KNO}_3$  granules and the mass of polymer film spraying of 40 g, the coating efficiency of polymer film was calculated to be 97.8%. The loss was resulted from the friction between granules and the entrainment of the fluidization gas. The coating amount of GO was estimated from the thickness of GOM in the composite film, as shown in Fig. 7. From Fig. 7, the thickness of GOM and polymer film were 350 nm and 29.5  $\mu\text{m}$ , respectively. The density of GOM and polymer film measured were 1.206  $\text{g}/\text{cm}^3$  and 1.049  $\text{g}/\text{cm}^3$ , respectively. Then the fraction of GOM to polymer film was calculated to be 1.43%. For 1000 g  $\text{KNO}_3$  granules, the actual coating amount of GO was calculated to be 0.5587 g. From 0.7 g of the amount of GOM sprayed, the coating efficiency

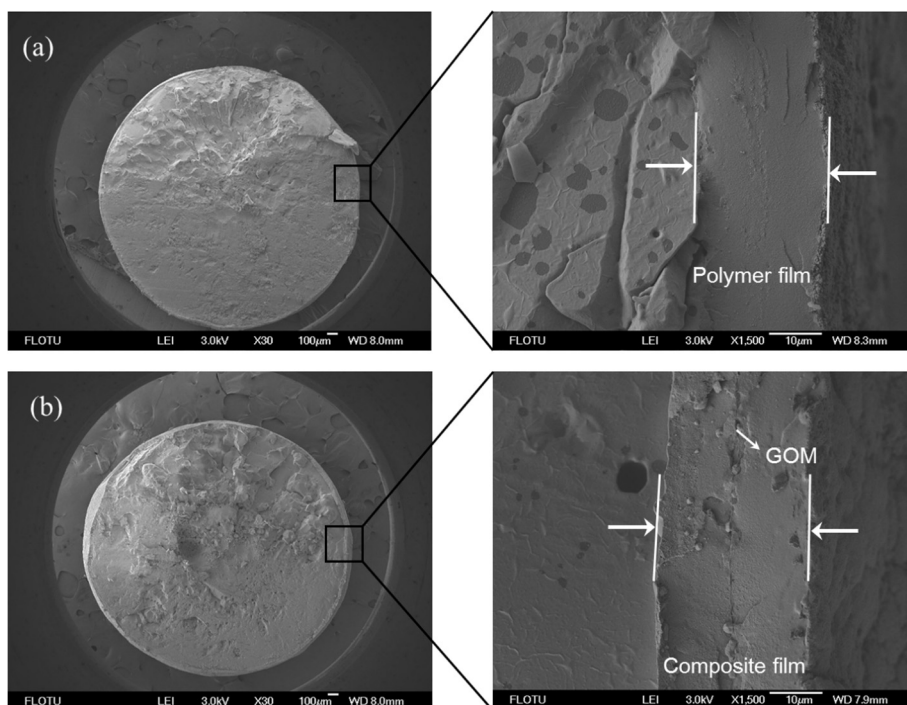


Fig. 5. Cross-sectional morphology of the film coated  $\text{KNO}_3$  granules: (a) the pure polymer film; (b) the composite film.

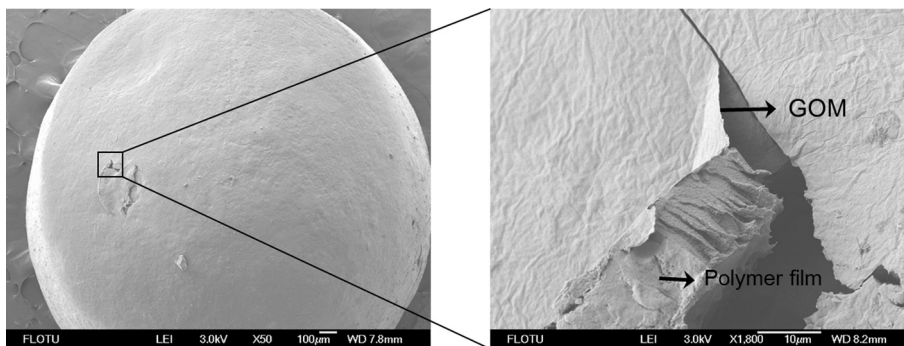


Fig. 6. Surface morphology of the GOM coated on the  $\text{KNO}_3$  granules (the incision was cut using a knife intentionally).

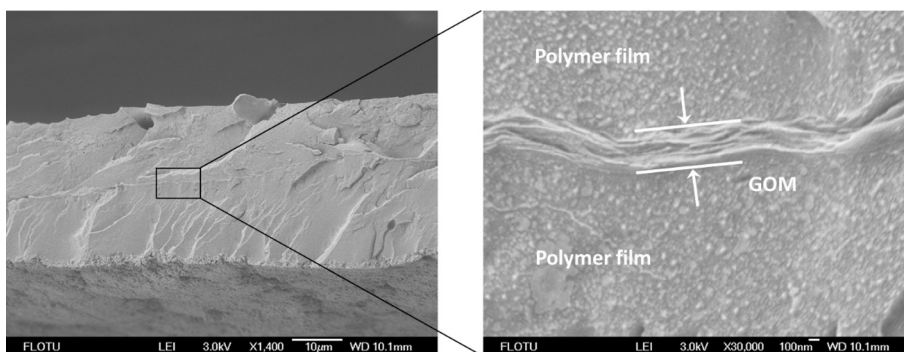


Fig. 7. Cross-sectional morphology of the composite film peeled from the coated  $\text{KNO}_3$  granules (the spraying amount of GOM is 1.75%).

of GO was calculated to be 79.8%. So the actual GOM coating amounts were 0.18%, 0.72%, 1.43% and 2.86% when sprayed 0.22%, 0.88%, 1.75% and 3.50%, respectively.

### 3.3. The release property of film coated $\text{KNO}_3$ granules

For pure film coated  $\text{KNO}_3$  granules, the mass of  $\text{KNO}_3$  core in the granule sample was  $10.0 \times (1 - \varphi) = 9.624$  g. For composite film coated fertilizer, the mass of GOM was ignored as the amount was very little, so the mass of  $\text{KNO}_3$  core was also taken to be 9.624 g. The cumulative release percentages of the coated  $\text{KNO}_3$  granules with different amounts of GOM in the coating are shown in Fig. 8. It was found that the addition of trace amounts of GOM in the polymer film extended the release duration of the coated  $\text{KNO}_3$  granules significantly. The larger the amount of the GOM in the composite film was, the longer the release duration of the film coated  $\text{KNO}_3$  granules was. Specifically, the release duration of the pure polymer film coated  $\text{KNO}_3$  granules was 24 days, while the release durations of the composite film coated  $\text{KNO}_3$  granules were 26, 29, 34 and 38 days when the amounts of GOM in the coating were 0.18%, 0.72%, 1.43% and 2.86%, respectively.

To clearly understand the slow release mechanism, the release rate, i.e., the release percentage per day (%/d), changing with time was calculated through the differential treatment of the cumulative release curve, as shown in Fig. 9. It was found that the release rate of the film coated  $\text{KNO}_3$  granules in the first several days was very fast, and the addition of the GOM slowed down the release rate, as shown in the inset of Fig. 9. It is known that the GO sheets contain pristine regions, oxidized regions and a small fraction of holes. In the pristine region, the C atoms are bonded in an  $\text{sp}^2$  hybridization. In the oxidized region, there are a large amount of oxygen-containing functional groups, including carboxyl, hydroxyl, epoxy and carbonyl, and the atoms are bonded in an  $\text{sp}^3$  hybridization [15,16,29]. The holes were formed during the preparation pro-

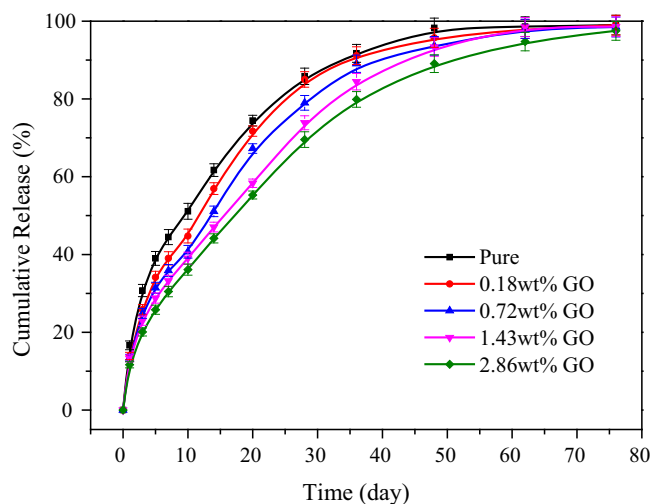


Fig. 8. Cumulative release curves of the film coated  $\text{KNO}_3$  granules.

cess because of the aggressive oxidation and exfoliation [29,30]. When the GO sheets stack together to form the GOM, the oxidized regions keep the adjacent GO sheets apart, while the pristine regions are connected to form networks of nanocapillaries within the GOM [31,32]. The interlayer spacing within the GOM in the fully wetted state is 9–10 Å [20,31], and the diameters of the hydrated  $\text{K}^+$  and  $\text{NO}_3^-$  are 6.62 Å and 6.7 Å, respectively [33], which are smaller than the interlayer space. Therefore, the hydrated  $\text{K}^+$  and  $\text{NO}_3^-$  could diffuse within the tortuous networks of the nanocapillaries in the GOM and permeate through the GOM, and the diffusion path in the composite film was longer than that in the pure polymer film. The hydrated  $\text{K}^+$  could interact with the

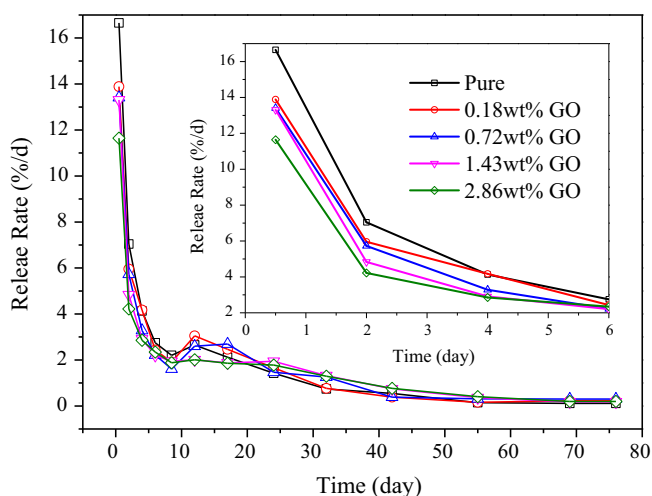


Fig. 9. Release rate vs time for the film coated  $\text{KNO}_3$  granules.

$\text{sp}^2$  clusters in the pristine regions of GO sheets through cation- $\pi$  interactions, which are noncovalent interactions between cations and the aromatic  $\pi$ -electron cloud [34–36]. The thermal post-treatment partially reduced the GO, leading the hydrated  $\text{K}^+$  to interact with more  $\text{sp}^2$  clusters. The cation- $\pi$  interactions resulted in the slow diffusion rate of the hydrated  $\text{K}^+$ , as well as the hydrated  $\text{NO}_3^-$ , because of the charge neutrality in the solution. The longer diffusion path and slower diffusion rate resulted in the reduced release rate of the composite film coated  $\text{KNO}_3$  granules compared with the pure film coated  $\text{KNO}_3$  granules. With the increase in the amount of GOM in the composite film, the length of the diffusion path increased, so the release rate decreased accordingly, as shown in Fig. 9. The decreased release rate of composite film coated fertilizer in the first several days can further reduce the loss of excess nutrient released, increase the nutrient utilization efficiency, and decrease the fertilizing cost and environment pollution effectively.

When the film coated  $\text{KNO}_3$  granules were soaked in water, the hydrophilic polymer film swelled over time [37]. It is reported that the swelling of a polymer film results in the narrowing of the diffusion channels of the polymer film, leading to a decrease in the permeability coefficients of molecules and ions through the polymer film [13]. Therefore, in the first several days, the polymer film started to swell, and the release rate decreased dramatically for the film coated  $\text{KNO}_3$  granules. Several days later, the swelling of the polymer film reached equilibrium and the permeability coefficient of molecules and ions remained constant [13], so the release rate then changed little afterward, as shown in Fig. 9. Compared with the pure film coated fertilizer, the composite film coated fertilizer with longer release duration supplies more nutrient to plants in the last days of release period, and it can meet the nutrient demand of plants with longer growth period, with a consequent of decreasing fertilizing frequency and the saving in spreading costs.

#### 4. Conclusions

Composite film coated  $\text{KNO}_3$  granules with the sandwich structure, i.e., polymer/GOM/polymer film, were prepared through spray coating in a fluidized bed. The GOM formed from the stacked GO sheets coated the entire granule completely, and GO was partially reduced in the thermal post-treatment process of the film coated  $\text{KNO}_3$  granules. The composition of the trace amounts of GOM in the polymer film extended the release duration of the film coated  $\text{KNO}_3$  granules significantly. The longer diffusion path for

the hydrated  $\text{K}^+$  and  $\text{NO}_3^-$  within the GOM and the slower diffusion rate caused by the cation- $\pi$  interactions between the hydrated  $\text{K}^+$  and the pristine regions of the GOM contribute to the longer release duration of the composite film coated  $\text{KNO}_3$  granules compared with that of the pure film coated  $\text{KNO}_3$  granules. With the increase of the amount of GOM in the coating, the length of the diffusion path increased, and the release duration was extended.

The decreased release rate especially in the first several days of composite film coated  $\text{KNO}_3$  granules could reduce the loss of excess nutrient and environment pollution effectively. The GO in the composite film was in the form of the GO membrane, which would hardly cause potential risks to soil environment [38,39]. The reduction degree of GO in this work was very low, since the reduced GOM with high reduction degree can delay ionic diffusion more effectively because of the decreasing of interlayer spacing of GOM [31,40], it is expected that increasing the reduction degree of GOM in the composite film can extend the release duration of the coated fertilizer. It is inferred that GO has a promising application in the field of controlled release fertilizers, particularly when the GO is produced in large scale at a relatively low cost.

#### Conflict of interest

The authors declare no competing financial interest.

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#### References

- [1] M.M. Hanafi, S.M. Eltaib, M.B. Ahmad, Physical and chemical characteristics of controlled release compound fertilizer, *Eur. Polym. J.* 36 (2000) 2081–2088.
- [2] A. Shaviv, *Advances in controlled-release fertilizers*, *Adv. Agron.* 71 (2001) 1–49.
- [3] Z.M. Easton, A.M. Petrovic, Fertilizer source effect on ground and surface water quality in drainage from turfgrass, *J. Environ. Qual.* 33 (2004) 645–655.
- [4] U. Bröckel, C. Hahn, Product design of solid fertilizers, *Chem. Eng. Res. Des.* 82 (2004) 1453–1457.
- [5] Y.P. Timilsena, R. Adhikari, P. Casey, T. Muster, H. Gill, B. Adhikari, Enhanced efficiency fertilizers: a review of formulation and nutrient release patterns, *J. Sci. Food Agric.* 95 (2015) 1131–1142.
- [6] M.E. Trenkel, *Controlled-Release and Stabilized Fertilizers in Agriculture*, International fertilizer industry association, Paris, 1997.
- [7] A. Shaviv, S. Raban, E. Zaidel, Modeling controlled nutrient release from polymer coated fertilizers: diffusion release from single granules, *Environ. Sci. Technol.* 37 (2003) 2251–2256.
- [8] M.M.E. Costa, E.C.M. Cabral-Albuquerque, T.L.M. Alves, J.M. Pinto, R.L. Fialho, Use of polyhydroxybutyrate and ethyl cellulose for coating of urea granules, *J. Agric. Food Chem.* 61 (2013) 9984–9991.
- [9] Q. Li, S. Wu, T. Ru, L. Wang, G. Xing, J. Wang, Synthesis and performance of polyurethane coated urea as slow/controlled release fertilizer, *J. Wuhan Univ. Technol.* 27 (2012) 126–129.
- [10] Y. Shen, C. Du, J. Zhou, Aqueous polyacrylate/poly (silicone-co-acrylate) emulsion coated fertilizers for slow nutrient-release application, *J. Appl. Polym. Sci.* 131 (2014) 40369.
- [11] R. Lan, Y. Liu, G. Wang, T. Wang, C. Kan, Y. Jin, Experimental modeling of polymer latex spray coating for producing controlled-release urea, *Particuology* 9 (2011) 510–516.
- [12] M. Tzika, S. Alexandridou, C. Kiparissides, Evaluation of the morphological and release characteristics of coated fertilizer granules produced in a Wurster fluidized bed, *Powder Technol.* 132 (2003) 16–24.
- [13] L. Yang, D. An, T. Wang, C. Kan, Y. Jin, A model for the swelling of and diffusion from a hydrophilic film for controlled-release urea particles, *Particuology*, DOI: <http://dx.doi.org/10.1016/j.partic.2016.03.005>.
- [14] Z. Zhou, C. Du, T. Li, Y. Shen, J. Zhou, Thermal post-treatment alters nutrient release from a controlled-release fertilizer coated with a waterborne polymer, *Sci. Rep.* 5 (2015) 13820.
- [15] D.R. Dreyer, S. Park, C.W. Bielawski, R.S. Ruoff, The chemistry of graphene oxide, *Chem. Soc. Rev.* 39 (2010) 228–240.
- [16] W.W. Cai, R.D. Piner, F.J. Stadermann, S. Park, M.A. Shaibat, Y. Ishii, D.X. Yang, A. Velamakanni, S.J. An, M. Stoller, J. An, D. Chen, R.S. Ruoff, Synthesis and solid-state NMR structural characterization of  $^{13}\text{C}$ -labeled graphite oxide, *Science* 321 (2008) 1815–1817.

- [17] D.A. Dikin, S. Stankovich, E.J. Zimney, R.D. Piner, G.H. Dommett, G. Evmenenko, R.S. Ruoff, Preparation and characterization of graphene oxide paper, *Nature* 448 (2007) 457–460.
- [18] D. An, L. Yang, T. Wang, B. Liu, Separation performance of graphene oxide membrane in aqueous solution, *Ind. Eng. Chem. Res.* 55 (2016) 4803–4810.
- [19] F. Guo, G. Silverberg, S. Bowers, S. Kim, D. Datta, V. Shenoy, R.H. Hurt, Graphene-based environmental barriers, *Environ. Sci. Technol.* 46 (2012) 7717–7724.
- [20] R.K. Joshi, P. Carbone, F.C. Wang, V.G. Kravets, Y. Su, I.V. Grigorieva, H.A. Wu, A. K. Geim, R.R. Nair, Precise and ultrafast molecular sieving through graphene oxide membranes, *Science* 343 (2014) 752–754.
- [21] P.Z. Sun, M. Zhu, K.L. Wang, M.L. Zhong, J.Q. Wei, D.H. Wu, Z.P. Xu, H.W. Zhu, Selective ion penetration of graphene oxide membranes, *ACS Nano* 7 (2013) 428–437.
- [22] L. Peng, Z. Xu, Z. Liu, Y. Wei, H. Sun, Z. Li, X. Zhao, C. Gao, An iron-based green approach to 1h production of single-layer graphene oxide, *Nat. Commun.* 6 (2015) 5716.
- [23] J. Chen, Y. Li, L. Huang, C. Li, G. Shi, High-yield preparation of graphene oxide from small graphite flakes via an improved Hummers method with a simple purification process, *Carbon* 81 (2015) 826–834.
- [24] A.P. Carvalho, L.A. Meireles, F.X. Malcata, Rapid spectrophotometric determination of nitrates and nitrites in marine aqueous culture media, *Analisis* 26 (1998) 347–351.
- [25] A.R. Kumarasinghe, L. Samaranyake, F. Bondino, E. Magnano, N. Kottegoda, E. Carlino, U.N. Ratnayake, A.A.P. de Alwis, V. Karunaratne, G.A.J. Amaratunga, Self-assembled multilayer graphene oxide membrane and carbon nanotubes synthesized using a rare form of natural graphite, *J. Phys. Chem. C* 117 (2013) 9507–9519.
- [26] L. Chen, Z. Xu, J. Li, Y. Li, M. Shan, C. Wang, Z. Wang, Q. Guo, L. Liu, C. Chen, X. Qian, A facile strategy to prepare functionalized graphene via intercalation, grafting and self-exfoliation of graphite oxide, *J. Mater. Chem.* 22 (2012) 13460–13463.
- [27] A.C. Ferrari, J. Robertson, Interpretation of Raman spectra of disordered and amorphous carbon, *Phys. Rev. B* 61 (2000) 14095.
- [28] X. Mei, X. Meng, F. Wu, Hydrothermal method for the production of reduced graphene oxide, *Phys. E* 68 (2015) 81–86.
- [29] K. Erickson, R. Erni, Z. Lee, N. Alem, W. Gannett, A. Zettl, Determination of the local chemical structure of graphene oxide and reduced graphene oxide, *Adv. Mater.* 22 (2010) 4467–4472.
- [30] J.T. Paci, T. Belytschko, G.C. Schatz, Computational studies of the structure, behavior upon heating, and mechanical properties of graphite oxide, *J. Phys. Chem. C* 111 (2007) 18099–18111.
- [31] R.R. Nair, H.A. Wu, P.N. Jayaram, I.V. Grigorieva, A.K. Geim, Unimpeded permeation of water through helium-leak-tight graphene-based membranes, *Science* 335 (2012) 442–444.
- [32] A.V. Talyzin, T. Hausmaninger, S. You, T. Szabó, The structure of graphene oxide membranes in liquid water, ethanol and water-ethanol mixtures, *Nanoscale* 6 (2014) 272–281.
- [33] E.R. Nightingale, Phenomenological theory of ions solvation: effective radii of hydrated ions, *J. Phys. Chem.* 63 (1959) 1381–1387.
- [34] A.S. Mahadevi, G.N. Sastry, Cation- $\pi$  interaction: its role and relevance in chemistry, biology, and material science, *Chem. Rev.* 113 (2013) 2100–2138.
- [35] J.C. Ma, D.A. Dougherty, The cation- $\pi$  interaction, *Chem. Rev.* 97 (1997) 1303–1324.
- [36] P.Z. Sun, F. Zheng, M. Zhu, Z.G. Song, K.L. Wang, M.L. Zhong, D.H. Wu, R.B. Little, Z.P. Xu, H.W. Zhu, Selective trans-membrane transport of alkali and alkaline earth cations through graphene oxide membranes based on cation- $\pi$  interactions, *ACS Nano* 8 (2014) 850–859.
- [37] A. Kostić, B. Adnadjević, A. Popović, J. Jovanović, Comparison of the swelling kinetics of a partially neutralized poly(acrylic acid) hydrogel in distilled water and physiological solution, *J. Serb. Chem. Soc.* 72 (2007) 1139–1153.
- [38] H. Zhang, C. Peng, J. Yang, M. Lv, R. Liu, D. He, C. Fan, Q. Huang, Uniform ultrasmall graphene oxide nanosheets with low cytotoxicity and high cellular uptake, *ACS Appl. Mater. Interfaces* 5 (2013) 1761–1767.
- [39] M. Lv, Y. Zhang, L. Liang, M. Wei, W. Hu, X. Li, Q. Huang, Effect of graphene oxide on undifferentiated and retinoic acid-differentiated SH-SY5Y cells line, *Nanoscale* 4 (2012) 3861–3866.
- [40] Y. Su, V.G. Kravets, S.L. Wong, J. Waters, A.K. Geim, R.R. Nair, Impermeable barrier films and protective coatings based on reduced graphene oxide, *Nat. Commun.* 5 (2014) 4843.