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Tuning shape of three dimensional graphene sheets

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ABSTRACT

3D graphene has been explored as an important material and catalyst for many applications. However, it is still a challenge to tune the shape of 3D graphene sheets. Herein, it is demonstrated that the shapes of 3D graphene sheets, which were synthesized from the reaction between Li_2O and CO, are strongly dependent on the particle size of Li_2O. When Li_2O particle size was very small (about 400 nm), the formed graphene sheets possessed a granulated shape. However, as Li_2O particle size increased, the shape of the synthesized graphene sheets changed to flower-structure and then to honeycomb-structure. Furthermore, the shape change of graphene from the granulated to the honeycomb-structured can increase its electro-catalytic efficiency as a counter electrode catalyst for dye-sensitized solar cells (DSSCs).

1. Introduction

Graphene is a promising two-dimensional (2D) material due to its high transparency, extremely high carrier mobility, large surface area, and excellent mechanical properties [1–7]. To prevent its self-aggregation, a graphene sheet is usually supported on a substrate [8–10]. However, the use of substrates limits its practical applications. To solve the issue, intense efforts have been devoted to synthesize 3D graphene architecture. Furthermore, 3D graphene architectures exhibited excellent performances as active material and catalysts for energy conversion and storage as well as environmental and biomedical applications, such as supercapacitors [11–13], batteries [14–16], solar cells [17,18], fuel cells [19], water purification [20], biosensors, and bioelectrochemical devices [21].

Graphene oxide (GO) solution has been widely employed to achieve 3D graphene scaffolds, including graphene aerogels [22,23], hydrogels [24,25], frameworks [26–28], fiber [29], and sponge [30,31]. Another common used approach is chemical vapor deposition with templates. Chen et al. synthesized graphene foam using porous Ni foam as a template for the chemical vapor deposition (CVD), followed by etching away the Ni skeleton [32]. The interconnected flexible network of the graphene foam provided the fast transport channel of charge carriers, leading to high electrical conductivity of graphene foam. Chang et al. [33] formulated MoS_x catalytic materials on 3D graphene/Ni foam structure to form a rigid 3D electrocatalytic architecture, which exhibited high efficiency for electrocatalytic hydrogen production. Cu foam [34] and Al_2O_3 [35] were also used as templates to construct 3D graphene architecture.

It is still a challenge to tune the shape of 3D graphene sheets with CVD and GO methods. Recently, we developed a novel approach to synthesize 3D graphene with controlled honeycomb-like structure based on our invented reaction between Li_2O and CO [17], which can be expressed as follows:

$$Li_2O + 2CO = C(\text{graphene}) + Li_2CO_3 \quad (1)$$

Furthermore, simultaneous generation of Li_2CO_3 with graphene can isolate graphene sheets from each other to prevent graphite formation during the process. On the other hand, the Li_2CO_3 particles will also play a role in determining the locally curved shape of graphene sheets [17]. This success has stimulated us to explore the possibility of tuning shapes of 3D graphene sheets by Li_2O particle sizes in this work. Furthermore, we found that the shape of 3D graphene can affect its performance as a counter electrode catalyst for a dye-sensitized solar cell (DSSC).

2. Experimental

2.1. Material preparation

The particle size of lithium oxide powder (Li_2O, Aldrich) is 10 μm. To obtain different particle sizes, the Li_2O powder was ball-milled with SPEX 8000 Mixer/Mill for a selected time (2 or 5 h).

The Li_2O powder (with or without ball-milling treatment) was located in a ceramic reactor and CO (with pressure of 50 psi) introduced into the reactor at room temperature. Then the reactor temperature was increased to 550 °C at a rate of 10 °C/min and

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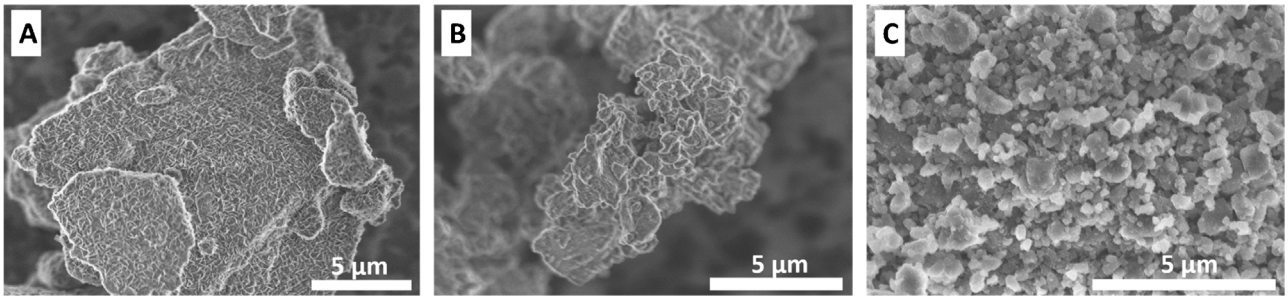

Fig. 1. FESEM images of Li_2O particles: (a) Li_2O without ball-milling, (b) Li_2O with ball milling for 2 h, and (c) Li_2O with ball milling for 5 h. (The images show that particle sizes are about 10 μm for Li_2O without ball-milling, about 1 μm for Li_2O with ball milling for 2 h, and about 0.4 μm for Li_2O with ball milling for 5 h).

kept at 550 °C for 12 h, followed by cooling down to room temperature. The obtained solid products after reaction were treated with 36.5 wt% hydrochloric acid (HCl) and washed with large amount of deionized water (DW). The remained solids were separated from deionized water by centrifugation (3600 rpm) and then dried overnight at 80 °C to obtain 3D graphene samples.

2.2. Characterization

The crystalline structure of Li_2O powders (with and without ball-milling treatment) and solid products after reaction were evaluated by X-ray diffraction (XRD) using a Scintag XDS 2000 Powder Diffractometer with Cu Kα (λ = 1.5406 Å) radiation in the range of $20 \leq 2\theta \leq 70^\circ$.

The morphologies of Li_2O powders and synthesized graphene were evaluated with a Hitachi-4700 field emission scanning electron microscope (FESEM). BET surface areas of synthesized graphene were measured by nitrogen adsorption at liquid nitrogen temperature (77 K) using a Micromeritics ASAP 2000 sorptometer. Before the adsorption measurement, samples were degassed at 110 °C. Sheet resistance of graphene film was measured by Jandel four-point probe system with RM3 test.

3. Results and discussion

Li_2O with and without ball-milling was subjected to FESEM characterization. As shown in Fig. 1, Li_2O particles without ball-milling possess a disk shape with average size of 10 μm. The particle size decreased to 1 and 0.4 μm by ball-milling for 2 and 5 h, respectively. Furthermore, XRD patterns were obtained for Li_2O samples (Fig. 2), and Li_2O crystal sizes were calculated with Scherrer equation:

$$\tau = \frac{K\lambda}{\beta \cos\theta}$$

where τ is the crystal size, λ the X-ray wavelength, K the dimensionless shape factor, θ the Bragg angle, and β the full width at half maximum (FWHM). The calculation showed that the crystal size of

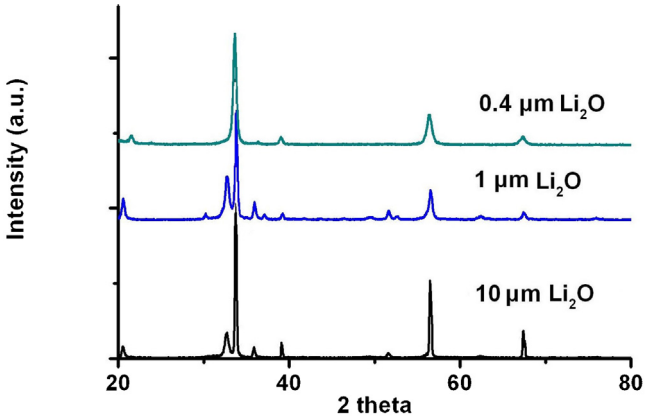

Fig. 2. XRD patterns of Li_2O with various particle sizes.

Li_2O without ball-milling was about 65 nm, and it decreased to 41 and 20 nm after ball-milling of 2 and 5 h, respectively. Those indicate that both the particle size and crystal size of Li_2O decreased with increasing ball-milling time.

Graphene sheets were synthesized from CO reaction with Li_2O of different particle sizes via an approach, in which the temperature of the reactor (containing CO and Li_2O) was increased to 550 °C and then remained for 12 h. As shown by FESEM images (Fig. 3), when large Li_2O particles (10 μm) were employed, synthesized graphene sheets possess a 3D honeycomb shape (with cell size in the range of 50–100 nm), which is consistent with our precious report [17]. However, when the particle size of Li_2O decreased, the shape of synthesized 3D graphene changed. Flower-like structured graphene was obtained from the reaction of CO with 1 μm Li_2O particles (Fig. 3b). Furthermore, when the Li_2O particle size decreased to 0.4 μm, the obtained graphene exhibited a granulated shape (Fig. 3c). This indicates that the shape of 3D graphene could be tuned by changing Li_2O particle size.

To understand the effect of Li_2O particle size on graphene shape, the reaction kinetics was examined. In the batch reactor system,

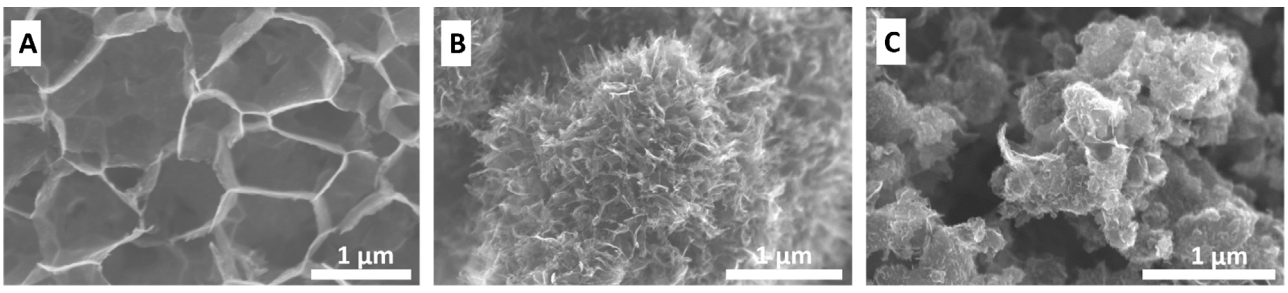

Fig. 3. FESEM images of graphene synthesized from CO reaction with (a) 10 μm Li_2O particles, (b) 1 μm Li_2O particles, and (c) 0.4 μm Li_2O particles.