Facile synthesis of graphene oxide-modified lithium hydroxide for low-temperature chemical heat storage

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ABSTRACT

LiOH·H$_2$O nanoparticles supported on graphene oxide (GO) were facilely synthesized by a hydrothermal process. The mean diameter of nanoparticles on the integrated graphene sheet was about 5–10 nm showed by SEM and TEM results. XRD results suggested that the nanoparticles are in good agreement with the data of LiOH·H$_2$O. The as-prepared sample showed a greatly enhanced thermal energy storage density and exhibit higher rate of heat release than pure lithium hydroxide, and thermal conductivity of composites increased due to the introduction of nano carbon. LiOH·H$_2$O/GO nanocomposites are novel chemical heat storage materials for potential highly efficient energy system.

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1. Introduction

The efficient utilization of thermal energy is essential today to decrease the depletion of fossil fuels and to reduce the greenhouse gas emissions [1]. Sensible, latent and chemical heat storage systems are of critical importance to decrease the gap between supply and demand of thermal energy and improve the efficiency of energy [1,2]. Among these systems, reversible thermochemical reactions are appropriate for thermal energy storage due to their high-energy storage densities [3]. Commonly, thermochemical materials (TCMs) used in chemical heat storage systems are metal hydrides, metal hydroxides, metal carbonates and inorganic hydrates [4–7]. However, hydration reaction rates of pure inorganic salts to hydrates are always slow in the low-temperature chemical heat storage system, and strong water sorption of hydrates-based composite TCMs is of great importance for exothermic reaction process [7].

Graphene oxide (GO) is an excellent substrate that can host phase change materials for latent heat storage. The composite materials which have many desirable properties, including high conductivity, large surface area and chemical stability [8]. Besides, GO is also a substance with outstanding hydrophilic property [9]. However, so far, the carbon-based composite nano-materials for chemical heat storage systems are rarely reported. Our recent work showed that lithium hydroxide monohydrate can decompose by using low-temperature thermal energy below 373 K. Besides it is quite a simple and safe reaction [10]. In this Letter, we present a facile approach to prepare LiOH nanoparticles supported on GO, which are used as TCMs in low-temperature chemical heat storage system for the first time. Subsequently, performance study on dehydration and hydration transformations of LiOH/GO–LiOH·H$_2$O/GO and LiOH–LiOH·H$_2$O was performed with a thermogravimetric and differential scanning calorimetric analyzer.

2. Experimental

Graphite oxide was prepared by a modified Hummers method with natural flake graphite as the carbon source (325 meshes, Alfa Aesar). Firstly, 3 g graphite was added into a solution of concentrated H$_2$SO$_4$ (30 mL), K$_2$S$_2$O$_8$ (2.5 g) and P$_2$O$_5$ (2.5 g) and the mixture was heated at 80 °C for 270 min. The pre-oxidized graphite was diluted with deionized (DI) water, filtered, dried and then added into 120 mL concentrated H$_2$SO$_4$. 15 g KMnO$_4$ was added slowly into the ice-cooled mixture (<10 °C) and the solution was stirred at 35 °C for 2 h. Then it was diluted with 250 mL DI water

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and stirred for additional 2 h. After adding 700 mL DI water, 30% H_2O_2 solution (20 mL) was added dropwise, and the color of the mixture turned to bright yellow. The product was collected by filtration and washed with 8 L H_2O/HCl (9/1, v/v) solution. Then the suspension was re-dispersed in DI water to 8 g L^{-1} and dialyzed for 1 week until the dialysate was neutral to obtain GO. The GO was exfoliated in DI water by sonication for 2 h, and the concentration of the solution was 1 mg mL^{-1}.

In a typical hydrothermal method, 21 mg lithium hydroxide monohydrate (300–400 μm, Aladdin, Ltd.) was dissolved in 40 mL of GO suspension to form a homogeneous solution under vigorously stirring at room temperature. The solution was transferred into a 100 mL Teflon lined stainless-steel autoclave and heated at 105 °C for 12 h. After cooled naturally to room temperature, the solids, denoted here as LiOH·H_2O/GO, were collected by centrifugation and lyophilization.

The surface morphology was examined by a field-emission scanning electron microscopy (SEM, LEO1530VP, LEO Company). Transmission electron micrographs (TEM) were obtained with a FEI Tecnai G^2 12 operated at 100 kV and a JEOL JEM-2010 operated at 200 kV. X-ray diffraction (XRD) analysis was performed on a D8-advance X-ray diffractometer (German Bruker) with Cu target (40 kV, 40 mA) at a scan rate of 0.02°/17.7 s. The thermal conductivity was measured by flash method at 30 °C (LFA 447, Netzsch Instruments Inc.). LiOH·H_2O content was measured by atomic absorption spectroscopy (AAS, Thermo Scientific S4AA).

Lithium hydroxide monohydrate and LiOH·H_2O/GO were respectively used as starting materials. Then, lithium hydroxide and LiOH/GO were respectively prepared by a temperature-programmed reaction and pyrolysis of the starting materials in a horizontal tubular quartz furnace with Ar gas at 150 °C for 2 h. Dehydrated samples were cooled to 30 °C in the same atmosphere, and water vapor with 2.55 kPa of partial pressure carried with N_2 flow was introduced into the tube for 10 min or 60 min as hydration operation. After hydration operation, endothermic heat and temperature of the samples were measured with the thermogravimetric and differential scanning calorimetric analyzer (Linseis STA PT1600), which was also used for measuring weight change during dehydration step at the same time. The TG/DSC thermal analyzer STA PT1600 was calibrated by measuring the heat enthalpy of Indium, which melting point satisfy the reaction temperature range required. Each TG/DSC measurement was repeated three times and took the average. The TGA and DSC curves were obtained by heating the samples from 30 °C to 170 °C at a heating rate of 5 K/min under nitrogen gas atmosphere. The endothermic heat was calculated from the area under the peak, and its temperature was estimated by a tangent at a point of greatest slope on the face portion of the peak.

3. Results and discussion

Figure 1 shows XRD patterns of the as-prepared LiOH·H_2O/GO sample. It is clearly shown that the sample with their characteristic diffraction peaks of 2θ values are at about 30.1 (011), 31.9 (101), 33.7 (220), 35.0 (130) and 37.0 (−121) (JCPDS 25-0486), respectively, indicating that LiOH·H_2O are successfully supported on GO. There are abundant oxygen-containing groups between graphite layers of GO, and interplanar spacing was widen due to the increased interlayer spacings. In the synthesizing process, GO carrier was partly reduced and the number of functional groups decreased, so the interlayer spacings become smaller than before. Therefore, the graphite (002) peak moved from 10.6° to 23–24° (see Figure 1) [11]. The typical SEM images of GO and LiOH·H_2O/GO are shown in Figure 2a and c. From the both figures, it is clear to see that the samples have a regular structure, and the

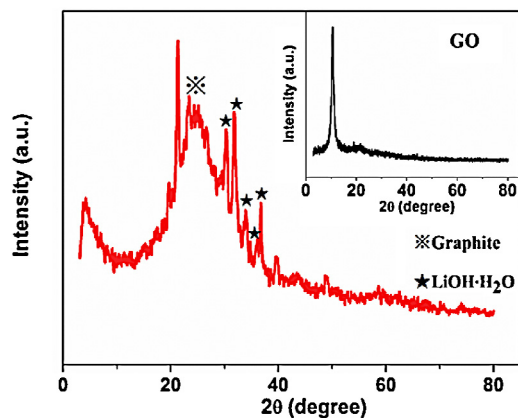**Figure 1.** XRD patterns of LiOH·H_2O/GO and GO.

introduction of LiOH·H_2O did not result in some unintegrated graphene sheets. Nanoparticles with a diameter of 5–10 nm are dispersed on GO in abundance, and clear particle structures can be observed, as indicated by Figure 2d. The content of LiOH·H_2O supported on GO was about 27.9 wt% by AAS. It is widely known that GO is a layer-structured material (see Figure 2b), and each fundamental layer of GO has two-dimensional carbonaceous skeletons with strong covalent bonding within the layers. Yet another intermolecular interaction such as hydrogen bonding may exist between GO and hydrate when they are synthesized into composites due to the presence of functional groups such as hydroxyl, carbonyl and carboxyl groups [12]. Since there are abundant oxygen functional groups, GO has an excellent stabilization ability for LiOH·H_2O. However, to our best knowledge, it is the first time to report its success in preparing LiOH·H_2O composites on nanoscale.

Subsequently, we conducted a comparative performance study for low-temperature chemical heat storage with LiOH·H_2O and LiOH·H_2O/GO. As shown in Figure 3a, the endothermic heat about 1460 kJ/kg at 65 °C was obtained by pure lithium hydroxide monohydrate, which started to dehydrate around 60 °C and finished dehydration at 98 °C, indicating that LiOH·H_2O has a potential to be the promising material for high density heat storage. However, it is found that lithium hydroxide reacted with water vapor very slowly and conversion of LiOH to LiOH·H_2O was only about 35% even after 1 h, which calculated by nearly 15% of H_2O mass loss shown in Figure 3b. Consequently, it led to the low energy storage density (511 kJ/kg) of LiOH after 1 h hydration, and the enhancement of hydration rate of LiOH is required toward practical application. As shown in Figure 3c, the evolution of DSC curve is observed on GO modified LiOH·H_2O when the hydration of LiOH/GO only lasted for 10 min. Surprisingly, ultrahigh heat storage density of 1980 kJ/kg normalized by LiOH·H_2O content (27.1 wt%) was obtained. This illustrates the GO provided a higher conversion of LiOH to LiOH·H_2O in a much shorter period of time. On one hand, LiOH·H_2O/GO showed better performance of hydration and dehydration due to the nanoscale of immobilized particles, which have increased surface area contacted with the water molecules. The number of surface atoms increased in magnitude as the particle diameter decreased to nanoscale, the crystalline field and binding energy of internal atoms are very different from that of surface atoms, which have many dangling bonds due to the lack of adjacent atoms. It is precisely the unsaturation that nanoparticles show better thermodynamic property, which included specific heat capacity [13] and latent heat [14]. On the other hand, graphene sheet could be a new reaction interface between LiOH particles and water molecules due to the hydrophilic nature of GO. Figure 3c also shows that LiOH·H_2O/GO had a single endothermic peak with wider range, and the dehydration temperature of LiOH·H_2O/GO