



Hydrogen storage kinetics: The graphene nanoplatelet size effect

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ABSTRACT

The kinetics of hydrogen storage in magnesium can be accelerated by nanocarbon additives. In this study, we show that loading magnesium by graphene nanoplatelets (GNP) enhances the kinetics by more than an order of magnitude. The GNP presence reduces the Mg agglomeration, induced by de/hydrating, and accelerates the kinetics by connecting between Mg particles. The GNP were prepared by top-down graphite ball-milling in the presence of various organic protective agents. We found that both the molecular structure of the protective agent and the milling energy dictated the GNP properties, namely, size, thickness, defect density and specific surface area. We demonstrated how manipulation of the GNP size has a major effect on the hydrogen storage kinetics in magnesium-GNP composites.

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1. Introduction

The use of hydrogen as energy carrier relies in part on its storage efficiency and delivery rate, according to the USA Department of Energy [1]. Metal hydrides, such as MgH₂, are considered as promising candidates for hydrogen storage applications, due to their high hydrogen capacity, light-weight and abundance [2,3]. However, Mg is characterized with slow reversible hydrating kinetics that hinders its use for these applications. Loading Mg with carbon species have dramatically enhance the hydrogen storage kinetics [4–6]. The major reported species include activated carbon [7,8], graphite [4,9], nanotubes [10,11] and graphene [12–14]. Furthermore, confinement of metal or metal hydride particles within a nanocarbon matrix has demonstrated the possibility to store hydrogen [12,15–20].

Graphite and its derivatives are typically integrated to Mg powder prior to long reactive ball milling (in the presence of hydrogen gas) [4–6,8,21–23]. The main role of these additives is to lubricate the Mg particles during milling [4–6]. The long milling

deconstructs the graphitic structure, resulting in dangling carbon atoms, which could consequently be hydrogenated [8,9,24].

Graphene is a two-dimensional carbonaceous allotrope, arranged in an sp²-bonded aromatic structure [25]. The pristine form of mono-atomic graphene layer is ideal for research purposes [26]. However, the production of a single-layered graphene is expensive and of low yield [27,28], which limits its industrial application. GNP consist of up to 100 graphene layers [29] and could be fabricated in large quantities. GNP possess attractive properties (thermal, mechanical and charge transport [30–33]), which depend on their size and quality. The quality of GNP could be quantified in terms of defect density, thickness and surface area, which determine their suitability for a specific application. For example, GNP make an ideal platform for clean energy applications, specifically for the improvement of hydrogen storage devices [34,35]. The main challenge in this study is to develop GNP with tailor-made properties that can be applied for energy conversion and storage devices [34,36–39].

Most scalable methods for GNP production are top-down, and based on exfoliating bulk, inexpensive graphite [40,41], such as ball milling [42–46], high-shear mixing [47], sonication [48,49] or electrochemical exfoliation [50,51]. Here, we focus on graphite ball milling in the presence of a protective agent. The weak van der Waals interactions between graphite layers and the strong coupling between the protective agent and the graphitic surface ensure the

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graphite exfoliation [46], while suppressing its fracture at the same time [52]. For example, it was shown that ball milling of graphite in the presence of melamine [53] or *N,N*-dimethylformamide [46] (as protective agents), results in low GNP production yield (<1%) with small lateral size (lower than 80 nm). In a more recent study, the ball milling of graphite in the presence of pyrene produced much higher yield graphene sheets with larger lateral dimension of ~1 μm [54].

In this study, we explored the *role of the protecting agent structure* on designing the produced GNP, and the route from GNP production to hydrogen storage applications. We demonstrated high-yield (>90%), size-manipulated fabrication of GNP, established by the integration of various protective agents during graphite ball milling. We examined three types of aromatic protective agents differing in their intermolecular hydrogen bonding. The produced pristine GNP were then added to a magnesium powder and explored for their effect on hydrogen storage kinetics.

2. Experimental

2.1. Materials

Graphite flakes (CAS 7782-42-5) were purchased from Sigma-Aldrich. Commercial GNP were obtained from XG Sciences, USA (M5, H5, H25 and C500). Melamine (CAS 108-78-1), 4-hydroxybenzoic acid (**4HA**; CAS 99-96-7) and pyrene (CAS 129-00-0) were purchased from Alfa Aesar, UK. Magnesium was purchased from Dead Sea Magnesium Ltd, ASTM-9980A; 99.8 wt% purity. All materials were used as received.

2.2. GNP production

Graphite flakes (36 mg) were ground in a planetary ball mill (Planetary Micro Mill Pulverisette 7 premium line by Fritsch) at atmospheric conditions. The graphite flakes were placed in 20 ml zirconia grinding bowl, $d = 45$ mm, with various protective agents (melamine, 4HA and pyrene) in a fixed weight ratio (protective agent-to-graphite flakes ratio of 28:1). Ten balls (zirconia) of 10 mm in diameter were used, with a balls-to-powder weight ratio of 23. The milling procedure was carried out for various milling times and at different rotational speeds. The ground powder was washed with a suitable solvent (melamine-deionized water; 4HA-ethanol and pyrene-acetone) and filtered on a membrane (Sartorius, 0.2 μm pores) to *completely remove* the protective agent from the carbonaceous product, as confirmed by thermogravimetric analysis (temperature range of 40–400 °C [53]; Fig. S1, Supplementary Information).

The milling energy (E_{mill} , Eq. (1)) calculation convolutes the milling time and the rotational speed into a single parameter. The milling energy is derived from the kinetic energy of the balls at a given geometry of the milling instrument (Pulverisette 7), bowl ($d = 45$ mm) and balls ($\rho = 5700$ kg m^{-3}) [55,56]:

$$E_{\text{mill}} = \left(8.1 \cdot 10^{-6} \cdot \omega_p^3 \cdot t \right) / m_{\text{graphite}} \quad [\text{J/g graphite}] \quad (1)$$

where ω_p is the rotational speed (rpm); t is total milling time (min), and m_{graphite} is the weight of the graphite flakes.

2.3. GNP characterization

Thermogravimetric Analysis (TGA) of GNP powders was performed on a Mettler Toledo analyzer with a Star^c software system (TGA/STDA85). The analysis was carried out under an air flow of 50 ml/min. The samples (2–6 mg in 70 μl alumina crucibles) were

heated from 40 to 500 °C at a rate of 10 °C/min and from 500 °C to 1000 °C at 5 °C/min. To simplify the comparison between various protective agents, we extracted a single parameter from the TGA curves: $T_{1/2}$ [57], the combustion temperature at which half of the weight loss is reached (see definition in Fig. S1, Supplementary Information). The $T_{1/2}$ values are correlated to a specific milling energy (Eq. (1)), and are independent of specific rotational speed (rpm) value or milling time (Fig. S2, Supplementary Information).

The defect density of the obtained GNP was determined by Jobin-Yvon HR LabRam micro-Raman operated at 514 nm, laser spot diameter of 1 μm (NA 0.65, X50) on a quartz slide. The Raman spectrum is characterized by three major bands [58]: (i) the intensity of the D band (~ 1350 cm^{-1}) is due to first-order phonons and indicates the in-plane and edges defect density; (ii) the G band (~ 1580 cm^{-1}) relates to the zone center Raman allowed band; and (iii) the 2D band relates to the second-order phonons, and its shift indicates the relative GNP thickness [59].

Scanning Electron Microscopy (SEM) was used on a high-resolution cold FEG SEM (JSM-7400F, JEOL) operated in a secondary electron mode. Samples were prepared by placing the powder on a sticky carbon tape mounted on an aluminum disk.

Transmission Electron Microscopy (TEM): TEM- FEI Tecnai 12 G2 TWIN microscope was operated at 120 kV and under focus of a few micrometers to increase the phase contrast. Dry samples were prepared on holey carbon-coated copper grids (300 mesh, lacey carbon, Ted Pella) by placing a drop of an aqueous dispersion of sodium cholate (1 mg/ml) on a grid and allowing it to dry under ambient conditions. The images were recorded on a Gatan 794 CCD camera and analysed by Digital Micrograph 3.6 software.

Atomic Force Microscopy (AFM) was used to determine the thickness of the GNP on a Dimension 3100 SPM instrument in tapping mode using Veeco RTESP silicon tips. The GNP powder was sonicated in an aqueous solution of sodium cholate (1 mg/ml). A drop of the obtained dispersion was then placed on a SiO_2 wafer and dried by evaporation at 150 °C for 4 h before the measurement.

Specific Surface Area (SSA) measurements were conducted by N_2 adsorption at 77 K with an automated adsorption apparatus (BELSOPRP-max from BEL JAPAN). Prior to the measurement, all samples were degassed at 473 K under vacuum (10^{-2} kPa) for 2 h. The SSA was calculated by the BET method [60] based on adsorption data in the relative pressure (P/P_0) range of 0.05–0.3.

X-Ray Powder Diffraction (XRD) was used to determine the crystallinity of GNP and Mg before and after de/hydrating cycles with a Panalytical Empyrean Powder Diffractometer equipped with position sensitive detector X'Celerator. Data were collected in the $\theta/2\theta$ geometry using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54178$ Å) at 40 kV and 30 mA (at ambient condition). Scans were run during ~15 min in a 2θ range of 10–70° with step equal to ~0.033°.

X-ray photoelectron spectroscopy (XPS) was used to characterize the graphite impurities (Table S1 and Fig. S3, Supplementary information) and the structure of GNP post de/hydrating procedure (Fig. S6, Supplementary information). The data was obtained by X-ray photoelectron spectrometer, an ESCALAB 250 ultrahigh vacuum (10^{-9} bar) apparatus with an AlK α X-ray source and a monochromator, operated at ambient condition. Powder samples were pressed into an indium foil. The spectra were recorded with pass energies of 150 eV or 20 eV (high-energy resolution).

2.4. Hydrogen storage

Sieverts-type apparatus was used to measure the rates of hydrogen absorption (hydriding) and desorption (dehydriding) in Mg-GNP powder (5 wt% GNP), at a final pressure of 20 and 1.2 bar, respectively, and $T = 300$ °C. Freshly prepared rough Mg powder was milled in a planetary ball mill (Fritsch Pulverisette 7, hexane

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