

ESI:

Buckyball-, carbon nanotube-, graphite-, and Graphene-enhanced dehydrogenation of Lithium aluminum hydride

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Experimental details

LiAlH₄ (97%) powder was purchased from Alfa Aesar and used as-received. C₆₀ (Aldrich; 98%), single-walled CNTs (Nanostructured & Amorphous Materials; 99%), graphite (Nippon Shiyaku Kogyo; 99.9%), graphene (preparation described below), Pd (Strem Chemical; 99.9%; 50 μm), Y₂O₃ (Strem Chemical; 99.9%; 5 μm), and Cu (Strem Chemical; 99.5%; 30 μm) were used as the additives. A ball-milling machine (SPEX 8000D) was adopted to mix the additives and LiAlH₄; the ball-to-powder weight ratio was 10:1. All the chemicals are preserved and handled in an Ar-purified glove box (Innovation Technology Co.), where both the moisture content and oxygen content were maintained below 0.5 ppm. After being sealed in the glove box, the ball-milling vessel was moved to the milling machine. The milling time was 30 min.

Graphene nanosheets were prepared using a modified Staudenmaier method [L. Staudenmaier, *Berichte der Deutschen Chemischen Gesellschaft*, 1898, **31**, 1481.]. Natural graphite powder (Alfa Aesar; with a particle size of ~70 μm and a purity of 99.999%) was chemically oxidized to form graphite oxide (GO) at room temperature. The graphite (5 g) was continuously stirred in a mixed solution of sulfuric acid (100 mL), nitric acid (50 mL), and potassium chlorate (50 g) for approximately 100 h. The resulting GO was rinsed with 5 wt.% HCl aqueous solution and then repeatedly washed with deionized water until the pH of the filtrate became neutral. The product was dried in air and pulverized. Finally, the GO was exfoliated by rapid heating (~30 °C/min) to 1050 °C in an inert Ar atmosphere. After thermal reduction (held at 1050 °C for 30 min), graphene nanosheets were obtained.

A temperature-programmed desorption (TPD) analyzer was used to evaluate the hydrogen desorption properties of the samples. In each test, 100 mg of LiAlH₄ was

loaded into a quartz crucible. The analysis was conducted at an argon gas flow rate of 90 mL/min under ambient pressure. The temperature was programmed from room temperature to 550 °C with a heating rate of 2 °C/min. The gas thermal conductivity change, corresponding to hydrogen release, was recorded as a function of the temperature. Hydrogen desorption isotherms were also measured using the TPD analyzer at 100 °C to examine the kinetic performance. The total hydrogen release amount was calibrated using Mg₂NiH₄, which has a known hydrogen capacity of 3.6 wt.% (confirmed by a Sievert's measurement). Moreover, the gas composition was analyzed using an Agilent 5975 Series gas chromatograph/mass selective detector (GC/MSD) system.

The microstructures of the samples were examined using a scanning electron microscope (SEM, JOEL 7000-F) and a transmission electron microscope (TEM, FEI Tecnai F20). Raman spectrometer (UniRAM MicroRaman with a spectral resolution of 0.5 cm⁻¹) was employed to study the bonding structure of [AlH₄]⁻; the spectra were excited by a diode-pump solid-state laser with a wavelength of 532 nm. To explore the catalytic mechanism of graphene for LiAlH₄ dehydrogenation, in situ X-ray diffraction (XRD) analyses at various temperatures were performed on beamline 01C2 at the National Synchrotron Radiation Research Center in Hsinchu, Taiwan. The storage ring was operated with an electron energy of 1.5 GeV and a current of between 100 and 200 mA. The powder sample was mounted in a capillary, which was filled with inert Ar gas to prevent oxidation during heating.

Differential scanning calorimetry (DSC) analyses of the samples were carried out using a Mettler Toledo DSC. About 7 mg of powder was loaded into a copper crucible in the glove box. Subsequently, the crucible was placed in a sealed glass

bottle in order to minimize oxidation during transportation from the glove box to the DSC apparatus. An empty copper crucible was used for the reference. The samples were heated at various rates (6 °C/min, 9 °C/min, and 12 °C/min) to 300 °C under an argon flow rate of 100 mL/min.

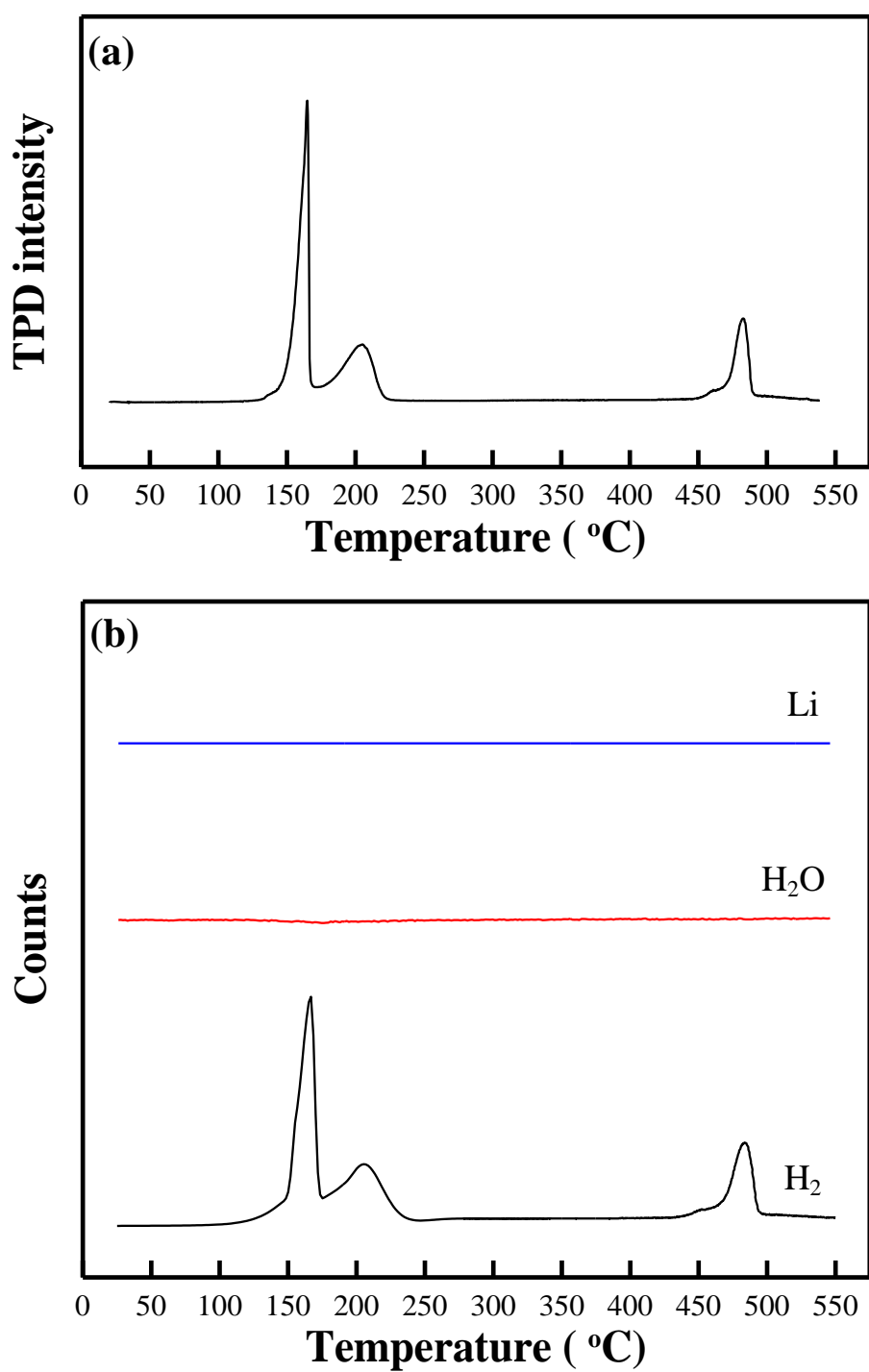


Figure S1. (a) Temperature-programmed desorption signals of ball-milled LiAlH₄. (b) H₂, H₂O, and Li released from ball-milled LiAlH₄ as a function of temperature.

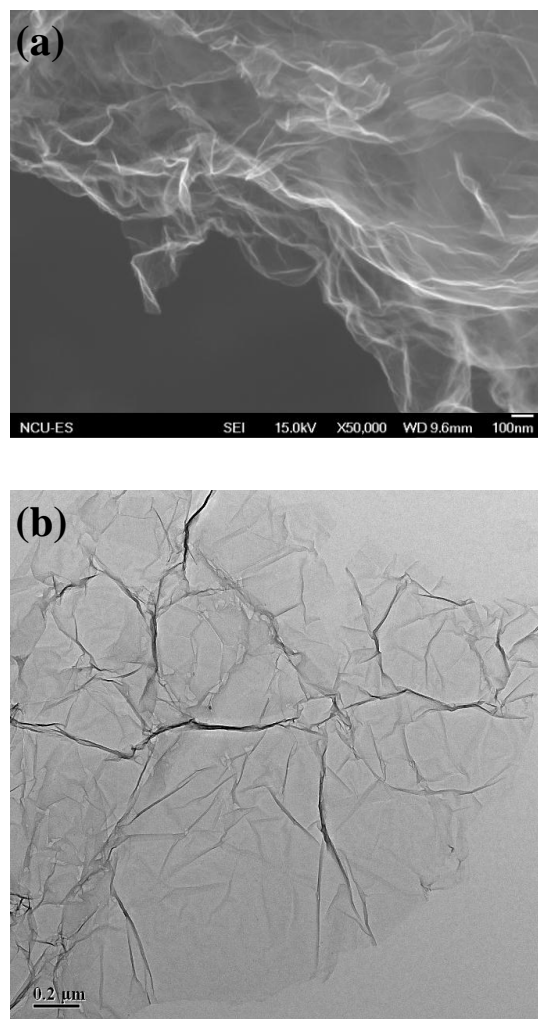


Figure S2. (a) SEM and (b) TEM images of graphene nanosheets synthesized in this study.

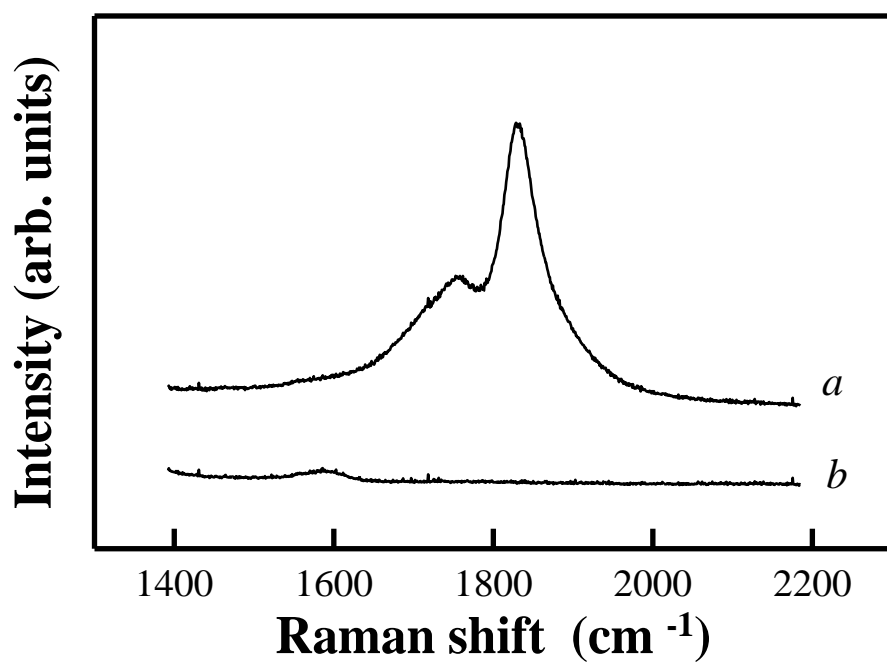


Figure S3. Raman spectra of LiAlH₄ ball-milled without (curve *a*) and with 10 wt.% of graphene (curve *b*).

(Discussion: The signals of Al–H stretching modes (at 1754 and 1829 cm⁻¹) were disappeared when graphene was incorporated, suggesting that the Al–H bonds were distorted [R. S. Chellappa, D. Chandra, S. A. Gramsch, R. J. Hemley, J. F. Lin and Y. Song, *J. Phys. Chem. B*, 2006, **110**, 11088.])

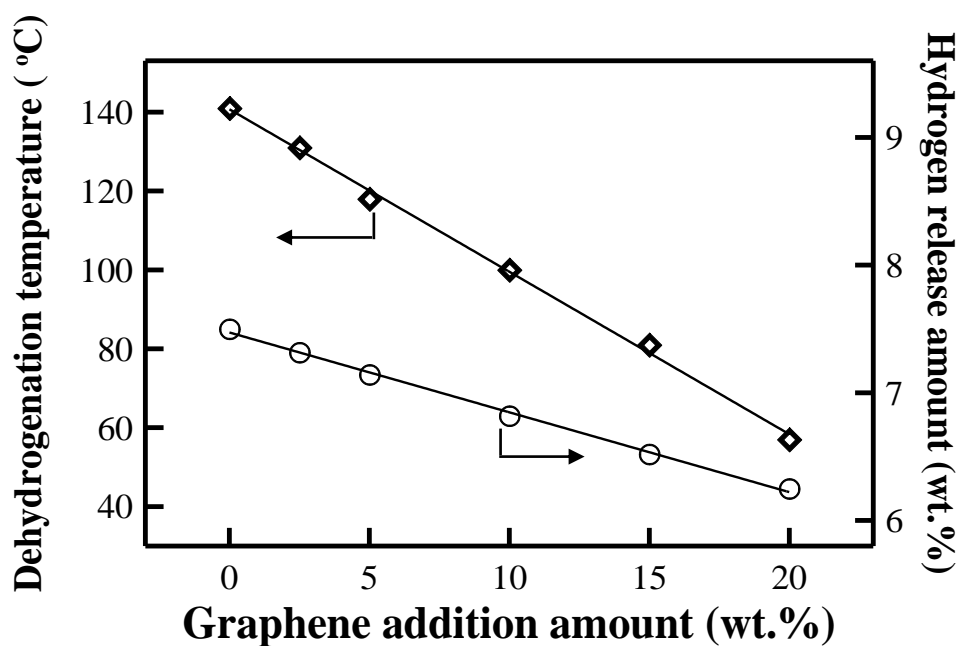


Figure S4. The initial dehydrogenation temperature and the specific hydrogen release capacity (including the first two dehydrogenations and based on the total weight of the composite) as a function of the graphene addition amount in the LiAlH_4 /graphene composites.

(Discussion: While a low dehydrogenation temperature can be achieved by increasing the graphene addition amount, the loss in specific hydrogen release capacity should be considered (because graphene does not release hydrogen).)

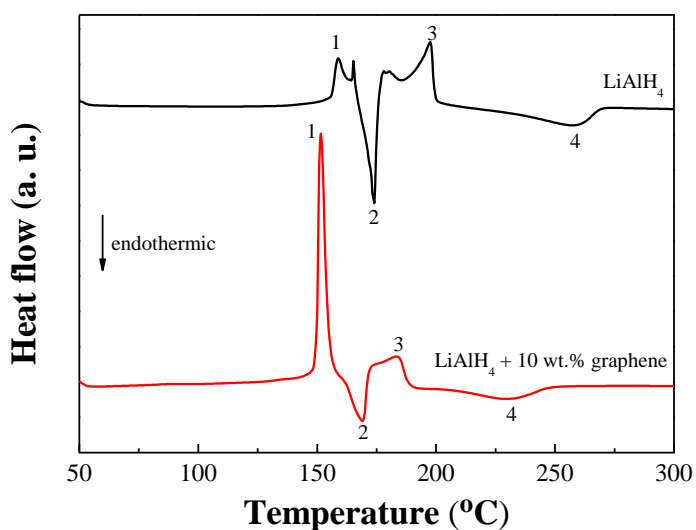


Figure S5. DSC profiles of LiAlH₄ ball-milled without and with 10 wt.% of graphene recorded at a heating rate of 12 °C/min. Peak 1: the interaction between LiAlH₄ and surface hydroxyl impurities. Peak 2: the melting of LiAlH₄. Peak 3: the first dehydrogenation step. Peak 4: the second dehydrogenation step. [M. McCarty, J. N. Maycock, V. R. P. Verneker, *J. Phys. Chem.*, 1968, **72**, 4009.; J. A. Dilts, E. C. Ashby, *Inorg. Chem.*, 1972, **11**, 1230.]

(Discussion: According to the DSC integrated peak area, both the reaction enthalpies for the first and second dehydrogenation are reduced due to the graphene incorporation, indicating that the presence of graphene is likely to destabilize LiAlH₄. However, the highly active LiAlH₄ would partially oxidize before and during the DSC measurement (which is difficult to be overcome in our current apparatus), the precise values of the dehydrogenation enthalpies should be further confirmed.)

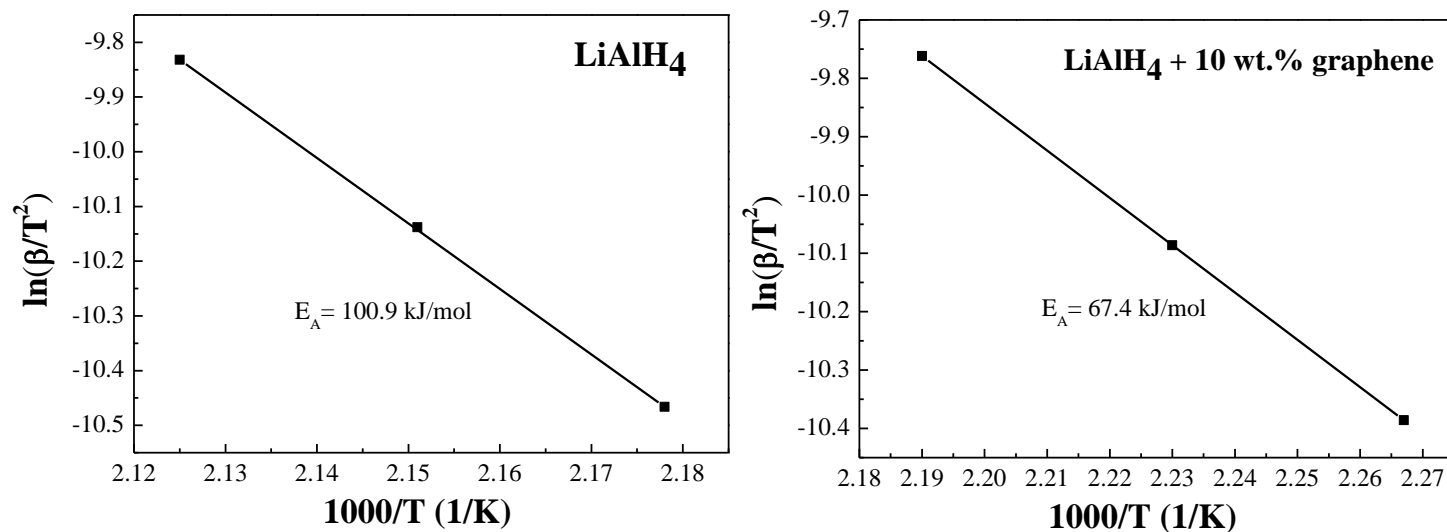


Figure S6. Kissinger plots [H. E. Kissinger, *Anal. Chem.*, 1957, **29**, 1702.] of LiAlH₄ ball-milled without and with 10 wt.% of graphene (β : DSC heating rate; T: DSC Peak 3 dehydrogenation temperature; E_A : activation energy for the first dehydrogenation reaction).

(Discussion: The results confirm that E_A for the first dehydrogenation reaction significantly decreases from 100.9 kJ/mol to 67.4 kJ/mol due to the graphene incorporation.)