NiCo nanoalloy encapsulated in graphene layers for improving hydrogen storage properties of LiAlH₄

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NiCo nanoalloy (4–6 nm) encapsulated in graphene layers (NiCo@G) has been prepared by thermolysis of a 3D bimetallic complex CoCo[Ni(EDTA)]₂·4H₂O and successfully employed as a catalyst to improve the dehydrogenation performances of LiAlH₄ by solid ball-milling. NiCo@G presents a superior catalytic effect on the dehydrogenation of LiAlH₄. For LiAlH₄ doped with 1 wt% NiCo@G (LiAlH₄-1 wt% NiCo@G), the onset dehydrogenation temperature of LiAlH₄ is as low as 43 °C, which is 109 °C lower than that of pristine LiAlH₄. 7.3 wt% of hydrogen can be released from LiAlH₄-1 wt% NiCo@G at 150 °C within 60 min. The activation energies of LiAlH₄ dehydrogenation are extremely reduced by 1 wt% NiCo@G doping.

Hydrogen storage is one of the most critical issues for fuel cell vehicular applications. Solid hydrogen storage materials such as carbon materials, MOFs, metal hydrides and complex hydrides have received significant attention as the safest and most effective storage media. Among them, lithium alanate (LiAlH₄) is considered as one of the most promising hydrogen storage materials due to its high hydrogen storage capacity of 10.5 wt%. In the last two decades, LiAlH₄ has received particular attention aiming at reducing the operation temperature to meet the DOE criteria because it can release a total amount of 7.9 wt% of hydrogen in two steps (eqs 1 and 2) below a relatively low temperature, e.g. 220 °C.

\[
\begin{align*}
3\text{LiAlH}_4 & \rightarrow \text{Li}_3\text{AlH}_6 + 2\text{Al} + 3\text{H}_2 (5.3 \text{ wt% } \text{H}_2, \quad 150–175 \degree \text{C}) \\
\text{Li}_3\text{AlH}_6 & \rightarrow 3\text{LiH} + \text{Al} + 3/2\text{H}_2 (2.6 \text{ wt% } \text{H}_2, \quad 180–220 \degree \text{C})
\end{align*}
\] (1) (2)

Different methods have been explored for decrease of the dehydrogenation temperature of LiAlH₄, including particle size reduction by ball milling, synthesis of multi-hydride composites, and doping with catalysts. Among these methods, doping with catalysts is considered as an effective approach for the dehydrogenation of LiAlH₄. Various catalysts have been investigated, such as Ti, Fe, Ni, V, Al, Al₃Ti, TiF₃, TiCl₃, NiCl₂, VCl₃, AlCl₃, FeCl₃, TiCl₃·1/3AlCl₃, TiH₂, NiFe₂O₄, carbon nanotube and so on. Ni based catalysts have been widely explored. Zheng et al. doped LiAlH₄ with Ni to reduce the temperature of the first dehydrogenation step by approximately 10–15 °C, with a great expense of the hydrogen storage capacity. Yuan et al. prepared 2 mol% NiCo₃O₄ nanorod doped LiAlH₄, which can release 6.47 wt% of hydrogen at 150 °C within 150 min. Nevertheless, most of the systems present the disadvantage of loss of the overall hydrogen storage capacity, due to either a hydrogen release during the ball milling process or the large additional weight of the catalysts. Thus, it is desirable to develop an effective catalyst for the dehydrogenation of LiAlH₄.

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Recently, metal/carbon composites has been developed for the dehydrogenation of LiAlH₄, including Co-decorated MWCNTs, Co@C, and Ni-containing mesoporous carbon scaffold (Ni-MCS). In the last two decades, bimetallic nanoparticles have received great interest for catalysis and electrocatalysis, due to their higher activity and selectivity than monometallic nanoparticles as a result of "synergistic effects". In addition, graphene more effectively improves the dehydrogenation behavior of LiAlH₄ than C₆₀, carbon nanotubes, and graphite. In this study, we used NiCo nano alloy encapsulated in graphene layers (NiCo@G) as a catalyst and investigated the effects of NiCo@G on the dehydrogenation behavior of LiAlH₄. Preliminary results showed that excellent dehydrogenation properties of LiAlH₄ were achieved by 1 wt% NiCo@G doping.

Results and Discussion
Preparation and characterization of NiCo@G. Briefly, a 3D bimetallic complex CoCo[Ni(EDTA)]·4H₂O, a precursor for NiCo@G, was firstly synthesized through solvothermal method. CoCo[Ni(EDTA)]·4H₂O precursor was thermally decomposed to NiCo@G as the final product at 500 °C in an argon flow. The Powder X-ray diffraction peaks (Fig. 1a) of the as-synthesized precursor CoCo[Ni(EDTA)]·4H₂O match well with the simulated pattern on the basis of the single crystal structure reported by Sapiña et al. (Supplementary Fig. S1). The Ni/Co molar ratio in NiCo@G is 1:1 as that in the precursor complex, which is confirmed by SEM-EDS data (Supplementary Fig. S2). As shown in Fig. 1b, the XRD pattern of NiCo@G shows peaks at 2θ = 44.48, 51.69 and 76.25°, matching those reported for (111), (200) and (220) planes of Ni₅₀Co₅₀ alloy with a fcc structure. Their positions are slightly higher than those of pure fcc Co (44.22, 51.52 and 75.86°) and slightly lower than those of pure fcc Ni (44.51, 51.85 and 76.37°). Broadness of the characteristic diffraction peaks for NiCo alloy is due to the formation of nanosized NiCo particles. Furthermore, the characteristic reflections corresponding to hexagonal close packed (hcp) metallic Co can not be observed. The broad peak around 2θ = 26° is the characteristic reflection for carbon. X-ray photoelectron spectroscopy (XPS) was used to examine the species present in the particles. The spectra of Ni 2p and Co 2p energy ranges were recorded (Supplementary Fig. S3). The positions of the 2p peaks are respectively 852.8 and 870.1 eV for Ni 2p, 778.3 and 793.3 eV for Co 2p, demonstrating Ni and Co in their zero-valent states. TEM images are shown in Fig. 1c,d, indicating that the NiCo nanoalloy is encapsulated in multilayered graphene shells (NiCo@G). The NiCo nanoalloy are spherical in shape, with a highly...
uniform size distribution ranging from 4 nm to 6 nm. In addition, the STEM corresponding element mapping (Supplementary Fig. S4) of NiCo@G confirms a homogeneous distribution of NiCo alloy over the sample.

**Dehydrogenation performances.** Figure 2a shows the non-isothermal dehydrogenation performances of as-received LiAlH$_4$, as-milled LiAlH$_4$, and LiAlH$_4$ doped with 1 wt%, 5 wt% and 10 wt% NiCo@G. Compared to as-received LiAlH$_4$, as-milled LiAlH$_4$ exhibits a similar dehydrogenation behavior. The as-received LiAlH$_4$ starts to decompose at 152 °C, while the as-milled LiAlH$_4$ exhibits a slight decrease of 4 °C. It is obvious that addition of NiCo@G extremely improves the onset dehydrogenation temperature of LiAlH$_4$. The onset dehydrogenation temperature and the amount of hydrogen released of all samples are shown in Fig. 2b. The onset desorption temperature decreases with the increasing NiCo@G percent. LiAlH$_4$-1 wt% NiCo@G starts to decompose at 43 °C, which is 109 °C lower than as-received LiAlH$_4$. For 5 wt% and 10 wt% NiCo@G doped samples, the onset dehydrogenation temperature is as low as 36 °C, which is 116 °C lower than as-received LiAlH$_4$. However, raising the NiCo@G percent results in a decrease of the amount of hydrogen released. Only 5.9 wt% and 3.7 wt% of hydrogen are respectively released for LiAlH$_4$-5 wt% NiCo@G and LiAlH$_4$-10 wt% NiCo@G, due to the increasing catalyst percent and the premature dehydrogenation during the ball milling process. It is noteworthy that the amount of hydrogen released for LiAlH$_4$-1 wt% NiCo@G reaches up to 7.3 wt%, which is identical to that of as-milled LiAlH$_4$. This phenomenon is attributed to the small NiCo@G percent and a good preservation of hydrogen during the ball milling process. Compared with the performance of other additives or catalysts, NiCo@G developed in this work exhibits high catalytic activity (Table S1†). For graphene, Hsu$^{29}$ and Jiang$^{36}$ suggested that the interaction between electronegative carbon and Li$^+$, high electronic conductivity promoting electron exchange between metal and [AlH$_4$]$^-$, and delocalized π bonds facilitates hydrogen release. Furthermore, in NiCo@G, graphene is the shell preventing NiCo nanoparticles aggregation, leading to NiCo nanoalloy with a uniform size distribution ranging from 4 to 6 nm. The beneficial effect of catalyst size on dehydrogenation behaviors has been confirmed in previous literatures.

Figure 3 shows the isothermal dehydrogenation kinetics measurements of as-milled LiAlH$_4$ and LiAlH$_4$-1 wt% NiCo@G at 150 °C. For as-milled LiAlH$_4$, only 1.6 wt% of hydrogen releases within 10 min. However, for LiAlH$_4$-1 wt% NiCo@G, the dehydrogenation goes on rapidly with 5.8 wt% of hydrogen released within 10 min. Furthermore, total 7.3 wt% of hydrogen can be thoroughly released within 60 min for LiAlH$_4$-1 wt% NiCo@G while 350 min for as-milled LiAlH$_4$. This result confirms that dehydrogenation kinetics are significantly improved by addition of NiCo@G.

**Dehydrogenation mechanism.** To obtain insight on the catalytic mechanism of NiCo@G for the LiAlH$_4$ dehydrogenation, morphologies and intergrain dispersion of both as-milled LiAlH$_4$ and LiAlH$_4$-1 wt% NiCo@G are investigated by SEM, as shown in Fig. 4. Compared to as-milled LiAlH$_4$, the particle size significantly
decreases after doping with 1 wt% NiCo@G, leading to more grain boundaries and larger surface area. This important observation suggests that NiCo@G readily influences the LiAlH4 texture at room temperature during the ball milling process, by preliminarily breaking their particle aggregation. Graphene has been confirmed as an effective grinding agent to reduce the crystal size of LiAlH4 owing to its high mechanical strength29,36. At that stage it is not yet clear whether the consequent decrease of the dehydrogenation temperature is due to the smaller LiAlH4 particles generated after ball milling or to another effect of the catalyst on the mechanism governing this decomposition. The strong catalytic effect of such a small percent of NiCo@G was further investigated by combining XRD and DSC.

Figure 5 shows the XRD patterns of NiCo@G, as-received LiAlH4, as-milled LiAlH4 and LiAlH4-1 wt% NiCo@G. The diffraction peaks of as-milled LiAlH4 match well with those of the as-received LiAlH4, demonstrating a high stability of LiAlH4 during the ball milling process. NiCo@G can not be distinguished in LiAlH4-1 wt% NiCo@G, due to the exceptionally small concentration (1 wt%) of NiCo@G. The weak peaks of Li3AlH6 (2θ~21.9°, 31.6°) and Al (111) (2θ~38.4°) appear in LiAlH4-1 wt% NiCo@G sample, indicating partial dehydrogenation of LiAlH4 during ball milling process (R1), in agreement with the small hydrogen capacity loss observed in the TGA visualization of the dehydrogenation process (Fig. 2). Furthermore, the diffraction peaks of LiAlH4 in the 1 wt% NiCo@G doped sample become broader than those of as-milled LiAlH4, indicating smaller particle size of LiAlH4.

DSC measurements were conducted to further verify the effect of NiCo@G on the dehydrogenation of LiAlH4, as shown in Fig. 6a. Compared to as-received LiAlH4, as-milled LiAlH4 presents a similar DSC profile including the melting peak of LiAlH4, indicating that the ball milling process does not alter its intrinsic properties. Surprisingly, the DSC profile of LiAlH4-1 wt% NiCo@G is totally different and shows three distinct endothermic peaks. In order to understand the phase changes at different stages of LiAlH4-1 wt% NiCo@G, we stopped the dehydrogenation of LiAlH4-1 wt% at temperatures (110 °C, 170 °C and 210 °C ) corresponding to three dehydrogenation stages in DSC profile and investigated the samples by XRD. As shown in Fig. 6b, Li3AlH6, Al and small amount of retained LiAlH4 are present in the sample which was stopped dehydrogenation at 110 °C. Thus, the first endo peak in the DSC profile of LiAlH4-1 wt% NiCo@G is attributed to the decomposition of solid LiAlH4 (eqn.1). This decomposition (eqn. 1) apparently ends around 110 °C, which explains the absence of any LiAlH4 melting. For the sample heated up to 170 °C corresponding to the second stage, Al, LiH, small amount of Li3AlH6,

Figure 3. Isothermal dehydrogenation curves of as-milled LiAlH4 and LiAlH4-1 wt% NiCo@G at 150 °C.

Figure 4. SEM images of: (a) as-milled LiAlH4, (b) LiAlH4-1 wt% NiCo@G.
and LiOH are observed. Al, LiH and small amount of LiOH are present in the sample decomposed at 210 °C. So we can declare that the second and third peaks are attributed to the decomposition of solid Li₃AlH₆ (eqn. 2).

**Activation energies.** To understand the dehydrogenation kinetics, the apparent activation energy ($E_a$) at each stage of LiAlH₄-1 wt% NiCo@G dehydrogenation was calculated using the Kissinger equation (eqn. 3), considering the three endothermic peaks in DSC profiles at heating rates of 2, 5, 10 and 20 °C min⁻¹, as shown in Fig. 7.

\[
\ln \left( \frac{\beta}{T_p^2} \right) = \ln (AR/E_a) - E_a/RT_p
\]

where $\beta$ is the heating rate, $T_p$ (K) is the DSC peak temperature, A is the pre-exponential factor, and R is the gas constant. $E_a$ for each dehydrogenation stage of LiAlH₄-1 wt% NiCo@G, was evaluated to be 54.8 ± 6 kJ mol⁻¹, 80.1 ± 1.3 kJ mol⁻¹ and 119.7 ± 2.8 kJ mol⁻¹ respectively. The activation energy $E_a$ for R1 involved in the catalytic dehydrogenation of LiAlH₄ is comparable to the lowest values of those reported catalysts.

Regarding the superior efficiency of NiCo@G, many factors obviously play a role. Such efficiency can either be attributed to the support (carbon)²⁹ or to a combination of properties associated with two different nanosized metals³⁷,³⁸ or to both¹⁹,³⁹,⁴⁰. The mechanism need further investigations for the particular NiCo bimetallic nanoparticles encapsulated in graphene used here.

As a summary, NiCo nanoalloy (4–6 nm) encapsulated in graphene layers (NiCo@G) was prepared and introduced into LiAlH₄ by solid-state ball milling. A tremendous improvement in the dehydrogenation properties of LiAlH₄ was achieved. When 1 wt% NiCo@G was doped with LiAlH₄, the onset dehydrogenation temperature is decreased to 43 °C with 7.3 wt% of hydrogen released below 200 °C. For LiAlH₄ doped with 10 wt% NiCo@G, the onset dehydrogenation temperature is as low as 36 °C, which is 116 °C lower than that of pristine LiAlH₄. $E_a$ of LiAlH₄-1 wt% NiCo@G for the first dehydrogenation step decreased to 54.8 kJ mol⁻¹. The significant catalytic effect makes NiCo@G a promising candidate for LiAlH₄ dehydrogenation. A more in depth study of the effect of NiCo@G on LiAlH₄ dehydrogenation, in particular regarding the critical roles of Ni/Co and catalyst/LiAlH₄ ratios, is in process.

**Figure 5.** XRD patterns of NiCo@G, as-received LiAlH₄, as-milled LiAlH₄ and LiAlH₄-1 wt% NiCo@G.

**Figure 6.** (a) DSC profiles of dehydrogenation of as-received LiAlH₄, as-milled LiAlH₄ and LiAlH₄-1 wt% NiCo@G at heating rate of 2 °C min⁻¹; (b) XRD patterns of LiAlH₄-1 wt% NiCo@G heated up to different temperatures (110 °C, 170 °C and 210 °C) corresponding to the DSC profile.
Methods

Chemicals. All reagents and chemicals were commercially available and of analytical grade without further purification prior to use, unless specifically stated elsewhere.

Preparation of NiCo@G. The precursor complex CoCo[Ni(EDTA)]·4H2O was synthesized by solvo-thermal method as reported previously30. Pyrolysis of CoCo[Ni(EDTA)]·4H2O was performed under an argon (99.999%) flow at 500 °C for 3 h. The final sample was denoted as NiCo@G.

Preparation of LiAlH4-NiCo@G samples. LiAlH4 (97%) was purchased from Alfa Aesar, and used without further purification. Typically, 0.5 g powder mixture composed of LiAlH4 and NiCo@G was loaded into a stainless milling pot with 10 steel balls (10 mm in diameter). Ball milling was carried out on a QM-1SP2 planetary under an argon atmosphere at 300 rpm for 30 min. All sample handlings were performed in a glove box filled with argon to avoid oxidation and moisture.

Characterizations. Powder X-ray diffraction (XRD) measurements were conducted on a PANalytical X’pert diffractometer operated at 40 kV and 40 mA with a Cu Kα radiation (λ = 1.5418 nm). The samples were covered by Mylar film in glove box to avoid oxidation and moisture. Scanning electron microscopy (SEM) images were obtained by using JSM-6360LV SEM (JEOL, Japan). Transmission electron microscopy (TEM) studies were performed on a FEI Tecnai F30 microscope and a G² microscope operated at 300 kV. The powders were dropped on an ultrathin carbon film supported on a copper grid by using ethanol as a dispersant. X-ray photoelectron spectroscopy (XPS) was recorded using a Thermo ESCALAB 250Xi instrument with Al Kα X-rays (1486.6 eV). Thermogravimetric analysis (TGA) was carried out on a Cahn Thermax 500 with a heating rate of 2 °C min⁻¹ in an argon flow. The isothermal dehydrogenation kinetics were measured using a Sieverts-type apparatus (Advanced Materials Corporation, USA) at 150 °C under an initial pressure of 10⁻⁵ MPa. Differential scanning calorimetry (DSC) data was collected from a TA Q1000 in a constant argon flow (50 mL min⁻¹) at different heating rates (2 K min⁻¹, 5 K min⁻¹, 10 K min⁻¹, 20 K min⁻¹).

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Author Contributions
L.X.S. directed the project and designed the experimental scheme. C.L.J. performed experiments and wrote the paper. F.X. revised the manuscript. S.S.L. analyzed the dehydrogenation mechanism. J.Z. analyzed the dehydrogenation performances. X.J. analyzed the activation energies. L.N.Y. helped with the experiment.

Additional Information
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