Facile self-assembly of light metal borohydrides with controllable nanostructures

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MATERIALS AND METHODS

Materials. HPLC grade tetrahydrofuran (THF) was purchased from Aladdin Reagents (Shanghai) and distilled over drying agents before use. Lithium borohydride (LiBH4, 95%), sodium borohydride (NaBH4, 96%) and calcium borohydride (Ca(BH4)2, 95%) were purchased from Sigma Aldrich and used without purification. Poly(methyl methacrylate) (PMMA, MW120,000) was purchased from Alfa Aesar.

Synthesis of Borohydride NPs. PMMA-capped borohydrides NPs were synthesized via an EISA method. All sample procedures were carried out in an Ar-filled glovebox equipped with a circulative purification system. In a typical synthesis procedure, borohydrides and PMMA were individually dissolved in THF with stirring vigorously until
the solution became transparency. Then 10 ml of the borohydrides/THF solution was added dropwise to a solution of PMMA (100 mg) in 10 ml of THF and stirred vigorously for 2 h to obtain a homogeneous solution. Finally, the solutions were maintained at ambient conditions for self-assembly and were dried upon self-evaporation of THF with a velocity of about $1.34 \times 10^{-4}$ g/s (the evaporation area of 12.56 cm$^2$).

**Synthesis of Size-altered LiBH$_4$ NPs via Changing the Concentration.** Varying amounts of LiBH$_4$ solution in 10 ml of THF were added (ranging from 1 mmol to 5 mmol). Then the LiBH$_4}$/THF solution was added dropwise over a period of 20 minutes into a solution of PMMA (100 mg) in 10 ml of THF, stirred vigorously for 2 h and maintained at ambient conditions for self-assembly which was induced by the self-evaporation of THF.

**Characterization.** To reveal the phase components and structure, XRD was carried out on a Rigaku D/max 2400 with Cu Ka radiation at 50 kV and 30 mA. FTIR spectroscopy was carried out to examine chemical bond variations on a PerkinElmer FTIR 1710 spectrometer. To examine the microstructural and elemental composition, TEM observations were carried out on a JEOL JEM-2100F which was equipped with an EDX spectrometer For TEM measurements, samples were prepared by placing a drop of solution on a porous carbon film supported on a copper grid which allowed the solvent to evaporate in an Ar atmosphere. The evolved hydrogen gas process was analyzed using a Netzsch STA 409 PC analyzer equipped with a QMS 403C mass spectrometer at a ramping rate of 10 ºC/min under a flowing Ar (99.999% purity) atmosphere. A stability test was performed by exposing the samples to the atmosphere with 60% relative humidity, and the photographic changes and weight increase were examined using a CANON camera and an electronic balance, respectively.
Fig. S1. A plausible mechanism for the formation of dispersed borohydride NPs capped by PMMA. (I) Both borohydride and PMMA dissolve in volatile THF to form a homogeneous solution; (II) upon self-evaporation of THF, the supersaturated borohydride recrystallizes into small clusters along with in-situ adsorption and precipitation of PMMA; (III) the borohydride clusters tend to aggregate and grow along with continued precipitation and self-assembly; (IV) with the completion of evaporation and phase separation, the precipitated PMMA converts to a polymer matrix in which facilitates the embedding of borohydride NPs.
Fig. S2. Photographs and the relative weight increase of bulk LiBH$_4$ and PMMA-capped LiBH$_4$ NPs that were set on a copper surface during atmospheric exposure with 60% relative humidity.

Fig. S3. (a, b) TEM images, (c) elemental EDX spectroscopy analysis and (d) SAED patterns for polygon NaBH$_4$ NPs.
Fig. S4. FTIR spectra for polygon NaBH₄ NPs and bulk NaBH₄.

Fig. S5. (a, b) TEM images and (c) elemental EDX spectroscopy analysis for hollow Ca(BH₄)₂ NPs.

Fig. S6. FTIR spectra for hollow Ca(BH₄)₂ NPs and bulk Ca(BH₄)₂.