Synthesis of core-shell $NaBH_4$@M (M = Co, Cu, Fe, Ni, Sn) nanoparticles leading to varied morphologies and hydrogen properties

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EXPERIMENTAL DETAILS

All operations were carried out under inert atmosphere in an Argon-filled LC-Technology glove box (< 1 ppm O_2 and H_2O).

Preparation of materials. $NaBH_4$, $NiCl_2$ (anhydrous), tetra-n-butylammonium bromide (TBAB), and dry solvents were purchased from Sigma-Aldrich and used as received. $FeCl_3$ (anhydrous) was purchased from Ajax Finechem and used as received. $CoCl_2$ (blue) and $CuCl_2$ (brown) were obtained from $CoCl_2.6H_2O$ (magenta) and $CuCl_2.2H_2O$ (cyan) from Ajax Finechem by heating for several hours under vacuum at 100 °C. $SnCl_2$ was obtained from $SnCl_2.2H_2O$ by reaction with acetic anhydride.

Synthesis of $NaBH_4$ nanoparticles. Nanoparticles of $NaBH_4$ were prepared by antisolvent precipitation. A saturated solution of $NaBH_4$ was prepared by dissolving 500 mg of $NaBH_4$ in 10 mL dry diglyme at 50 °C. 0.5 g of TBAB was added to enhance solubility and act as a stabilizing agent. The solution of borohydride was then filtered to remove any undissolved compound and added dropwise to a 50 mL solution of dry pentane kept at 5 °C under fast magnetic stirring. The resulting precipitate was separated by centrifugation, washed in tetrahydrofuran (THF) and dried under vacuum at room temperature leading to nanoparticles of $NaBH_4$ stabilized by TBAB at a concentration of 22 mass % as observed by TGA.

Synthesis of the core shell particles. 100 mg of as-synthesised $NaBH_4$ nanoparticles were suspended in 5 mL of THF. The desired concentration of anhydrous cobalt (II) chloride, copper (II) chloride, iron (III) chloride, nickel (II) chloride, or tin (II) chloride was suspended in 5 mL of THF and added dropwise to the suspension of nanoparticles. The suspensions slowly changed colour and were allowed to age overnight before separation by centrifugation, washing three times with THF and drying under vacuum at room temperature.

Material	**Concentration (mol L^{-1})**	**Mass of salt used (mg)**	**Colour changes**
$NaBH_4$@Co	0.02	26	Pink – purple – black
	0.04	52	
	0.06	78	
$NaBH_4$@Cu	0.02	26	White – red/black
	0.04	54	
	0.06	80	
$NaBH_4$@Fe	0.02	22	Yellow – beige – black
	0.03	43	
	0.04	65	
$NaBH_4$@Ni	0.02	25	Yellow/orange – grey – black
	0.04	50	
	0.06	75	
$NaBH_4$@Sn	0.02	38	Orange – grey
	0.04	76	
	0.06	114	

Characterization. The size, morphology and EDS analysis and elemental mapping of the particles were characterized by Transmission Electron Microscopy (TEM) using a Philips CM200 operated at 200 keV. TEM samples were dispersed in THF, sonicated for a few seconds and then dropped onto a carbon coated copper grid. Similarly samples pre-heated to 300 °C and 600 °C were dispersed in THF and dropped onto a carbon coated grid. Exposure to air was limited to transfer between an Ar filled sample tube containing the materials to the instruments.

The crystalline nature of the materials synthesized was determined by X-Ray Diffraction (XRD) using a Philips X'pert Multipurpose XRD system operated at 40 mA and 45 kV with a monochromated Cu Kα radiation (λ = 1.541 Å) - step size = 0.01, 0.02 or 0.05, time per step = 10 or 20 s/step. The materials were protected against oxidation from air by a Kapton foil.

Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetry (DSC) in conjunction with Mass Spectrometry (MS) were conducted at 10 °C.min^{-1} under an Argon flow of 25 mL.min^{-1} using a Mettler Toledo TGA/DSC 1 coupled with an Omnistar MS. Masses between m/e =2 and 100 were followed.

Hydrogen desorption kinetics were characterised with a high pressure magnetic balance of 1 μg resolution equipped with capability for simultaneous density measurements (Rubotherm). The material was first cycled once at 150 and 250 °C to allow a gradual dehydrogenation of the core-shells before cycling at 350 °C. 30 mg of material was used and a hydrogen pressure of 4 MPa for absorption and 0.01MPa for desorption. Hydrogen uptake and release were determined from the weight changes. For an accurate determination of the amount of hydrogen stored, a blank measurement with the empty sample holder was performed at 350 °C to determine the mass and volume of the sample holder. Further measurements were performed at 350 °C under a He atmosphere with the material fully desorbed to determine the density of the materials and corresponding parameters for buoyancy corrections.

SUPPLEMENTARY FIGURES

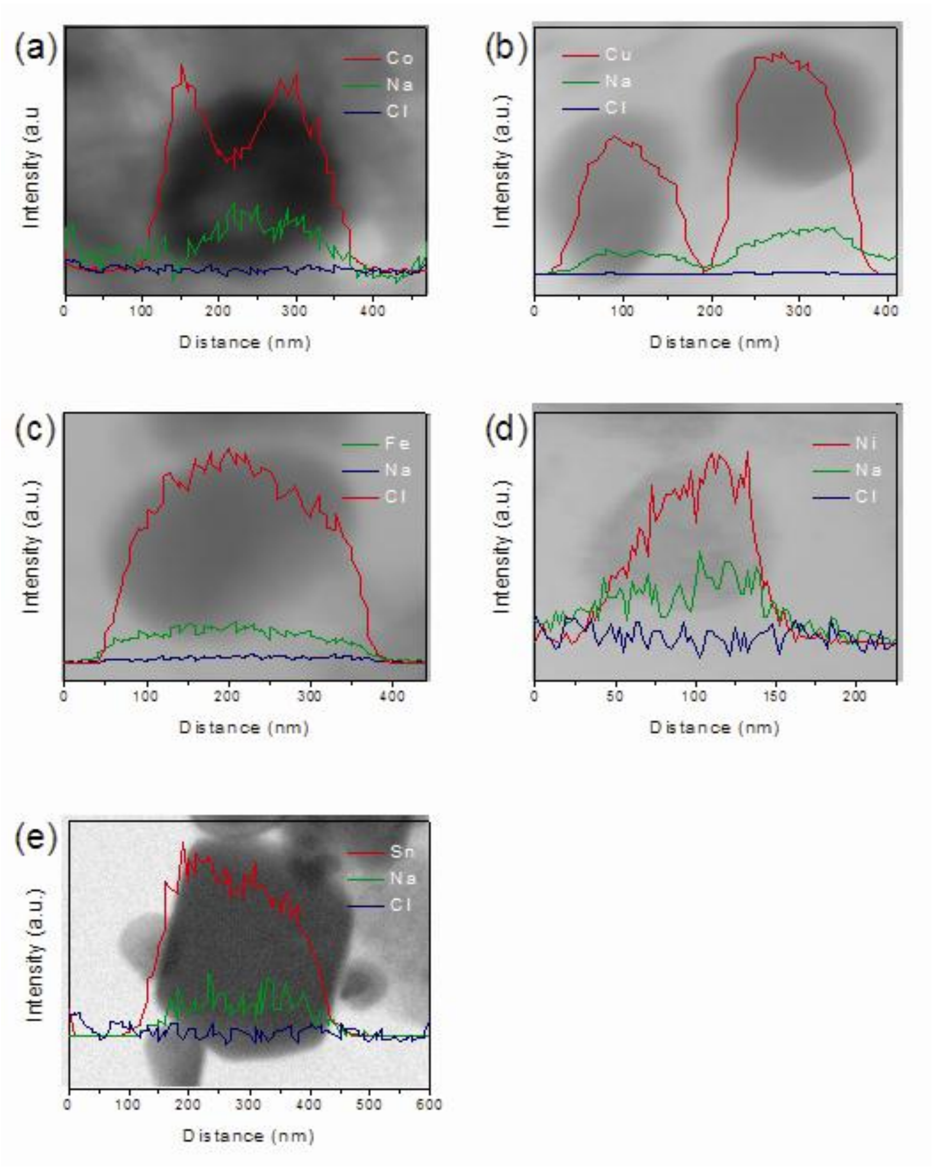

Fig. S1 Typical linescan analyses of (a) $NaBH_4$@Co, (b) $NaBH_4$@Cu, (c) $NaBH_4$@Fe, (d) $NaBH_4$@Ni, and (e) $NaBH_4$@Sn. No Cl was detected over any of the individual core-shell nanoparticles.

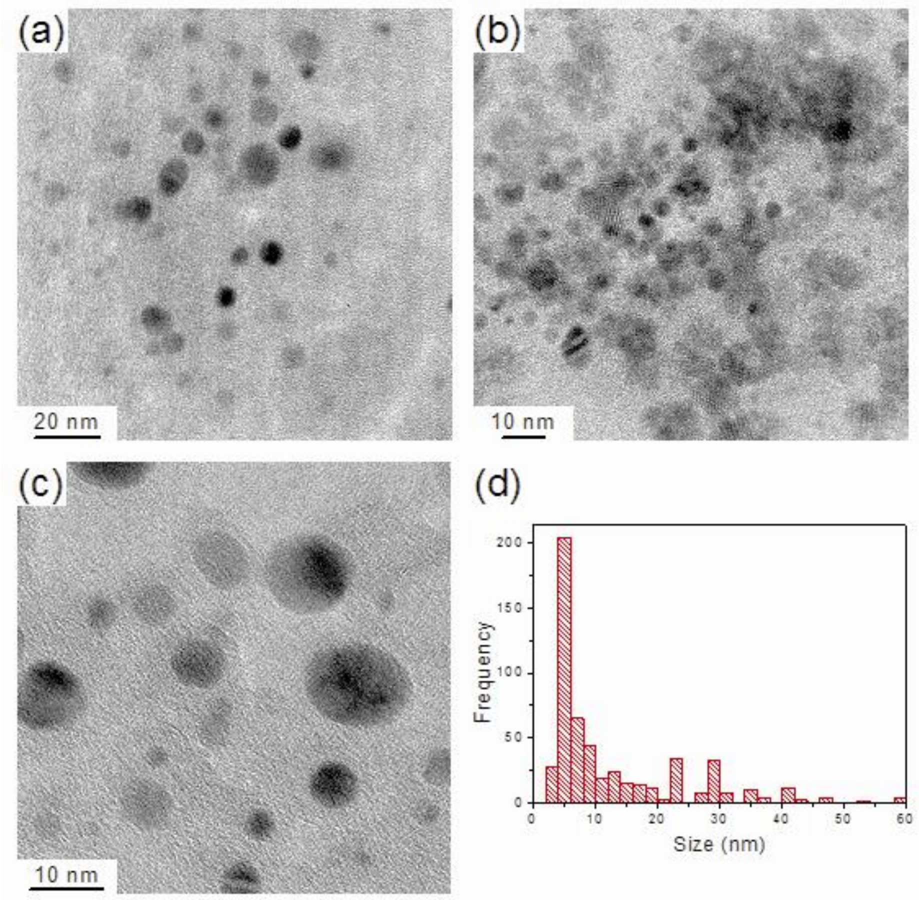

Fig. S2 (a)-(c) Typical TEM images of $NaBH_4$ nanoparticles before metal coating, and (d) typical size distribution as observed across the range of samples analysed by TEM.

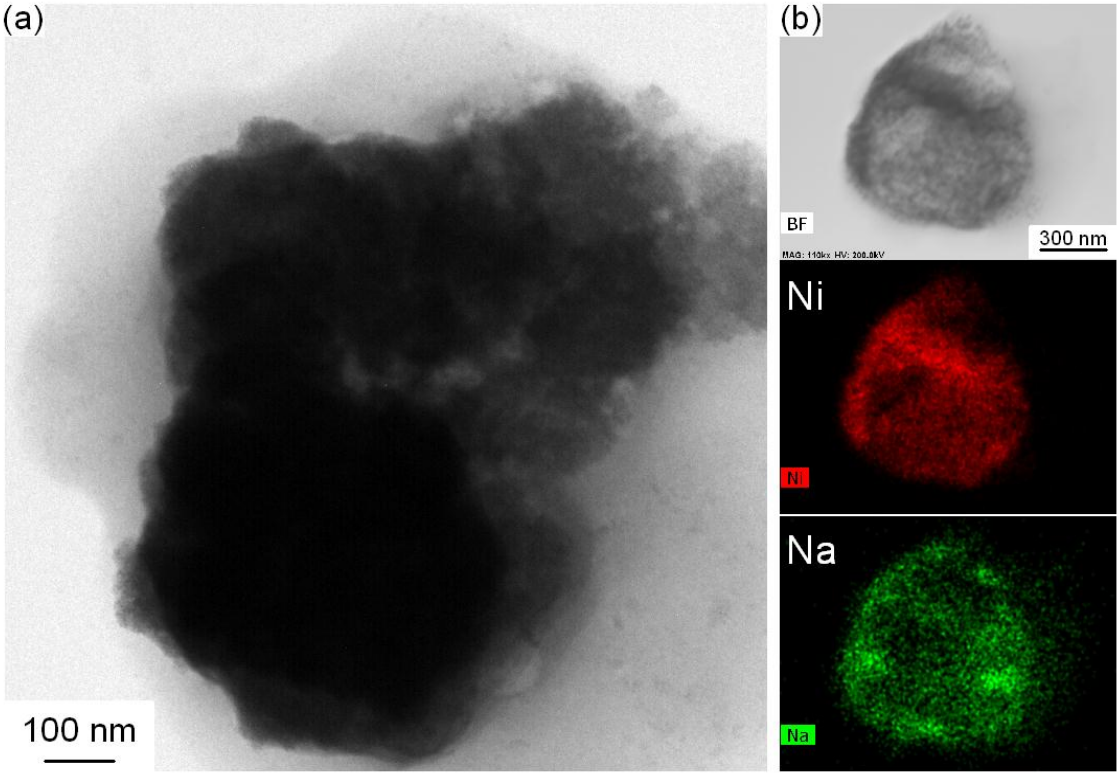

Fig. S3 (a) Typical TEM image of $NaBH_4$@Ni produced from 0.02 mol.L^{-1} $NiCl_2$ and (b) associated EDS mapping of the large particle/agglomerate (a), showing a combination of agglomerated Ni and $NaBH_4$.

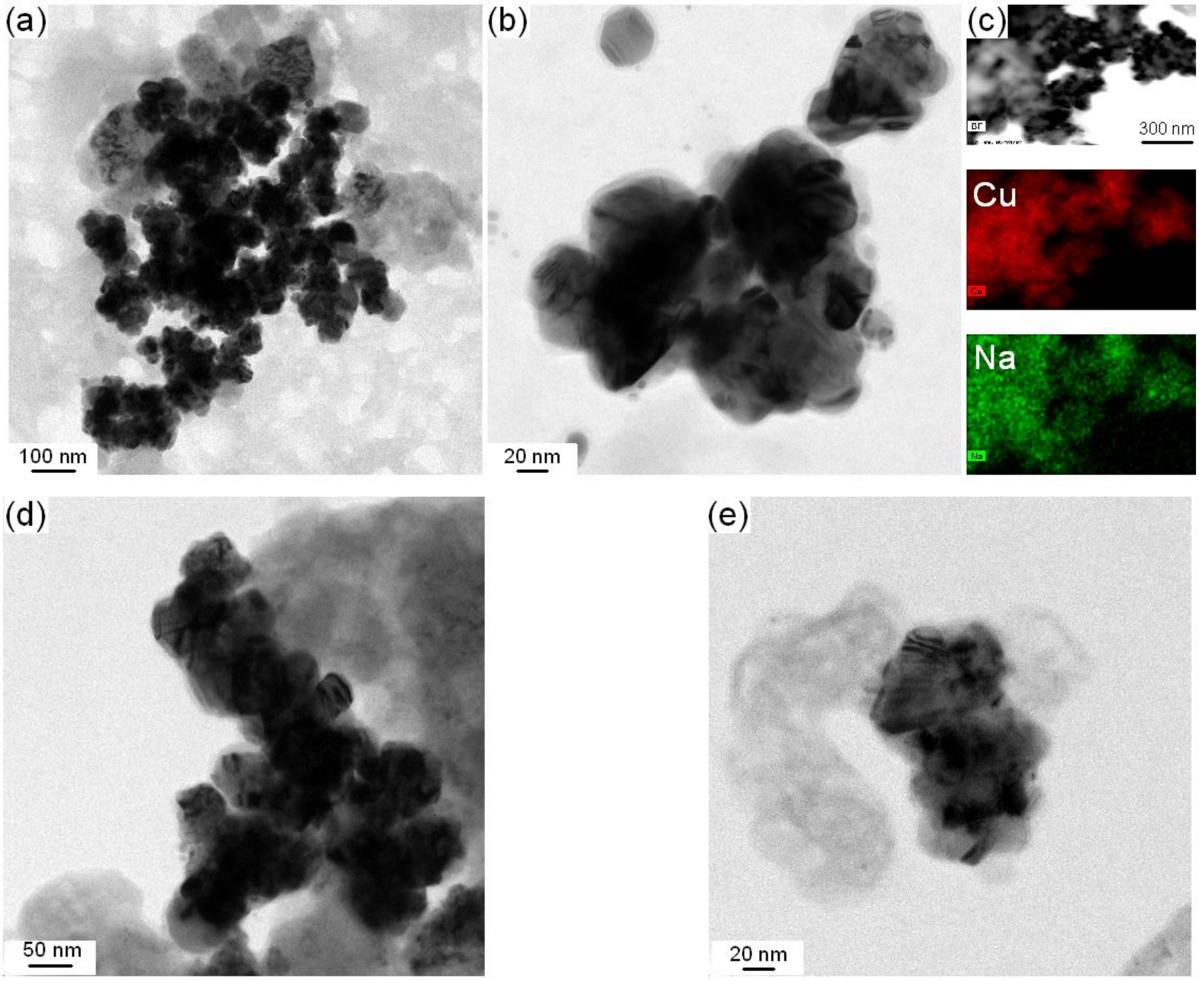

Fig. S4 (a)-(e) Typical TEM images of $NaBH_4$@Cu produced from 0.06 mol.L^{-1} $CuCl_2$ and (c) associated EDS mapping showing the formation of an irregular Cu surface at high $CuCl_2$ concentrations.

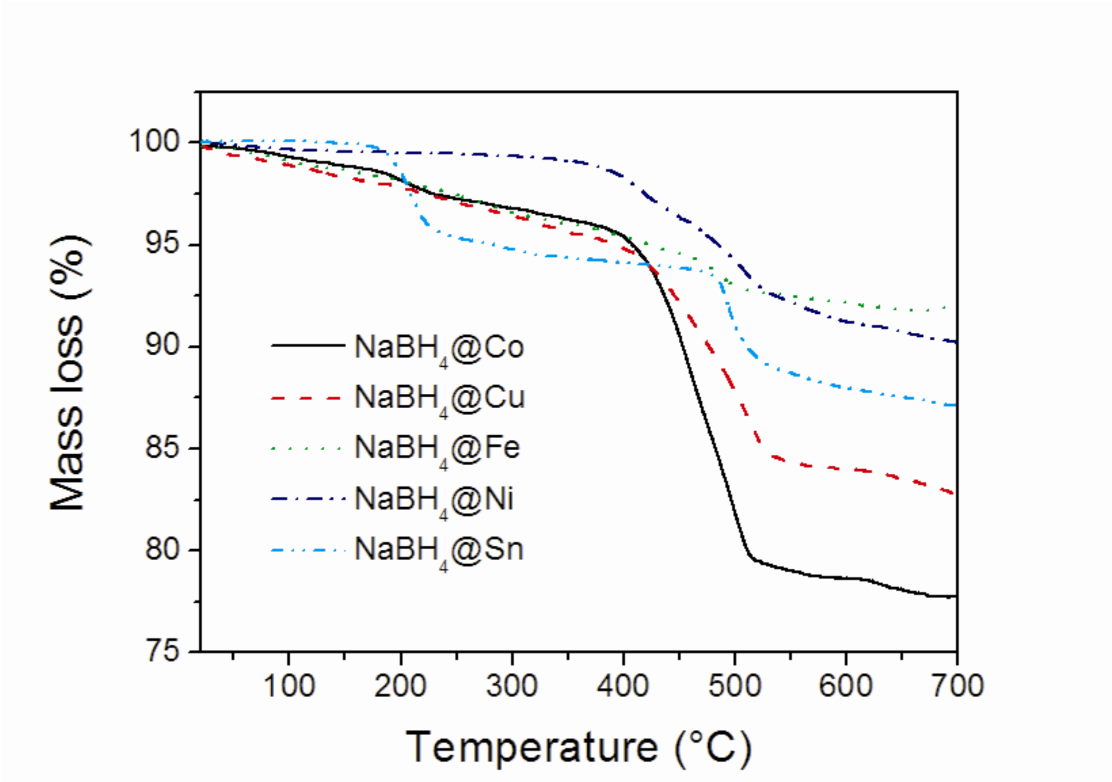

Fig. S5 TGA curves for the core-shell nanoparticles under a heating ramp of 10 °C.min^{-1}. Mass losses below 200 °C correspond to solvent evaporation.

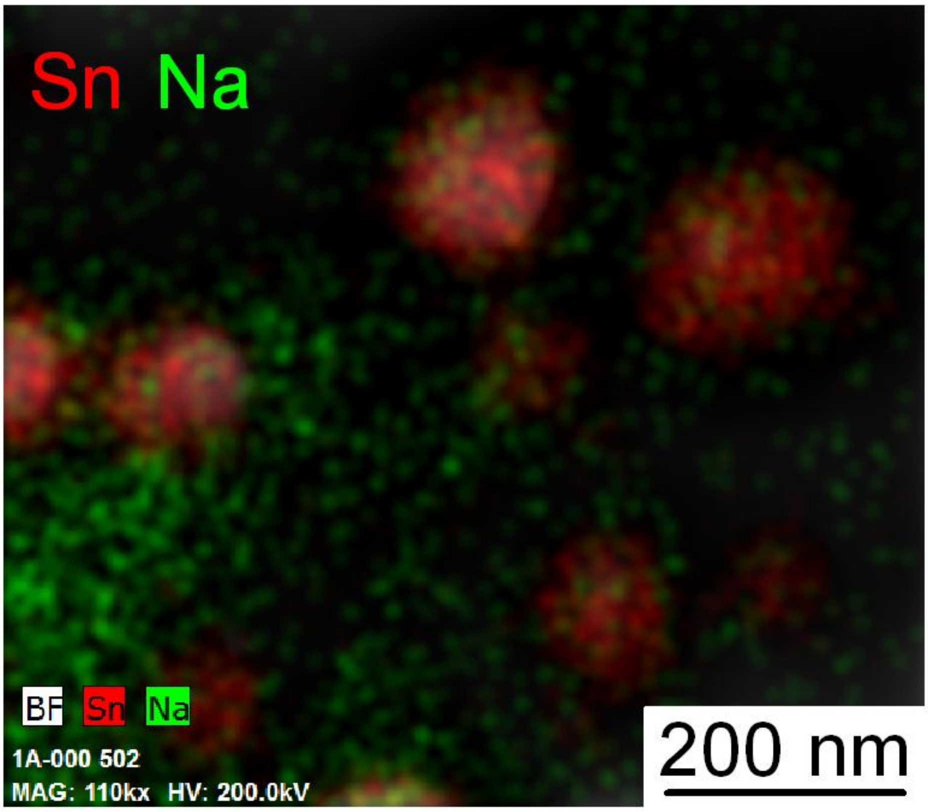

Fig. S6 Typical EDS mapping of $NaBH_4$@Sn heated to 300 °C showing the degradation of the original cubic-like structure to form a combination of spherical Sn nanoparticles and $NaBH_4$.

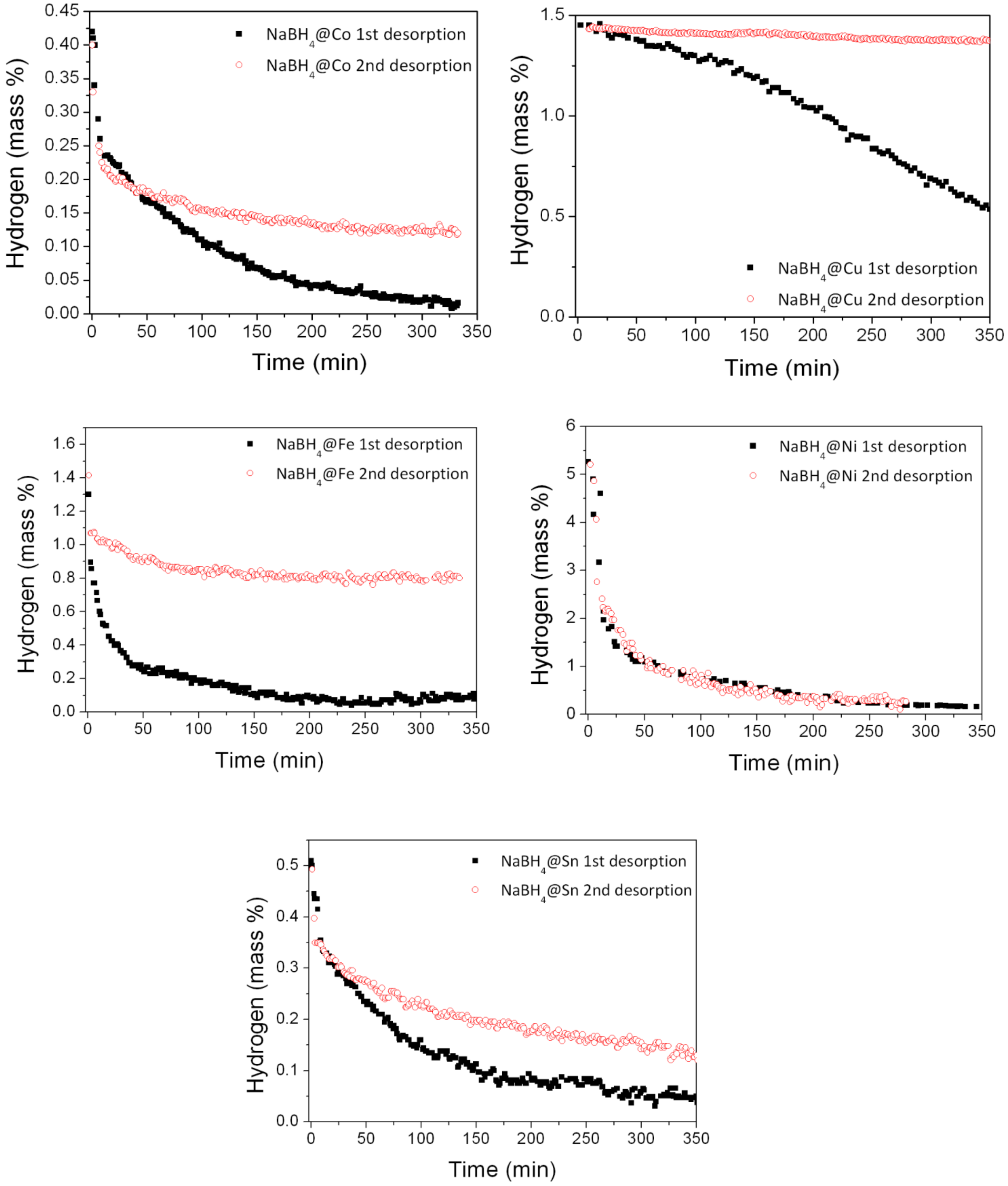

Fig. S7 Kinetics of successive hydrogen desorption at 0.01 MPa and 350 °C from (a) $NaBH_4$@Co, (b) $NaBH_4$@Cu, (c) $NaBH_4$@Fe, (d) $NaBH_4$@Ni, and (e) $NaBH_4$@Sn. Hydrogen absorption was performed under 40 MPa hydrogen pressure (not shown).