




Supplementary Materials

FCC/ α -Fe biphasic nano-sites synergize with CNTs to enhance reversible hydrogen storage of MgH_2

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Experimental

Synthesis of VTiFe alloy

All raw materials were commercially purchased and used without further purification. VTiFe alloy catalyst was synthesized via wet chemical mechanical milling under Ar atmosphere (99.999% purity). Briefly, a mixture of 1.625 g V, 0.680 g Ti and 2.695 g Fe (99% purity, Linyi Research and Innovation Materials Co., Ltd.) was milled in a planetary ball mill (FRITSCH Pulverisette 4) using stainless steel jar and balls. To prevent excessive cold welding, 15 mL of heptane was added as a process control agent. The milling was performed at a speed of 350 rpm with a ball-to-material weight ratio of 10:1. The milling was carried out in an alternating forward and reverse mode, with a 5 min pause every 15 min, for a total of 40 h. The as-synthesized VTiFe alloy catalyst was vacuum-dried at 100°C for 10 h.

Preparation of MgH₂-VTiFe and MgH₂-VTiFe-CNTs composites

The as-synthesized VTiFe alloy catalyst with various loading ratios ($x = 2, 6, 10,$ and 25 wt%) was mixed with commercial MgH₂ (98%, Shanghai Magnesium Power Technology Co., Ltd) by mechanical milling for 12 h under Ar atmosphere. The final prepared composite is defined as MgH₂- x wt% VTiFe. The ball-to-powder weight ratio was 30:1 and the milling speed was 400 rpm. The ball milling was performed in an alternating forward and reverse mode for 10 min each, with a 10 min pause between each milling period to prevent excessive temperature rise in the powder. Under unchanged processing conditions, MgH₂-6 wt% VTiFe composite material was first prepared by ball milling for 8 h. Subsequently, 3 wt.% multi-walled CNTs (3-15 nm diameter, Suiheng Technology Co., Ltd) was added and the mixture was further ball milled for 4 h to obtain the MgH₂-6 wt.% VTiFe-3 wt.% CNTs composite. As a control sample, MgH₂ without catalysts doping, denoted as milled MgH₂, was prepared in the same method.

Materials characterization and measurements

The phase composition of the samples was analyzed by X-ray diffraction (XRD, PANalytical X' Pert Powder) with Cu K α radiation with a scanning rate of 5 °C/min. The

microscopic morphology, microstructure, and elemental distribution of the catalyst and composites were investigated using an environmental scanning electron microscope (ESEM, Quattro S, FEI), a transmission electron microscope (TEM, Talos F200S, FEI) equipped with energy-dispersive X-ray spectroscopy (EDS), and a high-resolution transmission electron microscope (HRTEM). X-ray photoelectron spectroscopy (XPS) was performed on a Thermo SCIENTIFIC ESCALAB Xi+ spectrometer with monochromatic Al K α radiation (E=1486.68 eV) to analyze the chemical states of elements in the samples. All binding energies were calibrated with C1s peak (284.8 eV).

Hydrogen storage performance of the samples was tested by a full-automatic Sievert-type ab/desorption instrument (PCTPro, Setaram). Temperature-programmed-dehydrogenation (TPD) measurements were carried out to investigate the dehydrogenation behavior of samples at different heating rates from room temperature to 400°C. Isothermal dehydrogenation and hydrogenation were performed at 0.01 MPa and 3 MPa initial hydrogen pressure respectively. The thermodynamic properties of the samples were analyzed by pressure-composition-temperature (PCT) measurements. For each performance test, 50 mg of sample powder was loaded into the vessel in the argon-filled glove box.

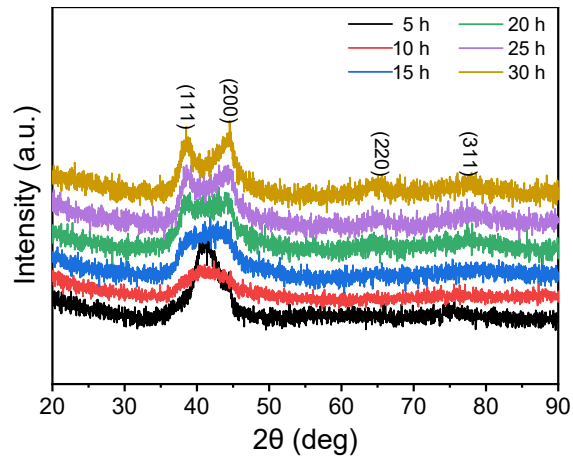


Fig.S1 XRD patterns of VTiFe alloy at different ball milling times.

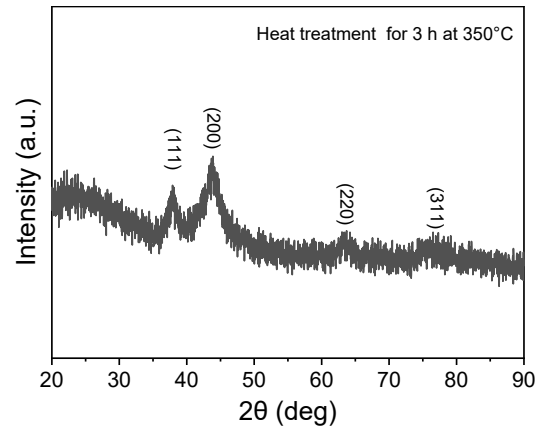


Fig.S2 XRD patterns of VTiFe alloy after heating treatment for 3 h at 350°C.

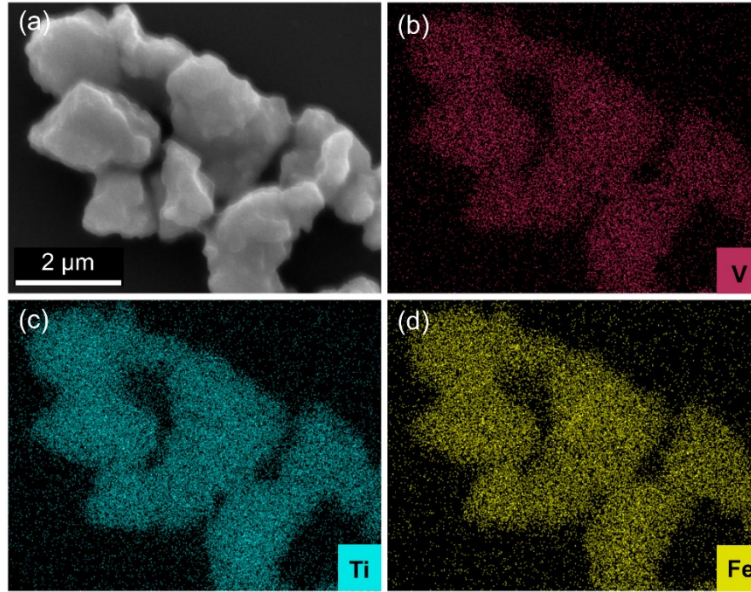


Fig.S3 (a) SEM images and corresponding EDS elemental mappings results of (b) V, (c) Ti and (d) Fe elements of the VTiFe alloy.

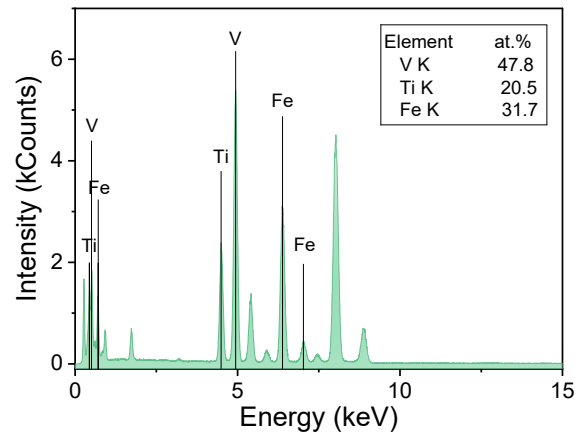


Fig.S4 EDS mapping results of VTiFe alloy.