

## Electronic Supplementary Information

### Excellent catalytic effects of multi-walled carbon nanotubes supported titania on hydrogen storage of Mg-Ni alloy

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#### Experimental

Original powders of Mg (99 wt.% in purity and < 74 μm in diameter), Ni (99 wt.% in purity and 2-3 μm in diameter), tetrabutyl titanate (CP, 98 wt.% in purity), hydrogen peroxide (AR, 30 wt.% in water) and multi-walled carbon nanotubes (>97 wt.% in purity and 40-60 nm in external diameter) were commercially gotten.

#### *MWCNTs treatment*

The surface of MWCNTs was treated to ensure functionalization. MWCNTs were added to 50 ml concentrated nitric acid under stirring in an oil bath, with an increase in the temperature to 413 K. It was further refluxed and stirred for 6 h to remove impurities, and washed with distilled water till the pH value of the rinsed solution reached around 7, and finally dried under vacuum.

#### *Synthesis of TiO<sub>2</sub>/MWCNTs catalyst*

The formation of TiO<sub>2</sub>/MWCNTs (mass ratio = 1:1) is based on a sol-gel method followed by an annealing process. Tetrabutyl titanate was added to deionized water with magnetic stirring for 30 min. The white product after stirring was collected by centrifugation and washed with deionized water and ethanol several times. Further,

H<sub>2</sub>O<sub>2</sub> was used to dissolve the product and the MWCNTs were dispersed into the solution by magnetic stirring for 24 h. After magnetic stirring, the suspension was transferred to blowing dry oven and dried at 353 K. Finally, the catalyst was heat-treated at 673 K and held for 2 h in a tube furnace under Ar.

#### *Preparation of Mg<sub>95</sub>Ni<sub>5</sub> and catalyzed Mg<sub>95</sub>Ni<sub>5</sub> composite*

Mg and Ni with atomic ratio of 95:5 were homogenized by ultrasonic vibration in acetone for 30 min. After being completely dried in air, the powders were directly used for hydriding combustion synthesis (HCS). During the HCS process, the samples were first heated up to 853 K at a heating rate of 10 K/min under 2 MPa hydrogen atmosphere and kept at that temperature for 1 h. It was then cooled down to 613 K and held for 4 h. Finally, the sample was cooled down to room temperature. The product of HCS was designated as Mg<sub>95</sub>Ni<sub>5</sub>. Then, the Mg<sub>95</sub>Ni<sub>5</sub> powder was mixed with 5 wt.% as-prepared TiO<sub>2</sub>/MWCNTs nanocomposite, and mechanically milled under 0.1 MPa argon atmospheres on a planetary ball mill with ball to powder ratio of 30:1 at 400 rpm for 600 min (mill 30 min then pause 6 min). The Mg<sub>95</sub>Ni<sub>5</sub> powder without additive was also milled under the same condition for comparison. In order to explore the effects of the TiO<sub>2</sub>/MWCNTs catalyst, the TiO<sub>2</sub> synthesized by sol-gel method and MWCNTs with the same mass percent of 5 wt.% were added separately into Mg<sub>95</sub>Ni<sub>5</sub> for comparison.

#### *Sample characterization*

The crystal structure and surface configuration of samples were determined by powder X-ray diffraction (XRD) with Cu K $\alpha$  radiation (40 kV and 35 mA) and high-

resolution transmission electron microscope (HRTEM, JEM-2010 UHR, 200 kV). X-ray photoelectron spectroscopy (XPS) was carried out in a Kratos AXIS ULTRA DLD system and operated at 10 mA and 15 kV. The specific surface areas and porous nature of the as-prepared TiO<sub>2</sub>/MWCNTs were further investigated by nitrogen adsorption/desorption measurements (ASAP-2020, Micrometrics instruments). The average crystallite sizes of the main phase MgH<sub>2</sub> in samples after MM and Mg after dehydrogenation were estimated according to Scherrer equation:

$$D = \frac{K\lambda}{\beta \cos\theta} \quad (1)$$

Where  $D$  is the crystallite size,  $k$  is the shape factor, typically 0.89,  $\lambda$  is the X-ray wavelength of 0.154 nm,  $\beta$  is the full width at half maximum of the diffraction peak and  $\theta$  is the Bragg angle.

The hydriding and dehydriding properties were measured by volumetric method, using the gas reaction controller (AMC). In order to prevent possible oxidation, the transfer of samples to the sample chamber was performed in a glove box under an argon atmosphere. Ahead of hydriding measurement, the samples were dehydrided completely under vacuum by heating up to approximately 603 K. Then, the hydriding kinetics at different temperatures was measured under the hydrogen pressure of 3.0 MPa. The dehydriding kinetics was measured under vacuum at 493 K and 0.005 MPa hydrogen pressure at temperatures higher than 493 K.

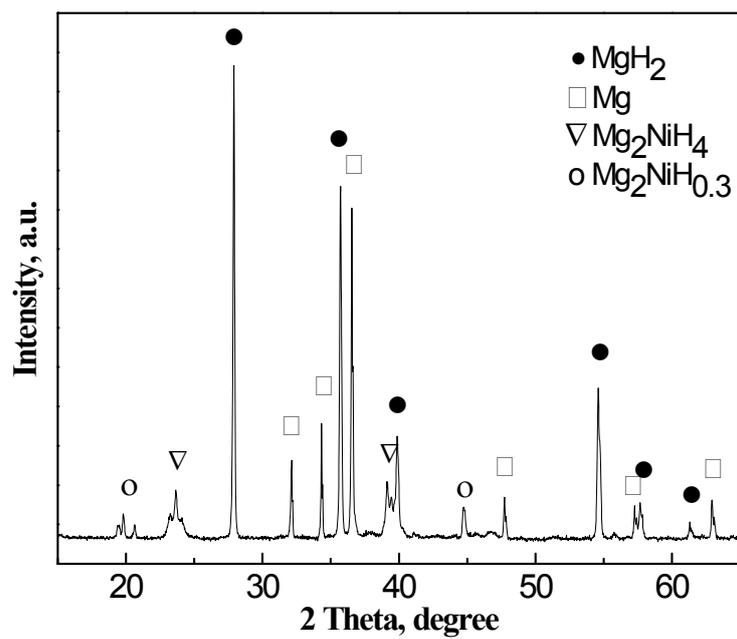
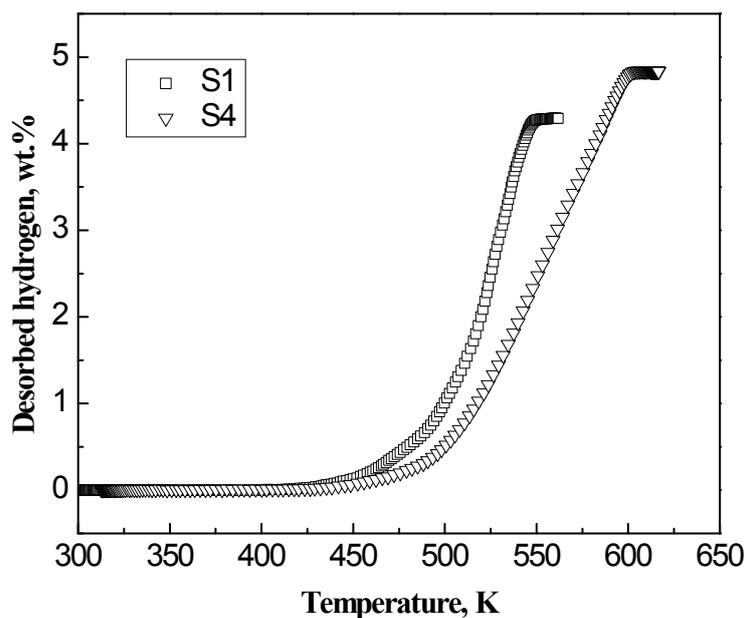


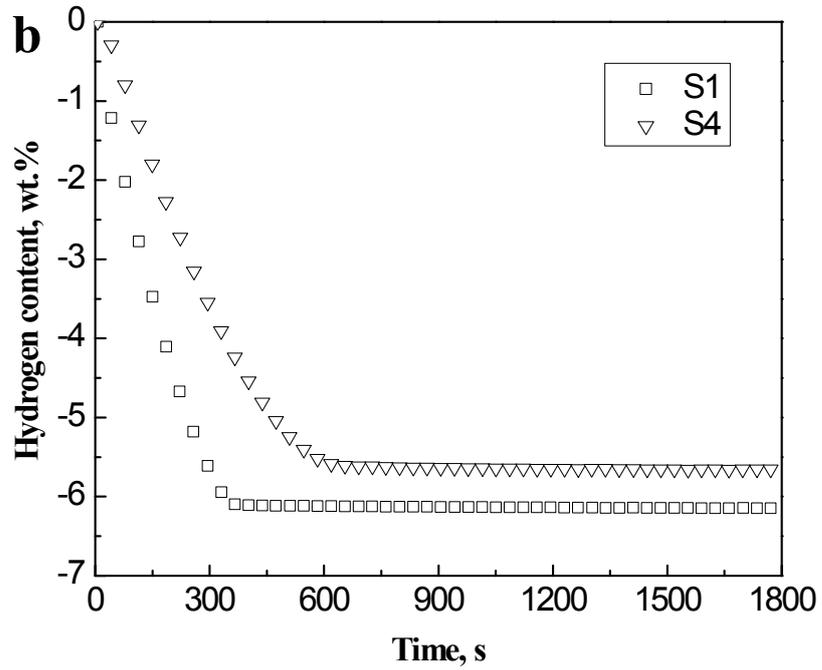
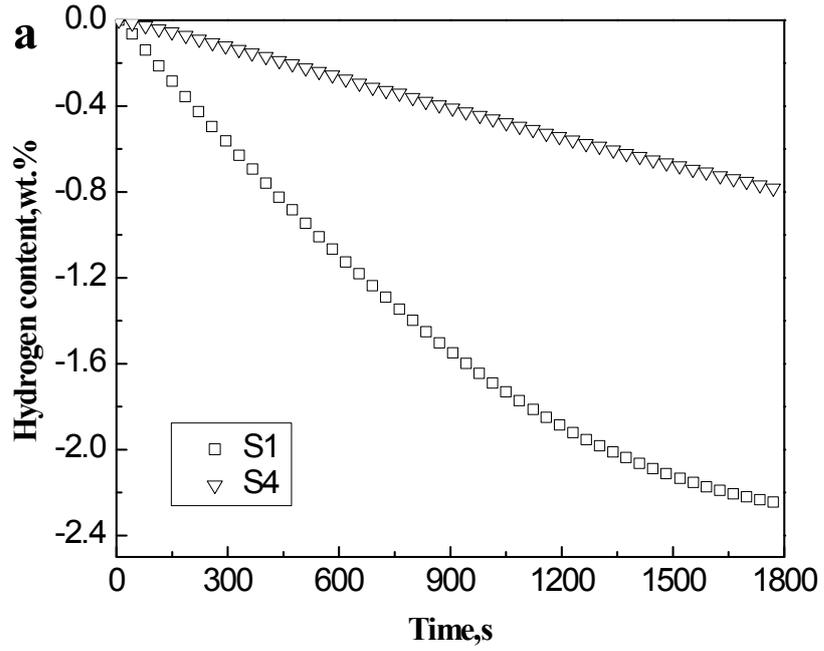
Fig. S1 XRD pattern of the HCS product of  $Mg_{95}Ni_5$



**Fig. S2** The amount of hydrogen desorbed as a function of temperature of the as-milled products: (S1)  $\text{Mg}_{95}\text{Ni}_5+5\text{wt.}\%\text{TiO}_2/\text{MWCNTs}$  and (S4)  $\text{Mg}_{95}\text{Ni}_5$ . The heating rate is  $20^\circ\text{C min}^{-1}$

**Table S1** Hydrogen absorption capacities of (S1)  $\text{Mg}_{95}\text{Ni}_5\text{-TiO}_2/\text{MWCNTs}$ , (S2)  $\text{Mg}_{95}\text{Ni}_5\text{-TiO}_2$ , (S3)  $\text{Mg}_{95}\text{Ni}_5\text{-MWCNTs}$  and (S4)  $\text{Mg}_{95}\text{Ni}_5$  at 373 K and 493 K under 3.0 MPa hydrogen pressure within 800 s

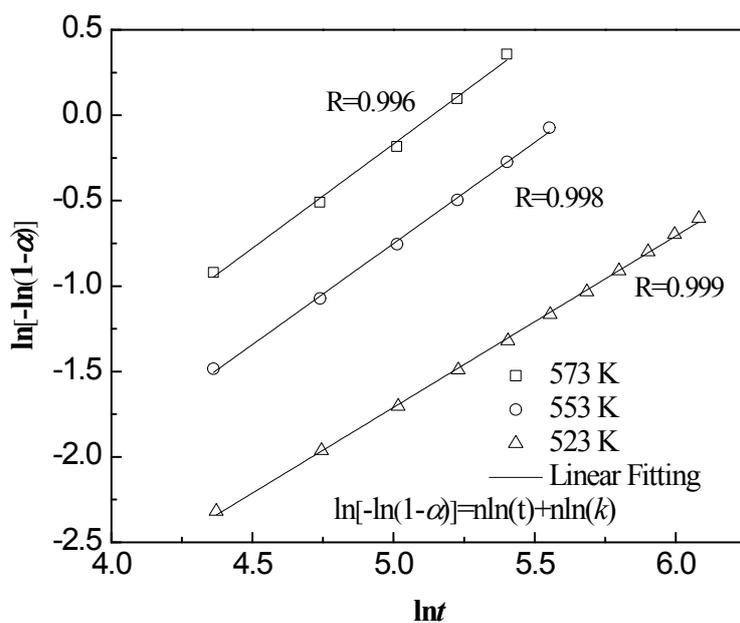
Temperature (K)	Hydrogen absorption capacity (wt.%)			
	S1	S2	S3	S4
373	5.62	4.71	2.96	4.07
493	6.25	5.48	6.03	5.77



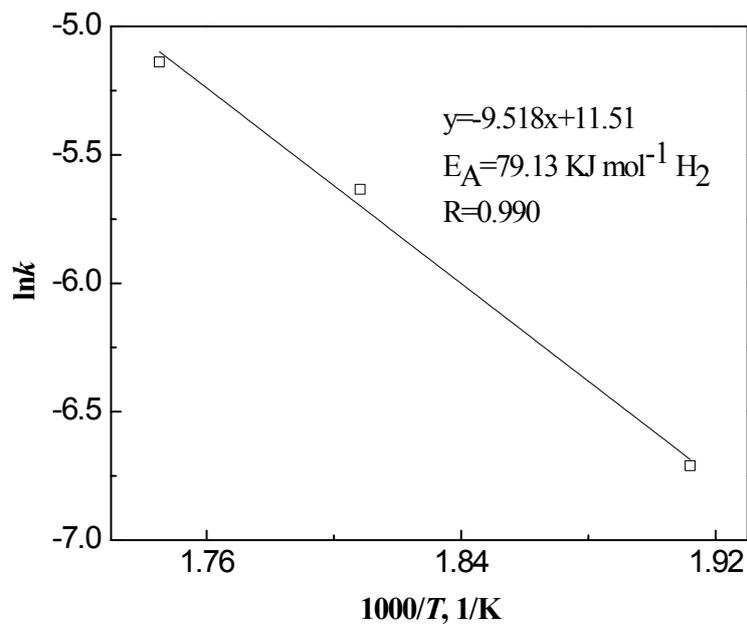
**Fig. S3** Isothermal dehydrogenation curves of (S1)  $Mg_{95}Ni_5-TiO_2/MWCNTs$  and (S4)  $Mg_{95}Ni_5$  at (a) 493 K under vacuum and (b) 573 K under the hydrogen pressure of 0.005 MPa

**Table S2** Hydrogen desorption capacities of the HCS+MM products of (S1) Mg<sub>95</sub>Ni<sub>5</sub>-TiO<sub>2</sub>/MWCNTs, (S2) Mg<sub>95</sub>Ni<sub>5</sub>-TiO<sub>2</sub>, (S3) Mg<sub>95</sub>Ni<sub>5</sub>-MWCNTs and (S4) Mg<sub>95</sub>Ni<sub>5</sub> at 493K, 523 K, 553 K and 573 K under 0.005 MPa hydrogen pressure within 1800 s

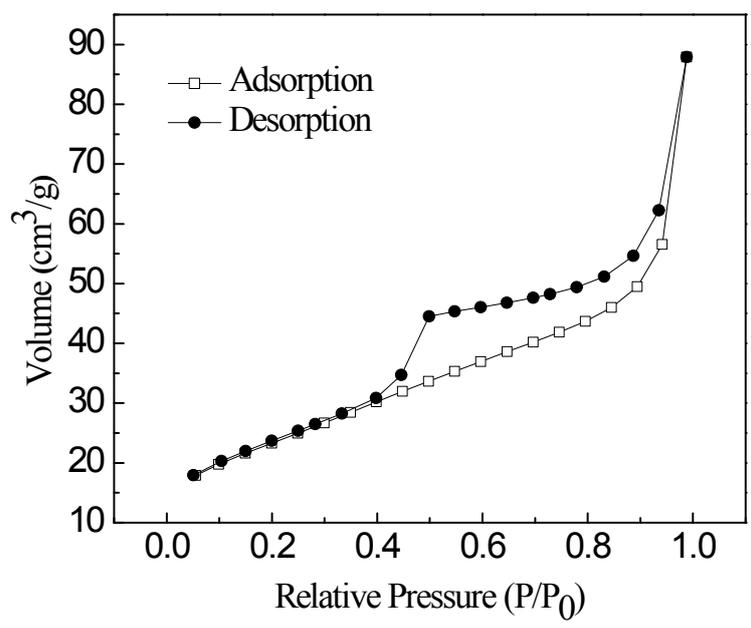
Temperature (K)	Hydrogen desorption capacity (wt.%)			
	S1	S2	S3	S4
493	2.24	-	-	0.78
523	5.95	5.24	3.54	4.47
553	6.08	5.87	5.50	5.32
573	6.15	-	-	5.66



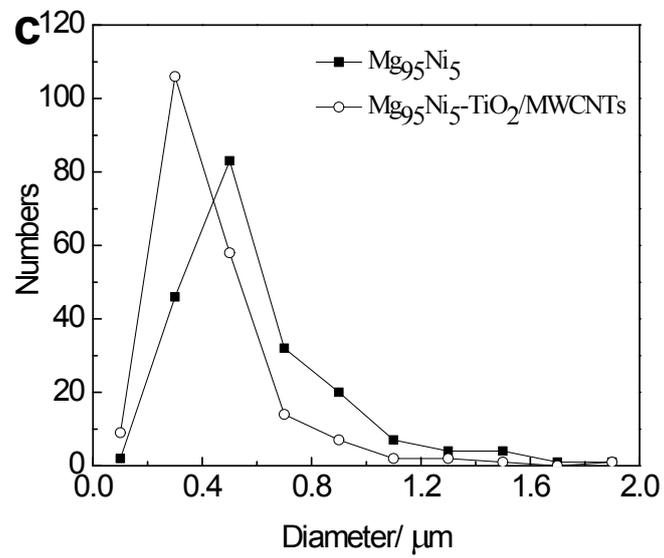
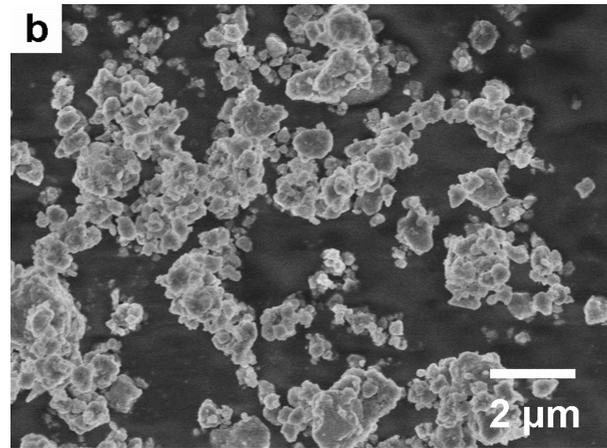
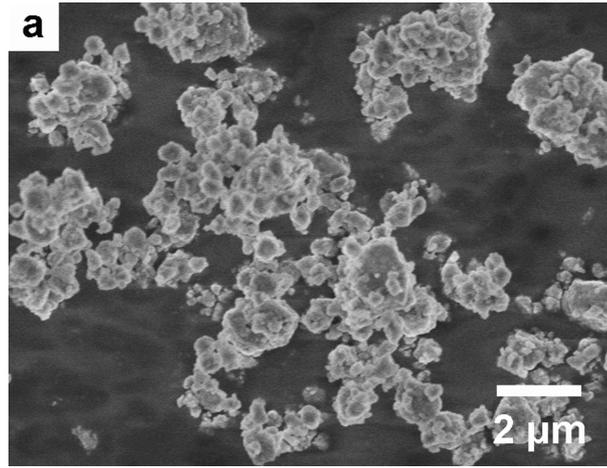
**Fig. S4** JMA plots of  $\ln[-\ln(1-\alpha)]$  vs  $\ln(t)$  for the dehydrogenation of the  $\text{Mg}_{95}\text{Ni}_5\text{-TiO}_2/\text{MWCNTs}$  composite at different temperatures. The samples with reacted fraction of  $0.1 < \alpha < 0.7$  was used



**Fig. S5** Arrhenius plots for the dehydrating kinetics of the  $\text{Mg}_{95}\text{Ni}_5\text{-TiO}_2/\text{MWCNTs}$  composite



**Fig. S6** Nitrogen adsorption-desorption isotherms curves of the TiO<sub>2</sub>/MWCNTs catalyst



**Fig. S7** SEM images of (a) Mg<sub>95</sub>Ni<sub>5</sub> and (b) Mg<sub>95</sub>Ni<sub>5</sub>-TiO<sub>2</sub>/MWCNTs after mechanical milling, and (c) the size distribution of samples

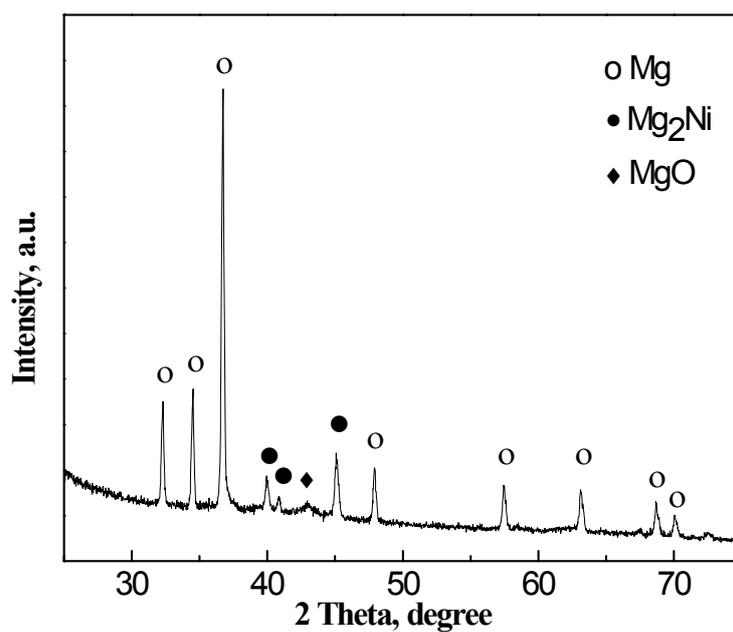


Fig. S8 XRD pattern of the  $\text{Mg}_{95}\text{Ni}_5\text{-TiO}_2/\text{MWCNTs}$  after dehydrogenation

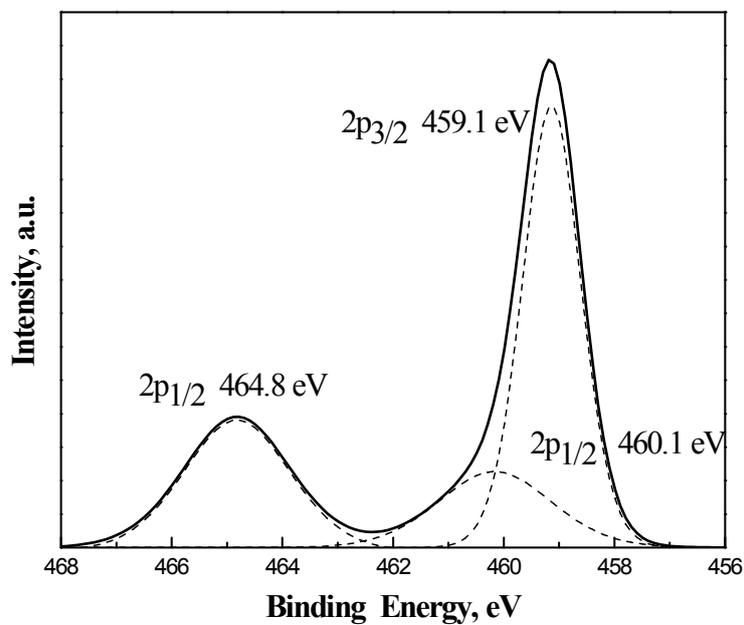


Fig. S9 XPS Ti 2p spectra from  $\text{Mg}_{95}\text{Ni}_5\text{-TiO}_2/\text{MWCNTs}$  after mechanical milling

**Table S3** XPS Ti 2p peak positions from reference data

Sample	Peak assignment	Position(eV)
Ti	Ti 2p <sub>1/2</sub>	460.0
	Ti 2p <sub>3/2</sub>	454.0
TiO <sub>2</sub>	Ti <sup>IV</sup> 2p <sub>1/2</sub>	464.6
	Ti <sup>IV</sup> 2p <sub>3/2</sub>	458.9