Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

1 Preparation of Mg-TM composites

All experiments and handling were carried out in glove box with an argon atmosphere to prevent possible Mg oxidation. A series samples named as Mg-Ti, Mg-Nb, Mg-V, Mg-Co, Mg-Mo and Mg-Ni were prepared by a reaction of the pre-milled Mg powder with corresponding chlorides ($TiCl_3$, $NbCl_5$, VCl_3, $CoCl_2$, $MoCl_3$, $NiCl_2$), separately (the detail experimental processes are shown in supporting information). All the raw materails are bought in Aldrich.

Firstly, fine Mg powder was prepared by ball-milling. As Mg powder is difficult to be broken down for its good plasticity and toughness, adding brittle MgH_2 powder into Mg powder is available for facilitating the particle breakage during the ball-milling. Besides, MgH_2 powder transform into Mg easily because of the heat effect during the ball-milling. However, adding too much of MgH_2 results that the as prepared Mg powder contains obvious MgH_2 which can not react with $TiCl_3$ in THF. Hence, the mixed powder of commercial Mg and MgH_2 with a weight ratio of 9:1 were milled in the 50 ml stainless steel vials with stainless steel balls (the weight ratio 30:1 of the ball to powder) and ~1ml THF solution at 800 rpm for 6 h (co-rotating 15min, stop 45 min, reversing 15min, stop 45 min, repeat 12 times in this way) under 0.1 MPa of argon by a vibratory milling apparatus. Then the powder is described as pre-milled Mg powder for the next step. Secondly, the as pre-milled powder (0.4g) was reacted with 0.833 mmol corresponding $TmCl_x$ ($TiCl_3$, $NbCl_5$, VCl_3, $CoCl_2$, $MoCl_3$, $NiCl_2$) in 20ml THF solution under electromagnetic stirring for 5h, separately. In the end, after 1h rest, the solution and insoluble substances were separated, then the solution was taken out by injector, and the insoluble substances were moved into a vacuum drying oven for drying 2 h under room temperature. Here, the sample after aforesaid treatments was correspondingly named as Mg-Tm (Mg-Ti, Mg-Nb, Mg-V, Mg-Co, Mg-Mo, Mg-Ni) for short. In addition, the pure MgH_2 were ball-milled with the same ball-milling parameters with pre-milled powder (co-rotating 15min, stop 45 min, reversing 15min, stop 45 min, repeat 4 times in this way) for comparison and named as ball-milled MgH_2. All the operations were under the protection of high-purity argon gas for avoiding oxidation.

2 Supporting XPS data

Fig. 1(SI) shows that Nb 3d signals of Nb, $NbCl_5$, NbO and Nb_2O_5 exsit both in the hydrogenated and dehydrogenated Mg-Nb sample after 5 cycles. And Co 2p signals of Co, $CoCl_2$ and Co can be detected both in the hydrogenated and dehydrogenated Mg-Co sample after 5 cycles as shown in Fig. 2(SI). Besides that, Ni 2p signals of Ni, $NiCl_2$ and NiO exsit in the as prepared Mg-Ni sample shown in Fig. 3(SI). However, diferent with as mentioned XPS data, Ni 2p signal of Ni despeared after the hydrogenation. Combinated with the XRD and TEM results, it can be suggested Mg_2NiH_4 after hydrogenation. This can also be proved by the left drifting of Mg 1s signal as shown in Fig. 4(SI) which stands for the metallicstateof Mg formed.

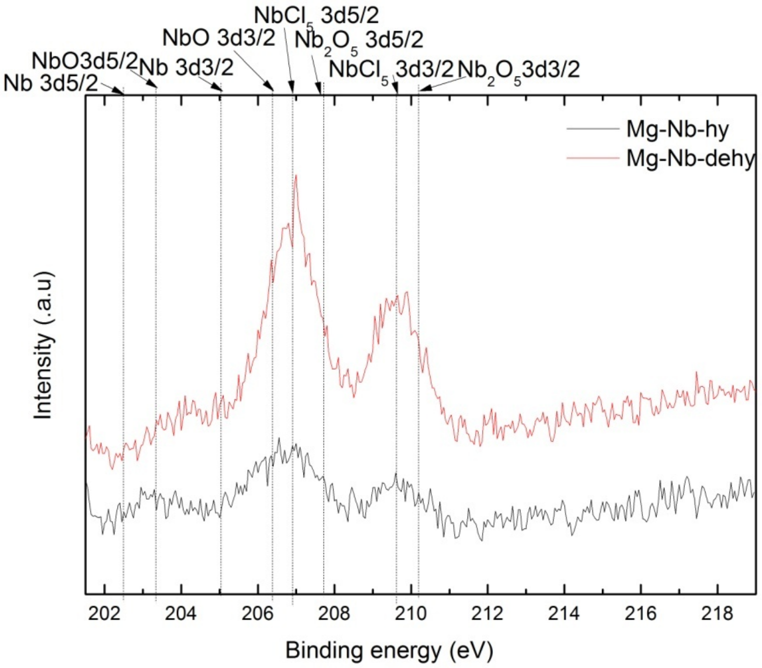

Fig. 1 Nb3d photo electron lines for the hydrogenated and dehydrogenated Mg-Nb samples after 5 cycles, repectively.

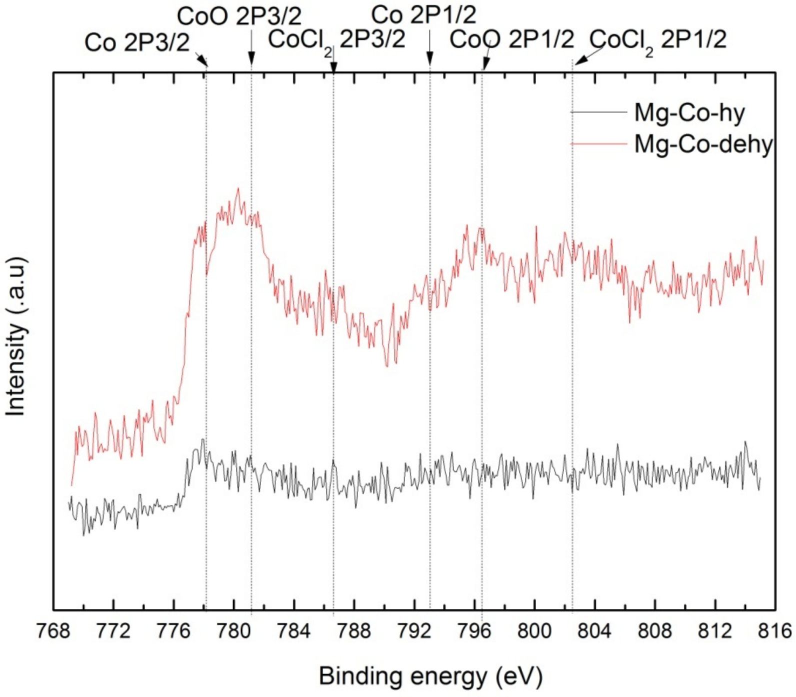

Fig. 2 Co 2p photo electron lines for the hydrogenated and dehydrogenated Mg-Ni samples, after 5 cycles, repectively.

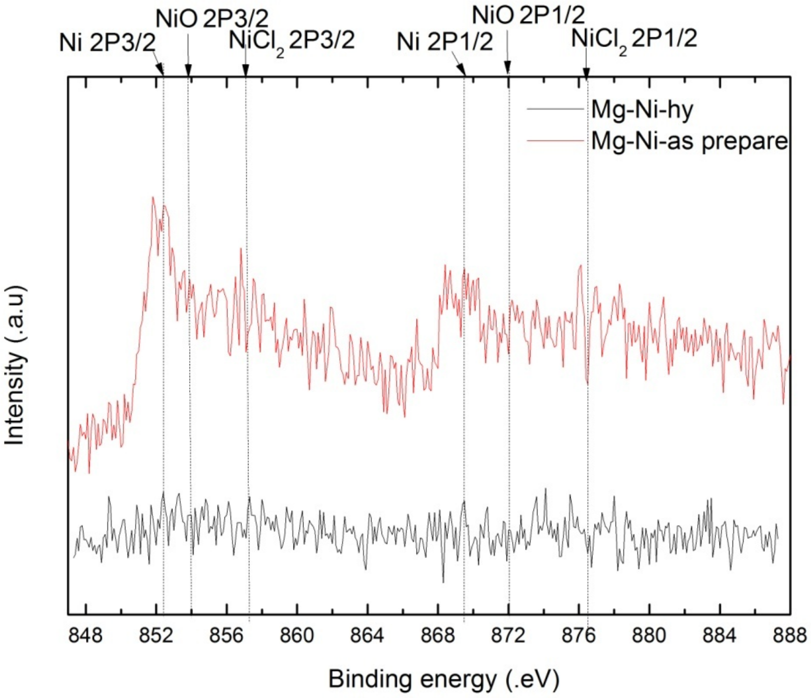

Fig. 3 Ni 2p photo electron lines for the as prepared and hydrogenated Mg-Ni samples, after 5 cycles, repectively.

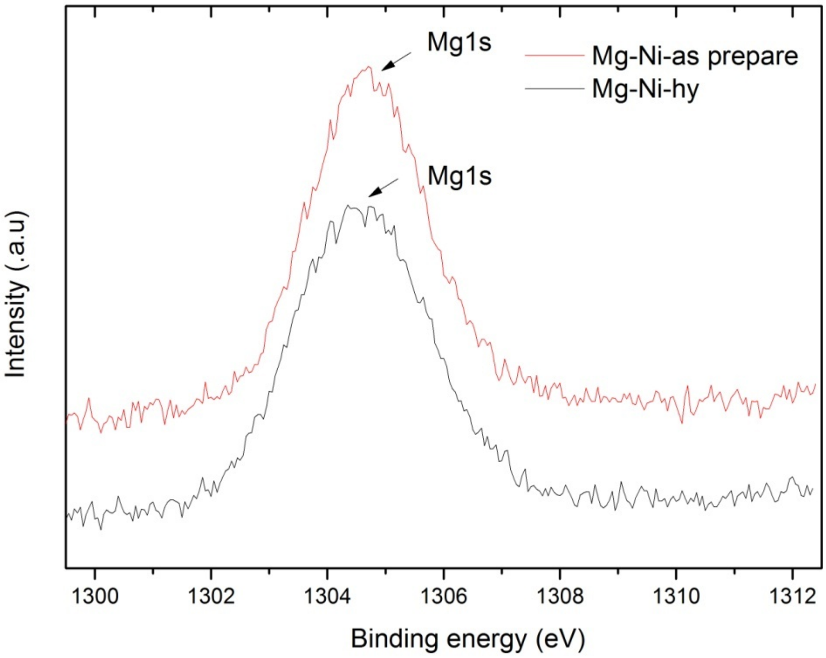

Fig. 4 Mg 1s photo electron lines for the as prepared and hydrogenated Mg-Ni samples after 5 cycles, repectively.