Supporting information

Promoting H_2 generation from the reaction of Mg nanoparticles and water by cations

Jie Zheng, DengChen Yang, Wei Li, Xingguo Li*

H_2 generation amount measurement

The setup to measure the H_2 generation is shown in Figure S1, which consists of a 250 mL sealed flask connected to a water filled U-shape tube. In a typical measurement, 0.024 g Mg nanoparticles are first placed in the flask immersed in the water bath. Under gentle stirring, 200 mL solution isothermal to the water bath is rapidly introduced into the flask via the side branch to initiate the reaction. The generated gas is allowed to pass the NaOH-CaO dessicator to remove the water vapor and the possible acidic gas (HCl). The generated H_2 will change the water level in the U-shape tube. By tuning the vertical position of the left branch, the water level in the two branches are always kept at the same level, so that the pressure of the sealed volume is kept The water level in the right branch is read every 30 sec. The amount of H_2 generated $n(H_2)$ (in mole) is calculated by the volume change ΔV read from the water level in the branch directly connected to the flask (the right branch in Figure S1):

$$n(H_2)=p_0\Delta V/(RT)$$

where p_0 is the ambient atmospheric pressure, $R=8.314\ J\cdot K^{-1}mol^{-1}$ is the gas constant, and T is the room temperature in K.

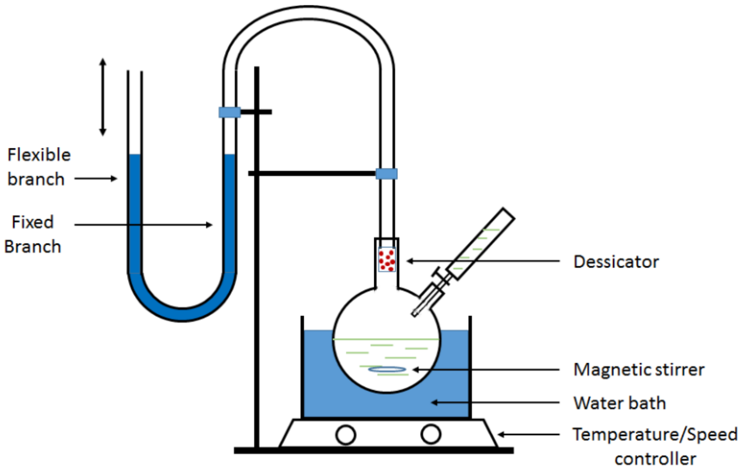

Figure S1 Schematic illustration of the setup for H_2 generation measurement.

Materials characterization

X-ray diffraction (XRD) patterns are collected using the Cu Kα line at scan rate of 4° min^{-1} (Rigaku 200Dmax diffractometer). Scanning electron microscopy (SEM) images are collected with acceleration voltage of 15 kV (Hitachi F4800).

The term to describe the OH^- affinity

Considering the following reaction:

$M(OH)_x \leftrightarrow M^{x+}\ xOH^-$

The equilibrium constant K is given by

$K= [M^{x+}][OH^-]^x$

Where $[M^{x+}]$ and $[OH^-]$ represent the equilibrium concentration of M^{x+} and OH^-, respectively.

Therefore:

$\lg [OH^-] = \lg K/x - \lg [M^{x+}]/x = -pK/x - \lg [M^{x+}]/x$

The above equation indicates that at given concentration of M^{x+}, higher pK/x value means lower $[OH^-]$. Therefore, the term pK/x can be used as an indicator to describe the affinity to OH^- of the cation M^{x+}. Strictly, this conclusion only holds for $[M^{x+}] = 1$ M. In our experiment, $[M^{x+}] = 0.1$ M. The more accurate description term should be $pK/x + \lg [M^{x+}]/x = (pK-1)/x$. Nevertheless, the term pK/x can still serve as a simple indicator with reasonable accuracy.

The effect of the Cl^- concentration

In our H2 generation experiments, the cation concentratino is kept the same for different chloride solution. The Cl^- concentration is different for cations with different valence. Chlorides are known to have corrosion effect of Mg and Mg based alloys. Therefore, the concentration of Cl^- should also be taken into account when designing the experiments to demonstrate the cation effect.

The corrosion effect of Cl^- is also visible in our experimental data. As shown in Figure 1, the H_2 generation rate is slightly enhanced by adding NaCl or KCl. However, this corrosion effect takes place in a longer time scale. As shown in Figure 1, the difference between water and NaCl is quite small, particularly in the first 10 min. The same phenomena were also observed in Ref 10 in this paper. The H_2 generation rate in the first 30 min is quite similar in NaCl solutions with different concentration.

For this reason, the difference of Cl^- concentration in different chloride solution will only cause slight influence on the generated H2 amount in the first 10 min. The conclusion in Figure 2 will not be significantly affected when taking the effect of the Cl^- concentration into account.

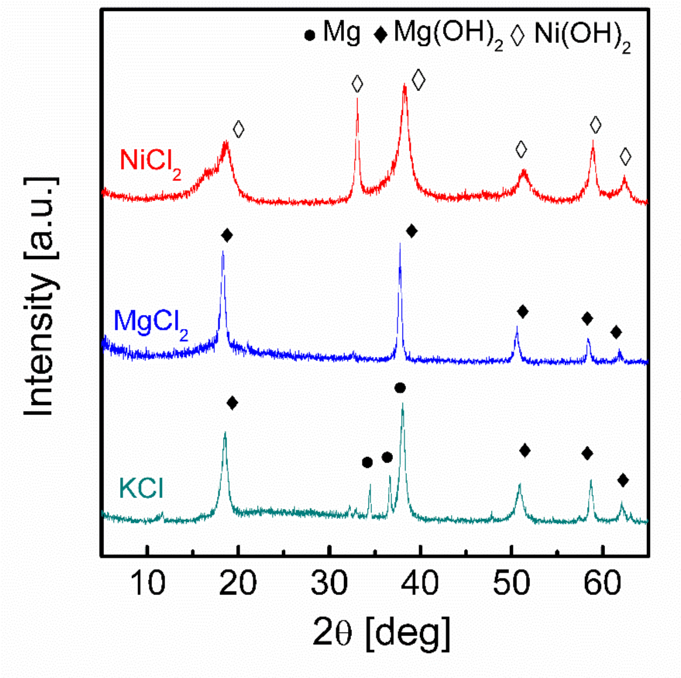

Figure S2 X-ray diffraction patterns of the reaction products from Mg nanoparticles in different solutions for 60 min. The solution concentration is 1 M. The JCPDS number for the phases indentified is: Mg 35-0821, $Ni(OH)_2$ 14-0117 and $Mg(OH)_2$ 44-1482.

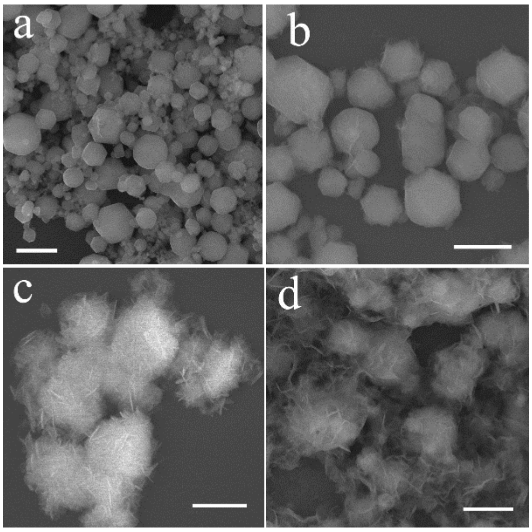

Figure S3 SEM images of the Mg nanoparticles after reaction in different solution: a) pristine Mg nanoparticles, b) 60 min in deionized water, c) 60 min in 0.1 M KCl solution, d) 5 min in 0.1 M $MgCl_2$ solution. Scale bar = 1 μm.

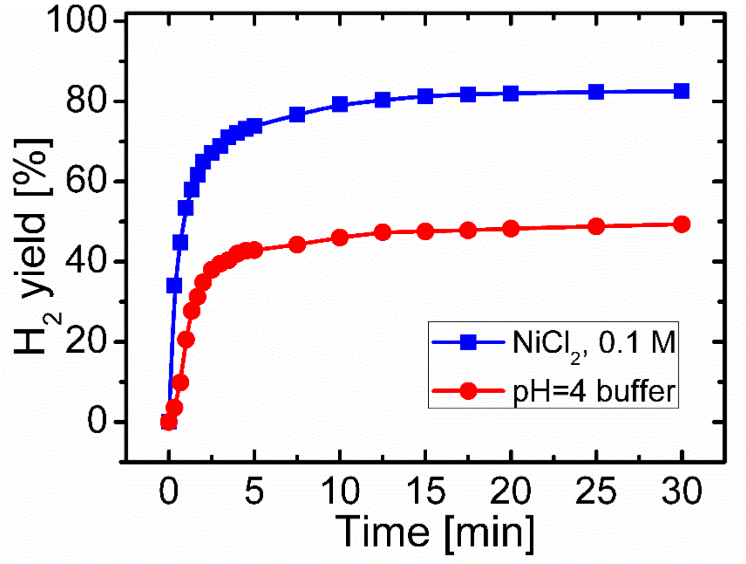

Figure S4 The H_2 generation kinetics from the reaction of Mg nanoparticles with 0.1 M $NiCl_2$ solution (initial pH = 5.0) and pH=4.0 buffer (benzene 1,2-dicarboxylic acid, mono passasium salt).

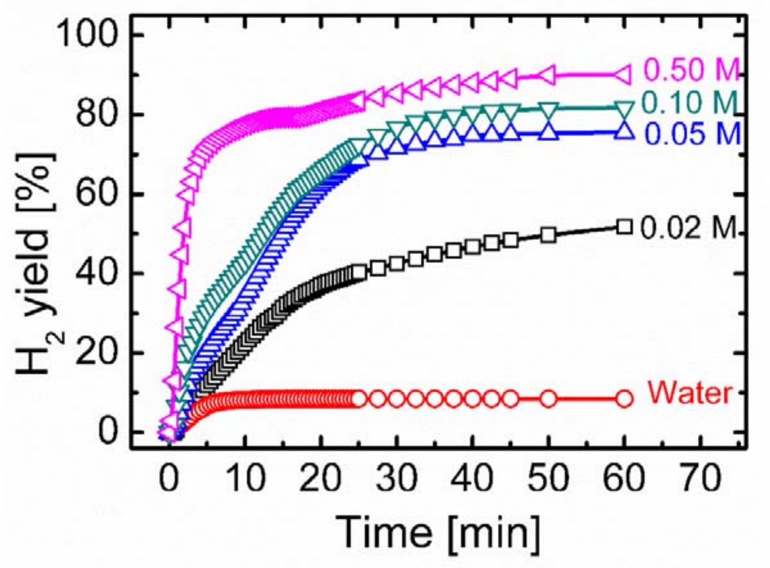

Figure S5 H_2 generation kinetics at 298 K from the reaction of Mg nanoparticles with $MgCl_2$ solution with different concentration.

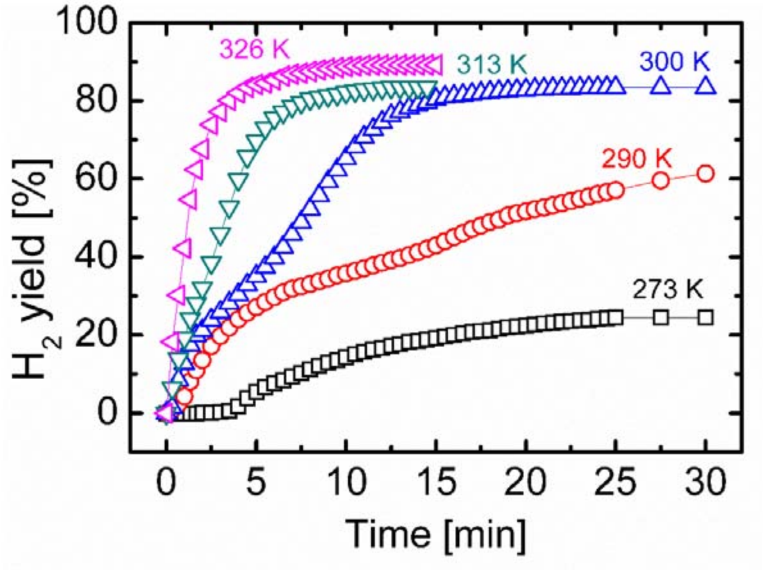

Figure S6 H_2 generation kinetics from the reaction of Mg nanoparticles with 0.1 M $MgCl_2$ solution at different temperature.