Electronic Supplementary Information

Electrochemical synthesis of ammonia directly from N_2 and water over iron-based catalysts supported on activated carbons

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Calculations

Thermodynamic electrolysis potentials for water splitting, oxide iron reduction to iron and ammonia synthesis with water are calculated from the unit activity thermochemical data for the individual species, using the convention to describe the positive potential necessary to drove a non spontaneous potential from the reactions: $\sum_{i=1\ to\ x} r_i R_i \rightarrow \sum_{i=1\ to\ y} c_i C_i$ using following equation 1-5:

$$E°(T)=-\Delta G°(T)/nF \tag{1}$$

$$\Delta G°(T)= \sum_{i=1\ to\ y} c_i\, G°(C_i,T) - \sum_{i=1\ to\ x} r_i\, G°(R_i,T) \tag{2}$$

$$G°(T)= H°(T) - TS°(T) \tag{3}$$

$$H°(T)-H°_{298.15}= A*t + B*t^2/2 + C*t^3/3 + D*t^4/4 - E/t + F - H \tag{4}$$

$$S°(T)= A*ln(t) + B*t + C*t^2/2 + D*t^3/3 - E/(2*t^2) + G \tag{5}$$

where

$E°(T)$——Electrolytic Potential at T (V);

T ——Temperature (K);

n——Transfer Electron Mole;

F——Faraday Constant(96485C/mol);

$\Delta G°(T)$——Standard Gibbs Free Energy Change at T (kJ/mol);

$G°(T)$——Standard Gibbs Free Energy at T (kJ/mol);

$H°(T)$——Standard Enthlpy at T (kJ/mol);

$S°(T)$——Standard Entropy at T (J/mol·K);

t——Temperature, T(K)/1000;

A~G ——Thermodynamic Parameters. Basic data is derived from NIST Chemistry WebBook.

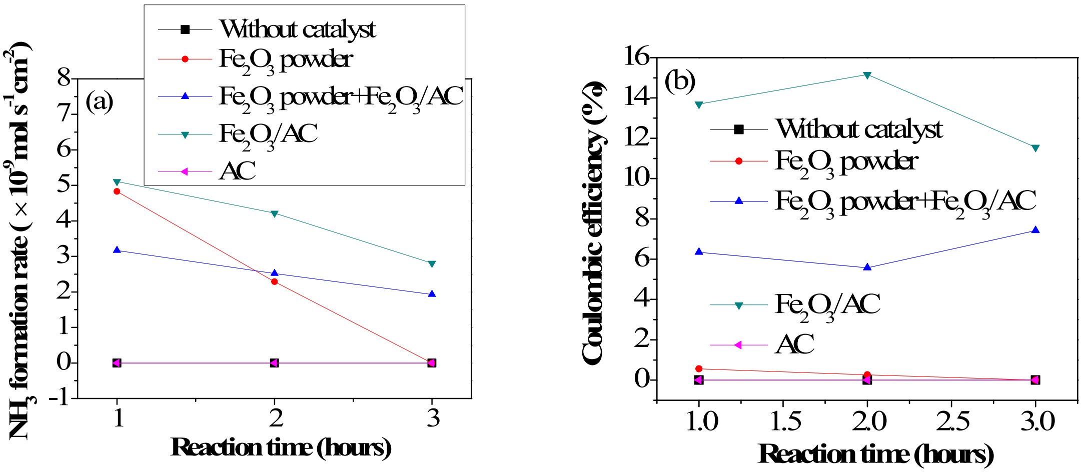

Fig. S1. The ammonia formation rate (a) and Coulombic efficiency (b) at 250◦C with different catalysts or without catalysts in wet N_2 when applied with voltage of 1.15 V.

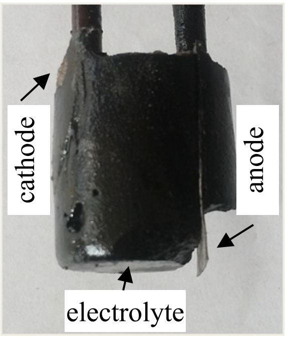

Fig. S2. Photograph of electrolyte containing Fe_2O_3/AC catalysts, cathode, and anode subsequent to electrolysis for 3 hours at a constant voltage of 1.15 V, cooling to room temperature and removing the crucible.

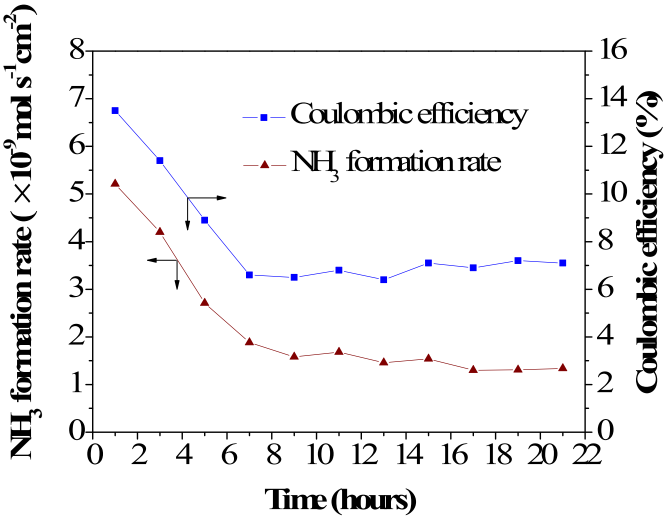

Fig. S3. The stability of ammonia formation rate and efficiency for the NH_3 electrolysis in wet N_2 in suspensions of Fe_2O_3/AC in a hydroxide electrolyte.

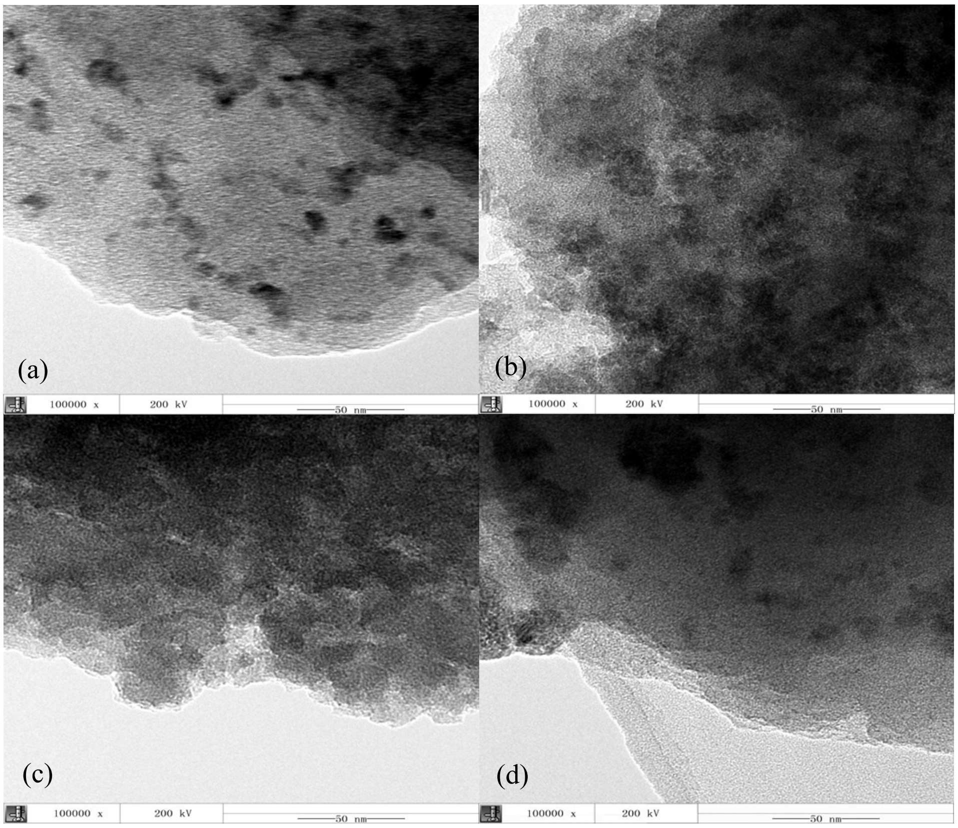

Fig. S4. TEM images of Fe_2O_3/AC (a) before electrolysis, (b) after 1hour electrolysis, (b) after 3 hours electrolysis, and (d) after 21 hours electrolysis.

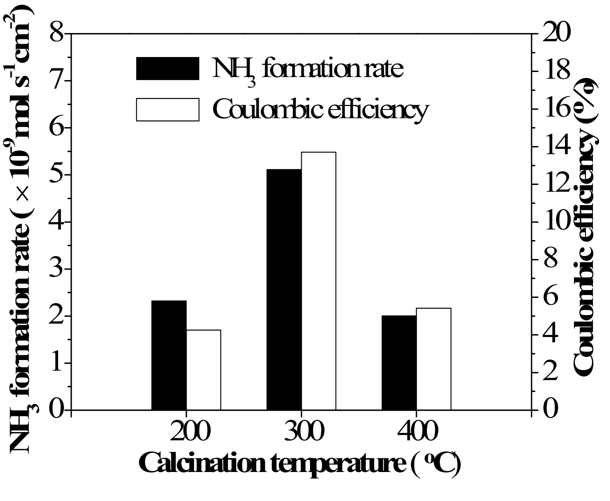

Fig. S5. The relationship between the ammonia formation rate or Coulombic efficiency and calcination temperature.

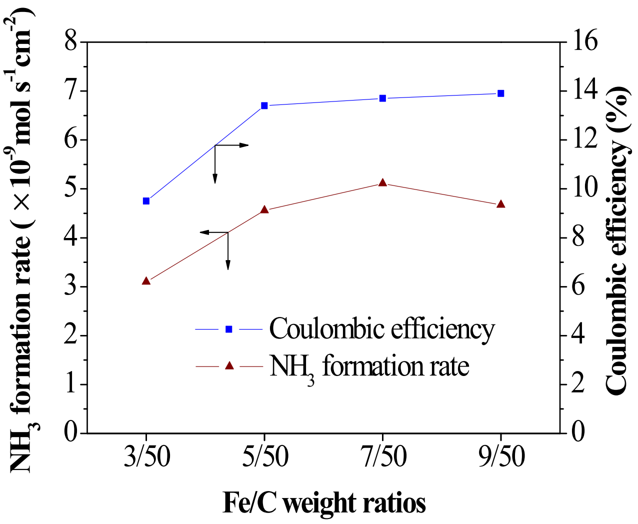

Fig. S6. Ammonia formation rate and Coulombic efficiency at different weight ratios of iron to activated carbon.