**Supplementary Information**

# Sandwich-like reduced graphene oxide/yolk-shell-structured Fe@$Fe_3O_4$/carbonized paper as efficient freestanding electrode for electrochemical synthesis of ammonia directly from $H_2O$ and nitrogen

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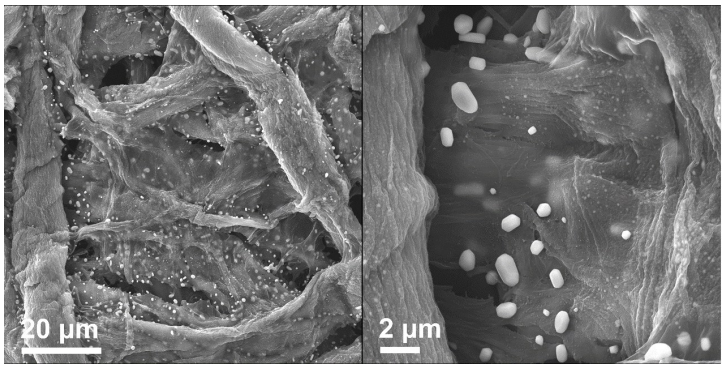


Figure S1. SEM images of Fe-rGO/CP.

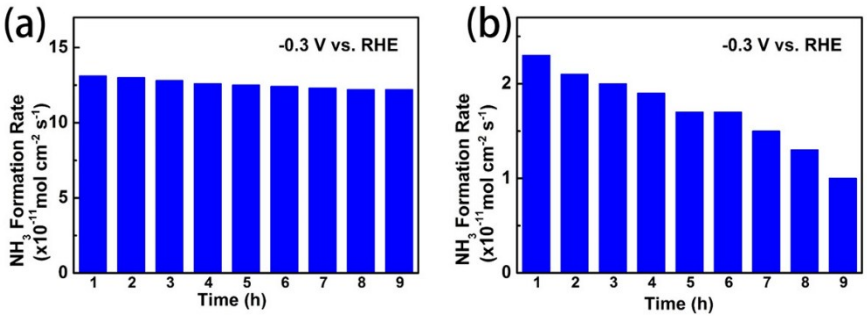


Figure S2. $NH_3$ formation rates of (a) rGO/Fe@$Fe_3O_4$/CP-1 and (b) Fe/CP in 9 hours.

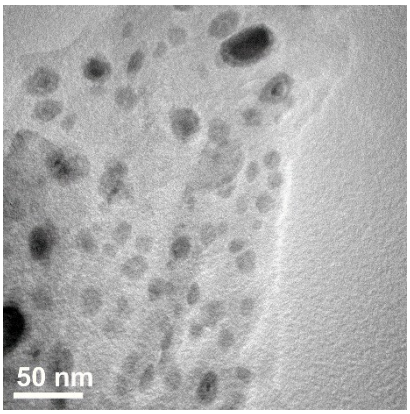


Figure S3. TEM image of rGO/Fe@$Fe_3O_4$/CP-1 after electrolysis.

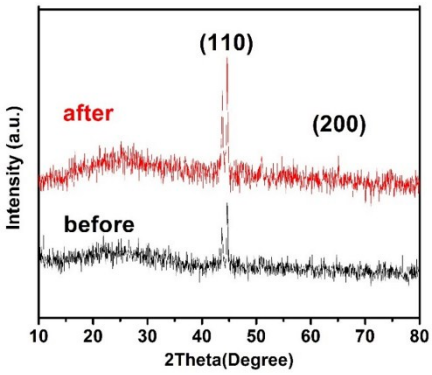


Figure S4. XRD patterns of rGO/Fe@$Fe_3O_4$/CP-1 before and after electrolysis.

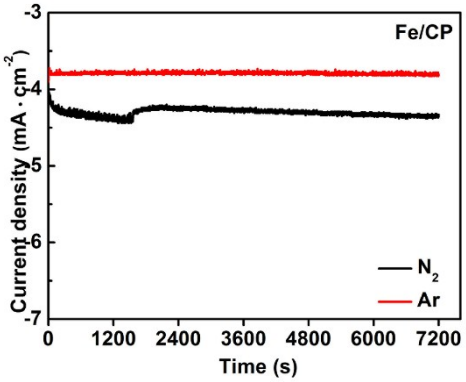


Figure S5. Current densities of Fe/CP in $N_2$ and Ar saturated electrolyte.

The method used for detection of low concentration ammonia was adapted from the standard methods for the examination of water and wastewater[1].

Apparatus: a spectrophotometer (Shimadzu UV-1800) was used at fixed wavelength ($\lambda$ = 420 nm) with a conventional 1 cm path length cuvette.

Regents used: Nessler's reagent, Auxiliary reagent: 50 g potassium sodium tartrate tetrahydrate dissolved in 100 ml boiled water and keep this solution in dark place, Standard ammonia solution.

Procedure: 10 mL of electrolyte was taken. Sterile syringe filters were used to filter the electrolyte to remove impurities. Then 200 μL of auxiliary reagent, 300 μL of Nessler's reagent were added in succession to the sample. After 10 minutes, absorbance measurements were

performed at λ = 420 nm. Series standard solutions of $NH_4^+$ were measured for calibration curve, which was used to calculate the concentration of ammonia. The measurements were repeated 3 times and the mean values were used as the final data.

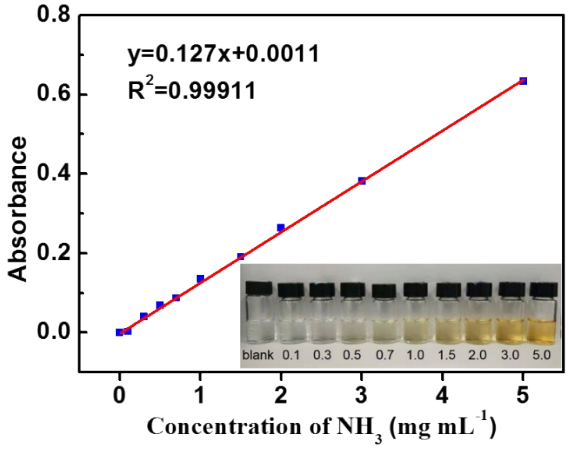


Figure S6. Calibration curve for colorimetric ammonia using Nessler's reagent.

Table S1. Comparison of studied NRR catalysts.

| T °C | Cathode/catalyst | Electrolyte | Reactants | Rate, mol $s^{-1}$ $cm^{-2}$ | FE, % | Ref. |
|---|---|---|---|---|---|---|
| 20 | Ru | 2 M KOH | $N_2/H_2O$ | $3.43\times10^{-13}$ (-1.1 V vs Ag/AgCl) | 0.28 | [2] |
| 25 | Pt/C | $Li^+/H^+/NH_4$ | $N_2/H_2$ | $1.14\times10^{-9}$ (1.6 V) | 0.55 | [3] |
| 250 | $Fe_2O_3$/AC | NaOH–KOH | $N_2/H_2O$ | $8.27\times10^{-9}$ (1.55 V) | 4.91 | [4] |
| 20 | $Fe_2O_3$-CNTs | Dilute $KHCO_3$ | $N_2/H_2O$ | $3.39\times10^{-12}$ (-2.0 V vs Ag/AgCl) | 0.15 at −1.0 V | [5] |
| 25 | Mo nanofilm | 0.5 M $H_2SO_4$ | $N_2/H_2O$ | $3.09\times10^{-11}$ (-0.5V) | 0.72 | [6] |
| 25 | ZIF-derived carbon | 0.1M KOH | $N_2/H_2O$ | $9.44\times10^{-10}$ (-0.3 V vs. RHE) | 10.2 | [7] |
| 25 | THH Au nanorods | 1 M KOH | $N_2/H_2O$ | $2.69\times10^{-11}$ (-0.2 V vs. RHE) | ~4.0 | [8] |
| 25 | Ni wire | 0.1 M LiCl/EDA | $N_2/H_2O$ | $2.15\times10^{-10}$ (1.8 V) | 17.2 | [9] |
| 25 | Amorphous Au on $CeO_x$/RGO | 0.1 M HCl | $N_2/H_2O$ | $1.28\times10^{-10}$ (-0.2 V vs. RHE, mol $s^{-1}$ mg $_{cat.}^{-1}$) | 10.1 | [10] |
| 25 | Au-$TiO_2$/Pt plate | 0.1 M HCl | $N_2/H_2O$ | $3.72\times10^{-10}$ (-0.2 V vs. RHE, mol $s^{-1}$ mg $_{cat.}^{-1}$) | 8.11 | [11] |
| 25 | N doped carbon | 0.05 M $H_2SO_4$ | $N_2/H_2O$ | $1.7\times10^{-10}$ (-0.9 V vs. RHE) | 1.5 | [12] |
| 25 | Iron-loaded carbon | 0.2 M $NaHCO_3$ | $N_2/H_2O$ | $1.3\times10^{-10}$ (0.3 V vs. RHE) | 6.25 | This work |

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