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Supplementary Information for

S-Doped Three-dimensional Graphene: A metal-free

Electrocatalyst for Electrochemical synthesis of Ammonia under

Ambient Conditions

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Figure S1. Pictures of the products at different stages (a) GO aqueous solution (b) Graphene hydrogels after water heats (c) S-3DG after drying



Figure S2. SEM of (a) Freeze-dried 3DG (b) Freeze-dried S-3DG



Figure S3. SEM of (a) 3DG (b) S-3DG (1 M Na₂S₂O₃) (c) S-3DG (2.5 M Na₂S₂O₃)



Figure S4. TEM of (a) 3DG (b) S-3DG (1 M Na₂S₂O₃) (c) S-3DG (2.5 M Na₂S₂O₃)



Figure S5. Raman spectrum of 3DG



Figure S6. TG of 3DG, S-3DG (1 M $Na_2S_2O_3$), and S-3DG (2.5 M $Na_2S_2O_3$)



Figure S7. SEM and EDS of S-3DG (2.5 M $Na_2S_2O_3$) After TG



Table S1 The element content of S-3DG after the TG Characterization



Figure S9. XPS spectra for 3DG in the (a) survey and (b) C 1s



Figure S10. XPS spectra for S-3DG (1 M $Na_2S_2O_3$) in the (a) C 1s and (b) S 2p



Figure S11. UV-vis absorbance spectra of electrolyte from different hours of use



Figure S12. UV-vis absorbance spectra of electrolyte from different concentration of Sulfur source S-3DG/CP 1 M $Na_2S_2O_3$ (black) and S-3DG/CP 2.5 M $Na_2S_2O_3$ (red)



Figure S13. UV-vis curves (a) and (b) concentration-absorbance curve of NH_4^+ ions solution with a series of standard concentration. The absorbance at 655 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with NH_4^+ ion concentration (y = 0.43102x + 0.00013365, $R^2 = 0.9999$).



Figure S14. UV-vis curves (a) and (b) concentration-absorbance curve of N_2H_4 solution with a series of standard concentration. The absorbance at 455 nm was measured by UV-vis spectrophotometer. The standard curve showed good linear relation of absorbance with N_2H_4 concentration (y = 0.36794x + 0.00518, $R^2 = 0.998$).