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High-efficiency Ammonia Synthesis via Electrochemical Nitrate Reduction over CeO₂/Fe₂O₃ Heterostructure





Ji Min Ahn, Jun Beom Hwang and Sanghan Lee*

Sustainable Energy and Electronic Devices Lab. (SEED) School of Materials Science and Engineering (SMSE) Gwangju Institute of Science and Technology (GIST)





Methods

Results

Summary

***** World Climate Crisis



Ref. BBC, What is climate change? A really simple guide





Ref. NASA Goddard Institute for Space Studies



Ref. For Earth, For Life, About Carbon Neutrality, Our Common Goal with the World

- World climate crisis
- → Rising global temperatures
- ➔ Rising sea levels
- → Changing ecosystem functions



Ref. hankyung article

Q&A

- New energy source
- → Hydrogen energy, Solar energy, Biomass ...





& low liquefying temperature & pressure

Essential chemical of industry and agriculture ٠



SEED

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♦ What is NRR and NO₃-RR?



It is imperative to develop electrocatalysts with high activity and selectivity.



Q&A

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Fe₂O₃ nanorod arrays by CeO₂ coating



Fe₂O₃

- + Abundance, stability, low cost
- + Strong electron-electron correlation and conductivity
 - Low selectivity
- Lack of active sites



+ Flexible transition between Ce³⁺ and Ce⁴⁺

Q&A

- + Efficiently regulation of oxygen vacancies
 - Low activity and selectivity









- 515 nm
- Intensity (arb. units) Intensity (arb. units) (012) A_{1g} (110) (104) ا Eg (300) (116)20 30 40 50 60 70 200 300 400 500 600 700 800 **2θ (°)** Raman shift (cm⁻¹)
 - Fe₂O₃ NRs were synthesized at 515 nm by hydrothermal method.
 - Both XRD and Raman clearly showed the peak of Fe₂O₃, confirming that the Fe₂O₃ NRs were well synthesized.



- TEM observations revealed that the CeO₂ NPs have a dodecahedron morphology and an uniform crystallite size of about 3 nm.
- TEM images of an CeO₂ show that the (002) and (111) directions are exposed and Powder XRD data reveals that the CeO₂ is polycrystalline.



Structural analysis: CeO₂/Fe₂O₃ heterostructure

< Energy Dispersive X-Ray Spectrometer (EDS) >



- The EDS image did not show that CeO₂ was distributed, as the size of CeO₂ was nano scale.
- The morphology of Fe₂O₃ remained unchanged, even after CeO₂ NPs coating,
- Even if Fe₂O₃/CeO₂ heterostructure is made through spin coating, it maintains nano size of CeO₂ NPs characteristics and is evenly dispersed.





- CeO₂ NPs are nano scale, so CeO₂ and CeO_{2-x} could not be identified in XRD spectra.
- In Raman spectra, both Fe₂O₃ and CeO₂ peaks show clearly at 465cm⁻¹, indicating that CeO₂/Fe₂O₃ heterojunction is well constructed.
- In Raman mapping, CeO₂ and CeO_{2-x} were present only at local sites.

10



Introduction	Methods	Results	Summary	Q&A

Sector Electrochemical measurement

< Linear Sweep Voltammetry (LSV) >



- Measure LSV and CA data in 0.1 M PBS + 0.1 M NaNO3 electrolyte using H-type cell
- Compared to the Fe₂O₃ sample, the onset potential of the CeO₂/Fe₂O₃ heterostructure sample was accelerated.





Ammonia quantitation (indophenol blue method)



- Through CA data, it can be confirmed that the stability of CeO₂/Fe₂O₃ heterostructure samples is also improved.
- Ammonia produced by the EC NO₃-RR reaction was quantitatively analyzed using the indophenol blue method.
- 12^{The calibration curve based on the UV-vis absorbance results showed a high accuracy of 99.6%. SEED}

Methods

Results







- ✓ Using 3-steps methods, we fabricated an
 CeO₂/Fe₂O₃ heterosturcture catalyst with potentials for NO₃⁻RR.
- ✓ XRD and raman spectra confirmed that the CeO₂/Fe₂O₃ heterojunction was well constructed.
- In the entire NO₃-RR mechanism, Fe₂O₃ affects the deoxygenation step, CeO₂ affects the hydrogenation step and shows good overall efficiency.
- ✓ As a Further work, we will calculate ammonia yield and FE to show that the NO₃-RR efficiency of this structure is improved.
- ✓ XPS will be measured to confirm that the oxygen vacancies of CeO₂ and CeO_{2-x} have a positive effect on the catalytic activity.

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Results

A&O



Thank you for your attention

jasmin2627@gm.gist.ac.kr





Proposed Reaction Mechanism for the NO₃RR to Ammonia

