Enhancing Water Oxidation with RuO_2–Graphene Composites for Economical Green Hydrogen Generation

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Green Industrial Futures
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Introduction

•The **hydrogen economy** plays a crucial role in decarbonizing sectors that are hard to electrify—like heavy industry, shipping, and aviation.
•**Hydrogen is clean at the point of use**, producing only water when used as a fuel.
•To meet global **net-zero targets by 2050**, we must shift from fossil-derived ("grey") hydrogen to **green hydrogen** made using **renewable-powered electrolysis**.
•**Water electrolysis** is a key technology for producing green hydrogen:
- Splits water into hydrogen and oxygen using electricity
- When powered by renewables (e.g., solar, wind), it is **zero-emission**

•Scaling up green hydrogen via electrolysis is essential to **cut CO_2 emissions**, stabilize energy systems, and enable **climate-resilient economies (Energy Harvesting and Systems, 11(1) 20220134, 2024, 1-28)**

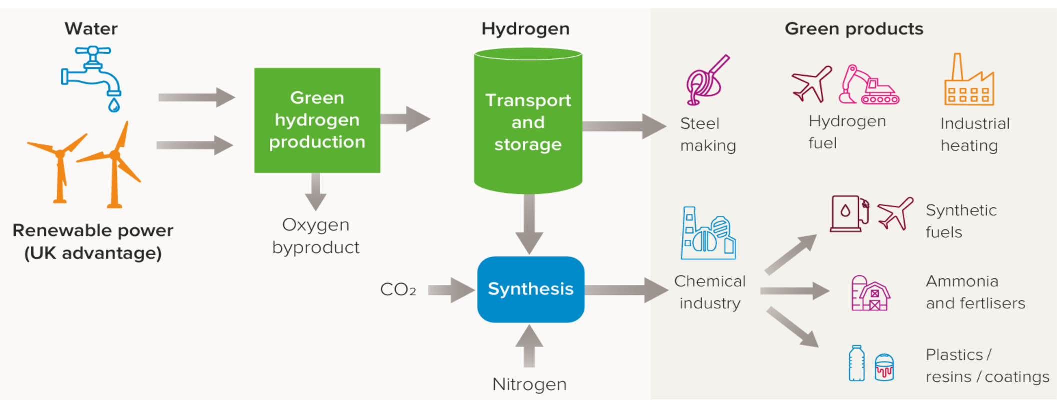


Figure 1. The complete green hydrogen value chain — from renewable inputs to final green products (Ref: Towards a green hydrogen roadmap for the UK – summary report, Royal Soceity, Sept. 2024).

Background

Electrolysis Water Splitting Oxygen and Hydrogen Generation

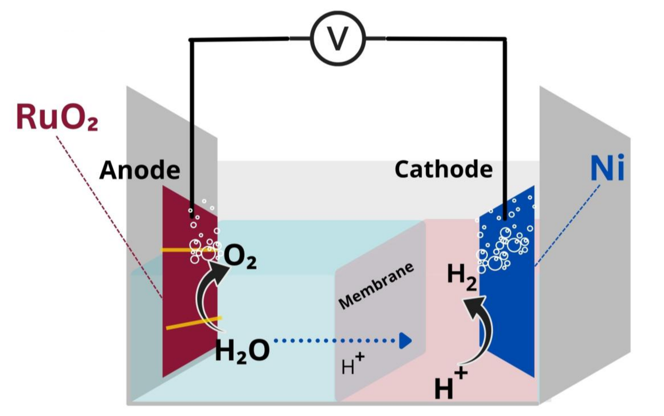


Figure 2. The electrolysis water splitting cells.

Why the Anode Matters in Electrolysis?

Oxygen evolution reaction (OER)

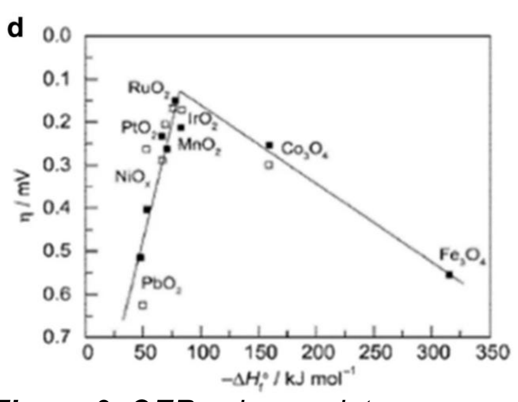
Anode: $H_2O \rightarrow 1/2O_2 + 2H^+ + 2e^-$

In water electrolysis, the anode drives the Oxygen Evolution Reaction (OER) — a slow, energy-intensive step that limits overall efficiency.
Improving anode performance is key to
(a) Lowering energy consumption, (b) Boosting hydrogen yield and (c) Enhancing long-term system durability

Hydrogen evolution reaction (HER):

Cathode: $2H^+ + 2e^- \rightarrow H_2$

Ruthenium Oxide (RuO2) Water Oxidation Catalysts



- High OER activity under acidic conditions
- Excellent electrical conductivity
- Good chemical stability in harsh electrolytic environments
- Well-suited for Proton Exchange Membrane (PEM) electrolysers

Figure 3. OER volcano plot.
(Ref: J. Electroanal. Chem. Interfacial Electrochem. 111, 1980, 125–131)

Challenges – RuO_2 Water Oxidation Catalysts

- High cost — Ruthenium is a rare and expensive platinum group metals (PGM)
- Ru dissolution under high anodic potentials
- Limited scalability due to cost and stability issues
- Material degradation affects long-term durability and performance

Research Focus

•**Reducing Ru content** using conductive additives like **graphene**
•**Nanostructuring** to increase active surface area
•**Composite design** for improved durability and cost-efficiency

Nano Energy, 2020, 78, 105185
Catalysis Science & Technology, 2018, 8(19), 4957-4974.
ACS Applied Nano Materials, 2020, 3(12), 12269-12277.

Objectives

•Develop and evaluate RuO_2 and RuO_2–graphene composite catalysts for acidic water electrolysis – solvothermal technique.
•Enhance catalytic activity while reducing the use of expensive RuO_2.
•Investigate the role of graphene in improving conductivity and lowering overall material cost.
•Benchmark electrochemical performance, durability, and cost-effectiveness for scalable hydrogen production.

Methodology

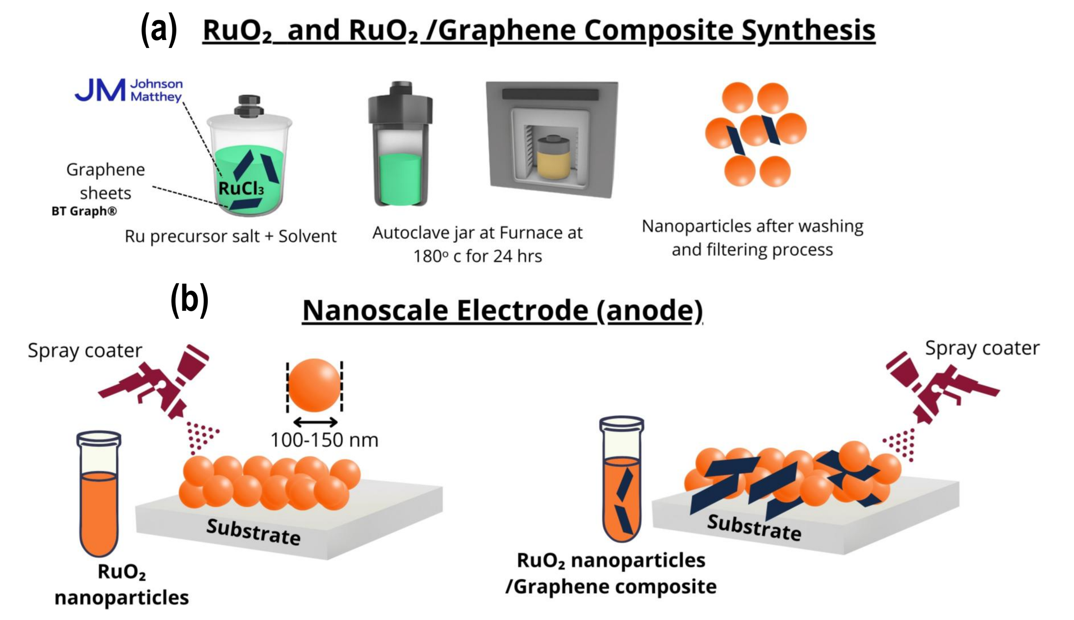


Figure 4. **(a)** Schematic of RuO_2 nanoparticles and RuO_2/graphene composite synthesis using a solvothermal method. **(b)** Fabrication of RuO_2 and RuO_2/graphene composite electrodes via spray coating onto carbon paper.

Results and Discussion

Surface Morphology Analysis

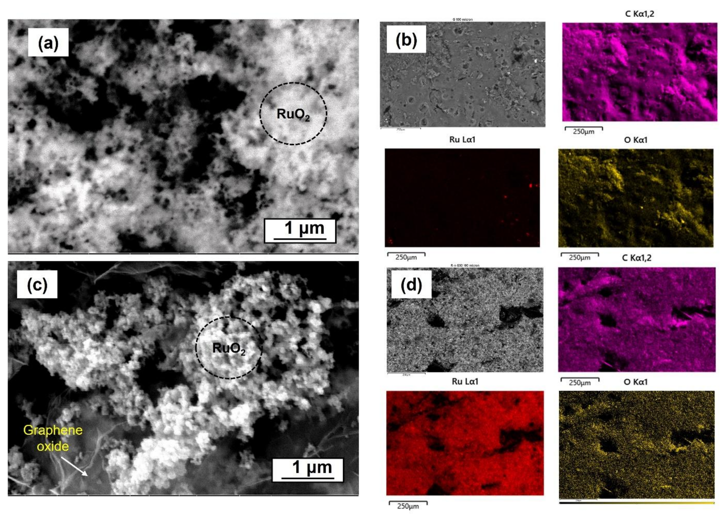


Figure 5. SEM images at 1 μm scale: (a, b) RuO_2-coated carbon paper and its elemental mapping (C, Ru, O); (c, d) RuO_2/graphene (50:50 wt%) composite coating and corresponding elemental mapping confirming C, Ru, and O distribution.

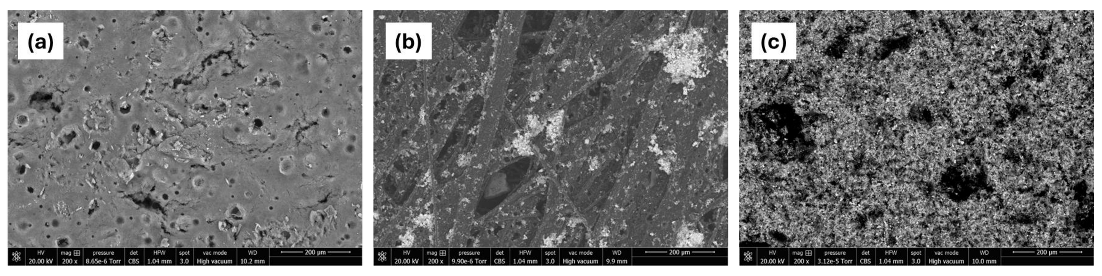


Figure 6. SEM images at 200 μm scale: (a,) carbon paper, b) RuO_2-coated carbon paper, and (c) RuO_2/graphene composite coated carbon paper.

•Uniform distribution of RuO_2 nanoparticles along carbon fibers.
•Good surface coverage and adhesion observed.
•RuO_2 nanoparticles: spherical, ~100–150 nm in size.
•Graphene sheets: larger, micron-scale lateral dimensions.
•Clear nanoscale integration of RuO_2 within graphene matrix.
•Graphene content leads to a more interconnected and rougher coating structure.

Electrochemical performance

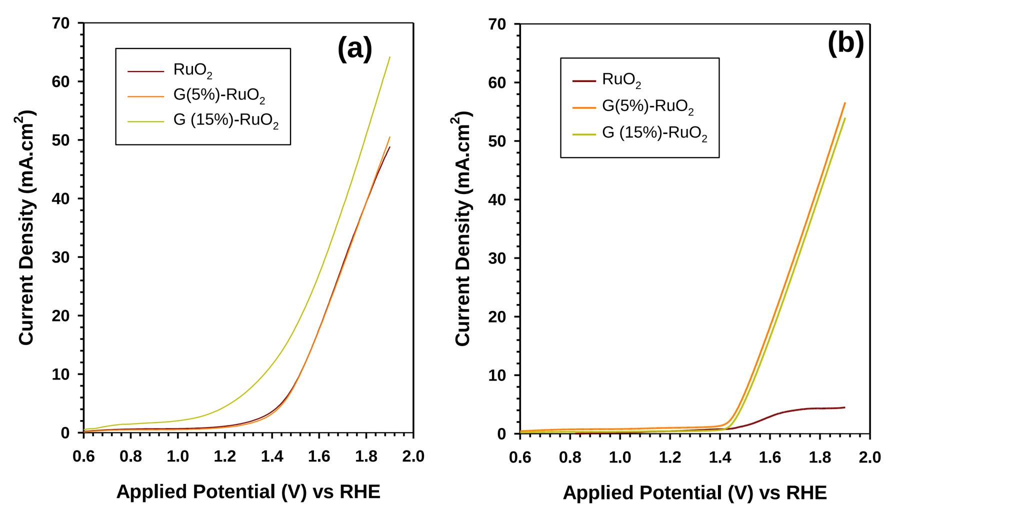
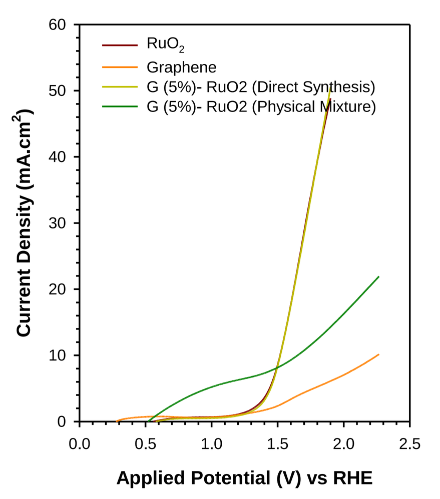


Figure 7. (a) and (b) show the linear sweep voltammetry (LSV) curves of RuO_2, G(5%)-RuO_2, and G(15%)-RuO_2 anodes recorded in 0.5 M H_2SO_4 before and after a 1-hour stability test, respectively.

Figure 7 (a) shows the LSV profiles of RuO_2, G(5%)-RuO_2, and G(15%)-RuO_2 anodes before a 1-hour stability test, where **G(15%)-RuO_2 exhibits the highest current density and the lowest onset potential**, indicating superior electrocatalytic activity for OER. In contrast, pristine RuO_2 shows the lowest performance. After the 1-hour stability test (Figure 7b), both G(5%)- and G(15%)-RuO_2 retain their activity with minimal loss, while RuO_2 demonstrates significant degradation. These results confirm that graphene incorporation not only enhances the OER activity but also significantly improves the electrochemical durability of RuO_2 in acidic media.



The comparison highlights (Fig.8) the influence of synthesis route on the electrocatalytic performance toward the oxygen evolution reaction (OER) in 0.5 M H_2SO_4. The G(5%)-RuO_2 prepared by **direct synthesis exhibits higher current density** and lower onset potential, indicating improved activity compared to both the physically mixed counterpart and pristine RuO_2.

Figure 8. Comparative LSV analysis of direct and indirect synthesis of RuO_2 and Graphene-RuO_2 composite

Results and Discussion - Continued

Tafel plots

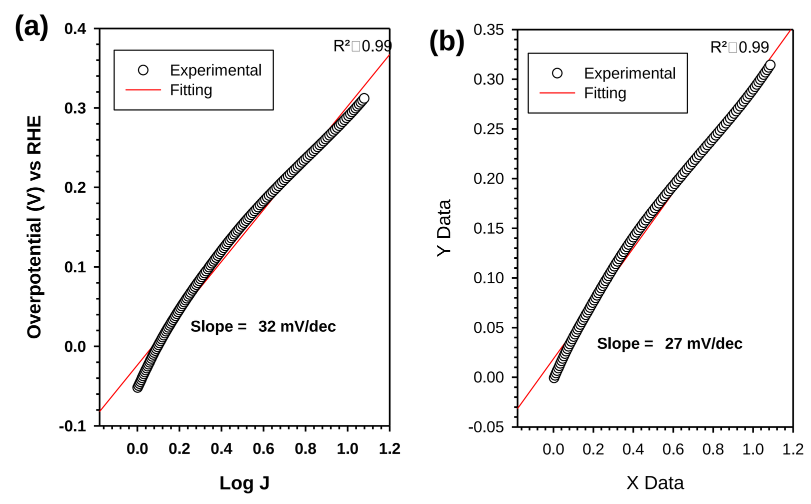


Figure 9. (a) Tafel plots of RuO_2 and (b) RuO_2/Graphene composite.

The Tafel slope is a key electrochemical parameter used to assess the kinetics of electrochemical reactions, especially the OER & HER in water splitting. It is derived from the Tafel equation: **$\eta = a + b.\log(j)$**
η = overpotential (V); j = current density (mA/cm²); b = Tafel slope (mV/dec); a = intercept (related to exchange current density) **(Nano Convergence, 8(1), 2021, 1-23)**

- The Tafel slope is the number of mVs required to increase the current by a factor of 10 (mV/dec). Low Tafel slopes are desired as it's an indication of an active catalyst, as a small overpotential is needed to reach high current densities **(Nano Convergence, 8(1), 2021, 1-23)**
- From Figure 9, it shows that RuO_2-Graphene composites have faster electrocatalytic reaction kinetics when comparing pure RuO_2 nanoparticle. Also, the slope values of the RuO_2/Graphene composite is lower than 24 mV/dec the other reports in the literature (RuO_2: 54 mV/dec & RuO2/Graphene: 30 mV/dec) **(Journal of Materials Chemistry A, 9(28), 2021, 15506-15521)**

Charge transfer resistance (Nyquist Plots)

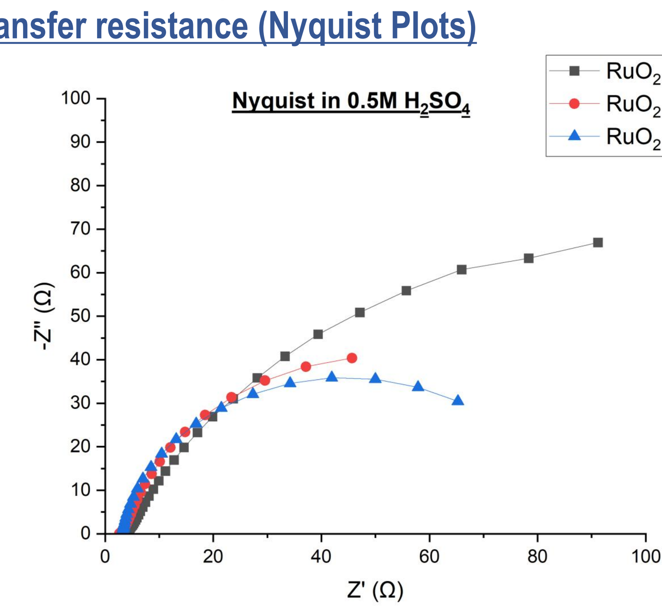


Figure 8. Nyquist plots of (a) RuO_2 and (b) RuO_2/graphene composite electrodes, measured in 0.5 M aqueous H_2SO_4 at open-circuit potential (OCP).

- The Nyquist plots presented show the electrochemical impedance spectra of pristine RuO_2, RuO_2 G5, and RuO_2 G15 in 0.5 M H_2SO_4. The semicircle diameter in the high-frequency region corresponds to the charge transfer resistance (R_{ct}), which is an indicator of the ease with which electrons are transferred at the electrode/electrolyte interface.
- Among the three, **RuO_2 - G15** (blue triangles) exhibits the **smallest semicircle**, indicating the **lowest charge transfer resistance** and thus the **fastest electron transfer kinetics. RuO_2 G5** (red circles) shows an intermediate R_{ct}, while **pristine RuO_2** (black squares) has the largest semicircle, corresponding to the highest resistance and poorest conductivity.

Conclusion

- RuO_2 and RuO_2–graphene composites were successfully synthesized via a solvothermal method, producing nanoparticles sized between 100–150 nm. Their electrochemical performance was evaluated as anodes for water splitting, focusing on the oxygen evolution reaction (OER) in acidic media.
- Graphene incorporation significantly improved the electrocatalytic activity of RuO_2. G(15%)-RuO_2 showed the highest current density and lowest onset potential before stability testing, indicating excellent initial performance. After a 1-hour stability test, both G(5%)- and G(15%)-RuO_2 retained their activity with minimal loss, while pure RuO_2 showed notable degradation.
- The composite synthesized via direct solvothermal route outperformed the physically mixed version, underscoring the importance of synthesis approach. Nyquist plots confirmed lower charge transfer resistance for G(15%)-RuO_2, indicating better conductivity and faster electron transfer. Tafel slope analysis also showed improved reaction kinetics and lower overpotentials for the composites.
- Overall, graphene integration enhances performance, **reduces Ru usage**, and supports the development of cost-effective, durable catalysts for green hydrogen production in acidic electrolyzers.

Acknowledgements

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