

Graphene/ZnO/Cu₂O catalyst for highly selective CO₂ electroreduction in aqueous solution to isopropyl alcohol

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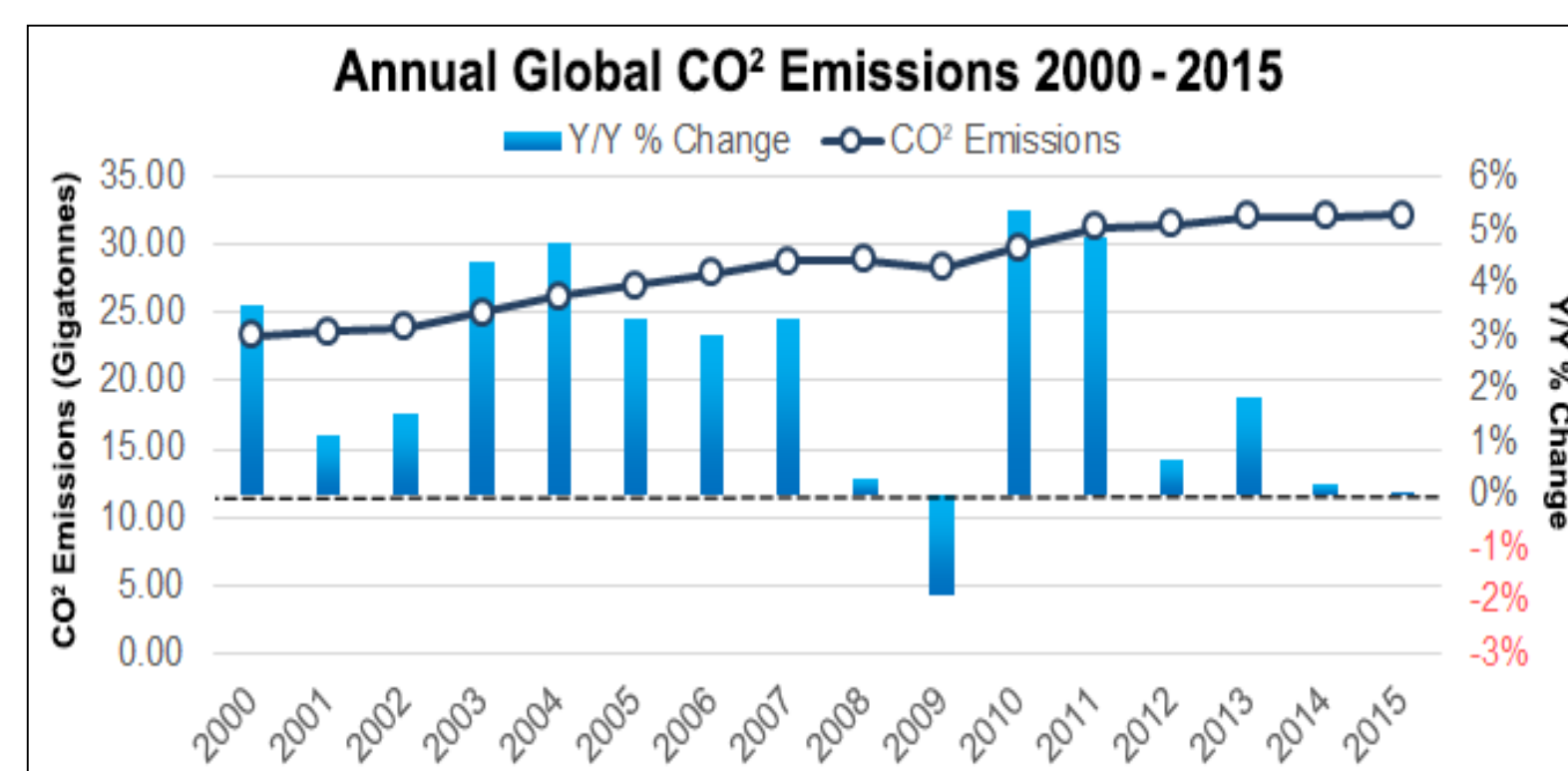
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Why CO₂??

- Carbon dioxide is the major greenhouse which contributes significantly to the global warming.¹⁻³
- Air pollution cause a thousands additional deaths and many cases of respiratory illness and asthma.



Preserving our ecosystem

- CO₂ is a typical renewable feedstock for manufacturing valuable chemicals.
- Electrochemical method is a promising for CO₂ conversion to valuable chemicals.⁴
- Efficient electrocatalyst should be developed for efficient and selective desired product.

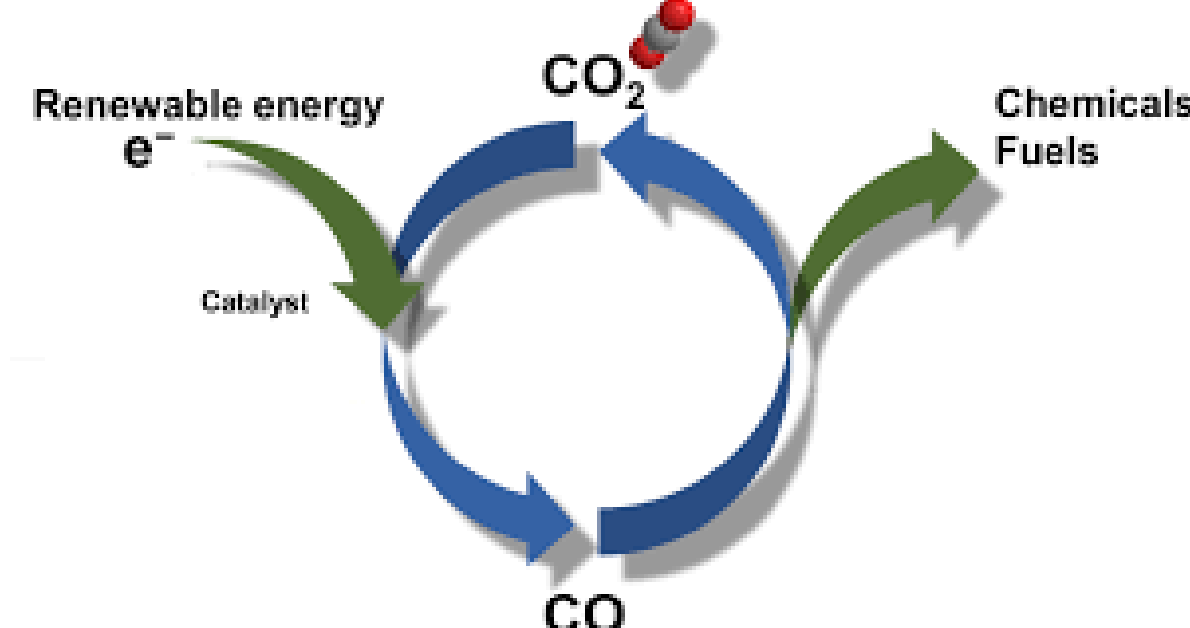
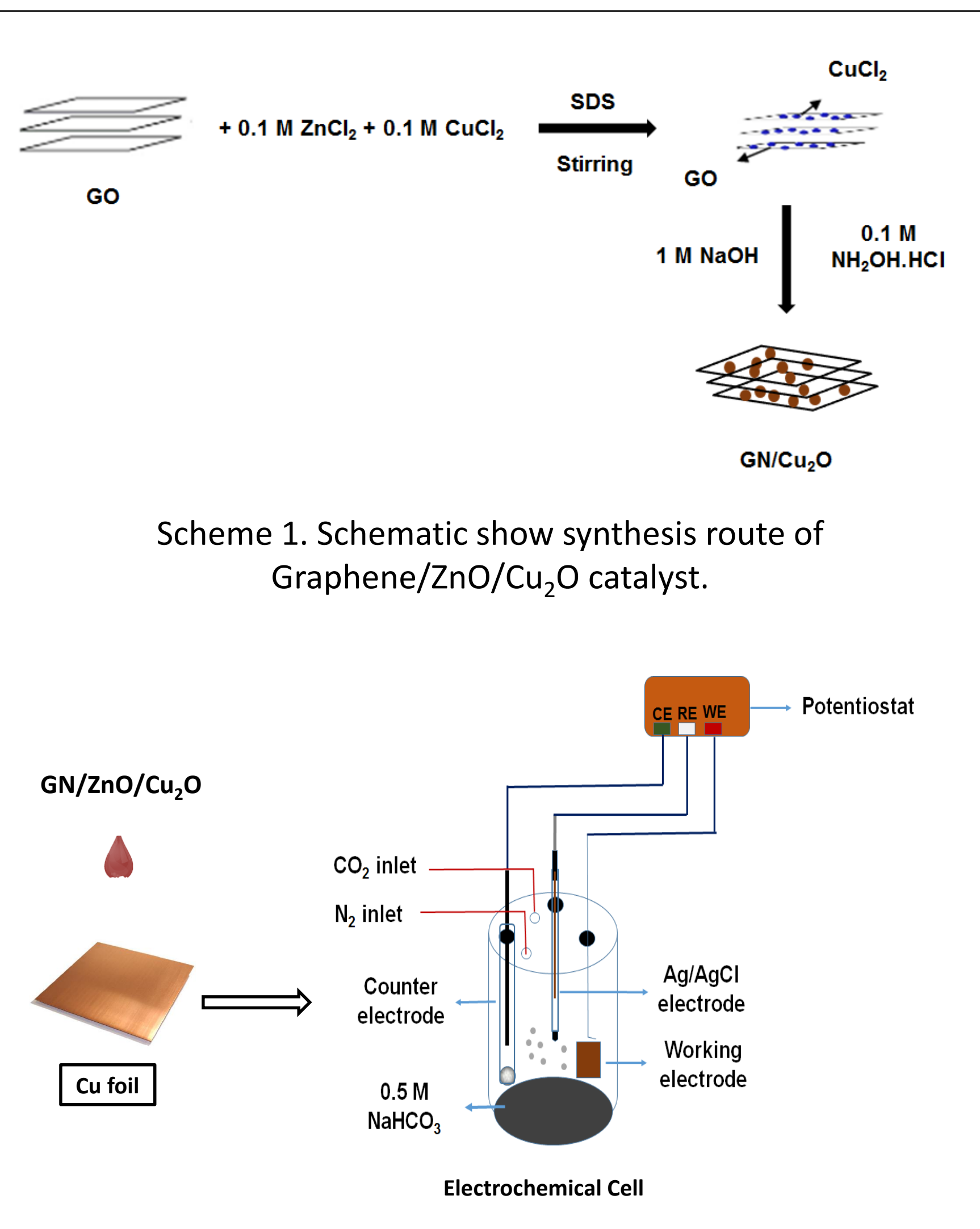


Fig. 1. Design electrocatalyst to reduce CO₂ to value-added chemicals.

Synthesis of catalyst



Characterization

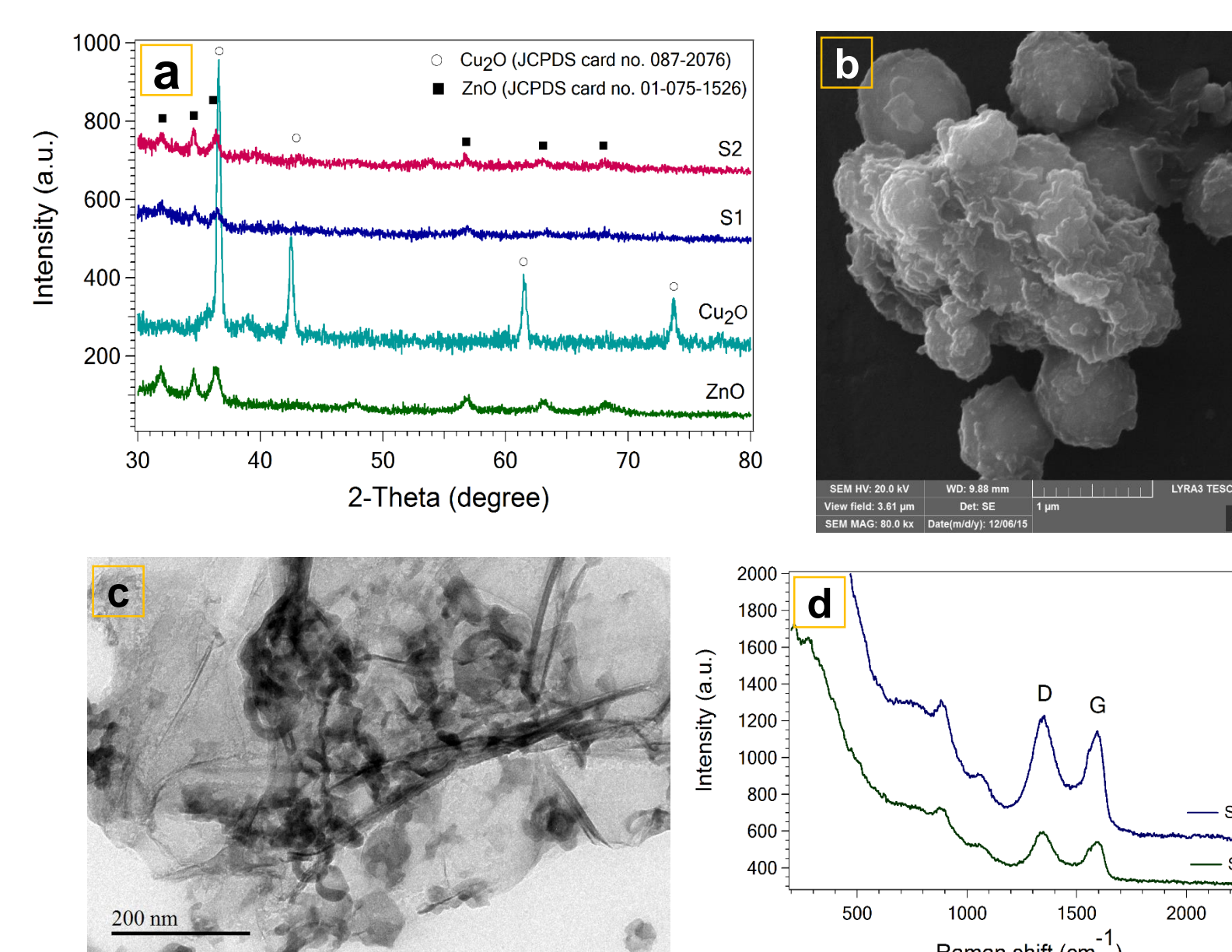


Fig. 2. (a) XRD patterns of GN/ZnO/Cu₂O composites. (b) SEM and (c) HR-TEM images of S2 composite. (d) Raman spectra of S1 and S2 composites showing the intensity ratio of D & G bands.

- S1 → ZnO/Cu₂O weight ratios of 2:1
- S2 → ZnO/Cu₂O weight ratios of 1:2

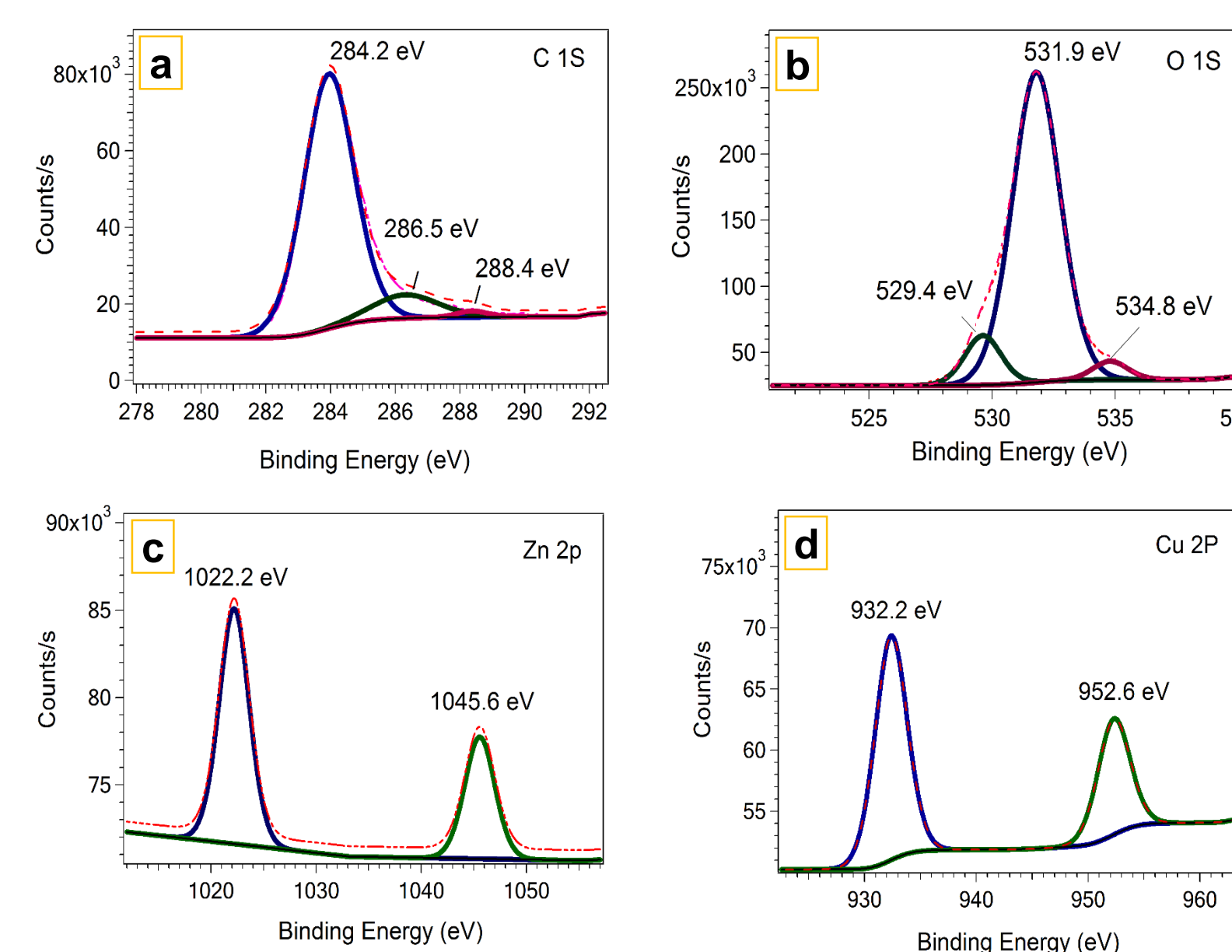


Fig. 3. XPS spectra of S2 catalyst: (a) C 1s scan, (b) O 1s scan, (c) Zn 2p scan, (d) Cu 2p scan after 90 sec etching.

- C 1s peaks at 284.2, 286.6, and 288.4 eV were attributed to C-C, C-O, and C=O bands, respectively. O 1s binding energies at 529.6, 531.9, and 534.8 eV (Fig. 3b), peaks characteristic of Zn-O, OH, and C-O bands, respectively.
- Peaks at 1022.2 and 1045.6 eV were assigned to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively which agree with the Zn (II) oxidation state for ZnO.
- Moreover, a peak characteristic of Cu 2p_{3/2} of the Cu (I) oxidation state at 932.2 eV.

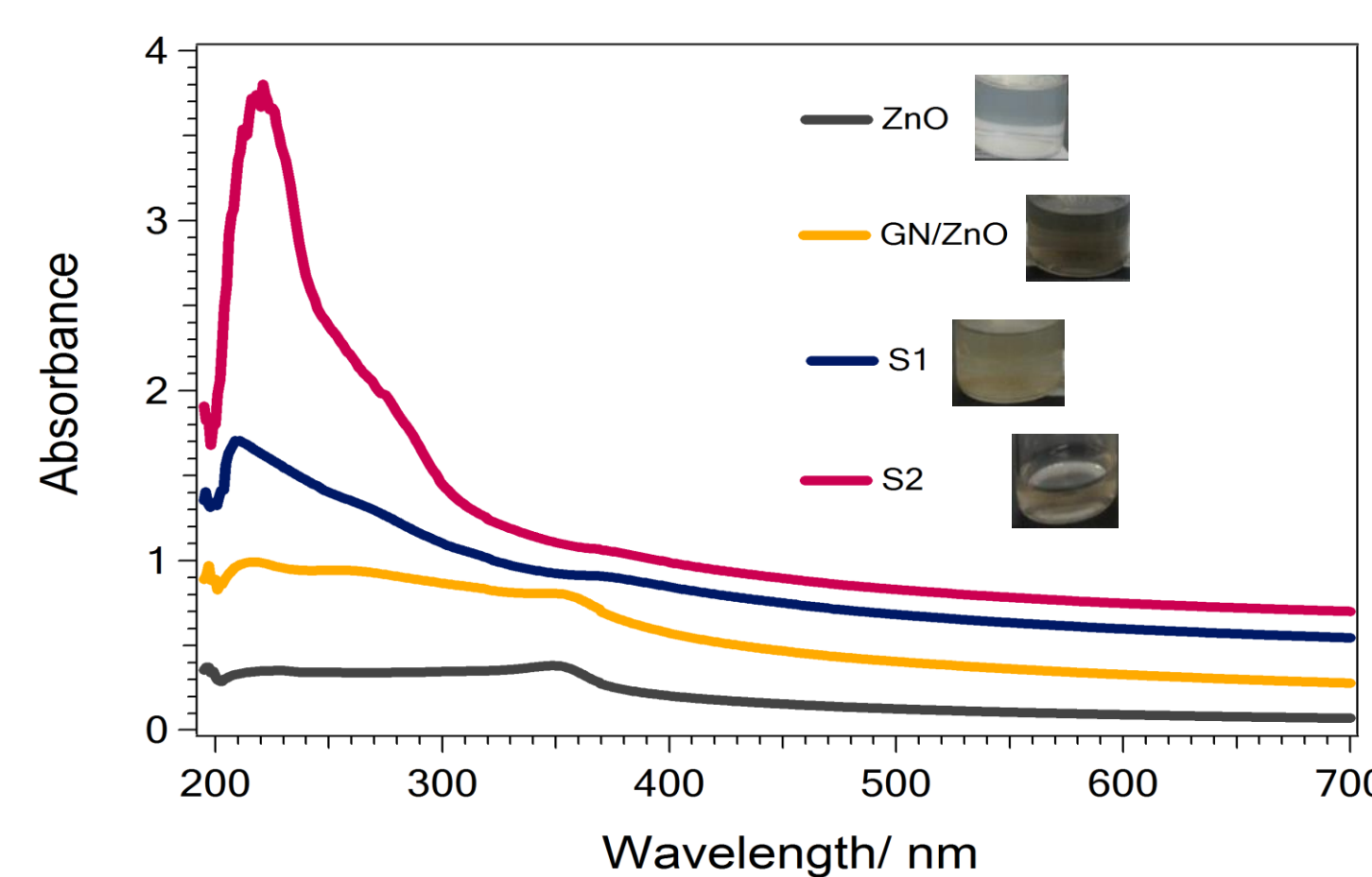


Fig. 4. UV-vis absorption spectra of as-prepared ZnO, GN/ZnO, and GN/ZnO/Cu₂O catalysts.

- The effect of introducing Cu₂O into GN/ZnO appeared as broadening peak covers the range from 200 to 300 nm.⁵

Electrochemical activity

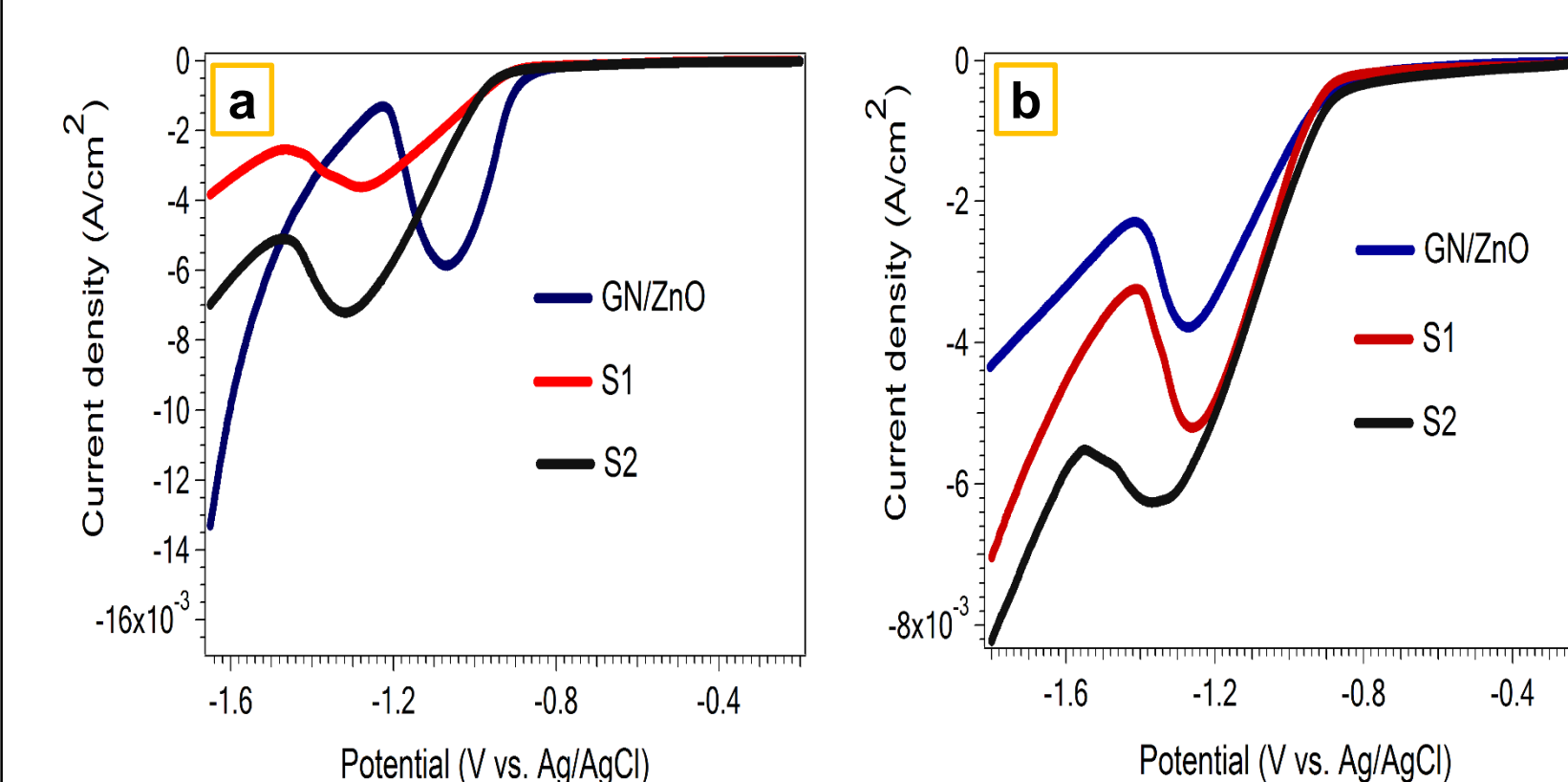


Fig. 5. LSV curves of GN/ZnO/Cu₂O catalysts under (a) N₂ and (b) CO₂ saturated 0.5 M NaHCO₃ solution (pH= 7.25) at scan rate of 20 mV/s.

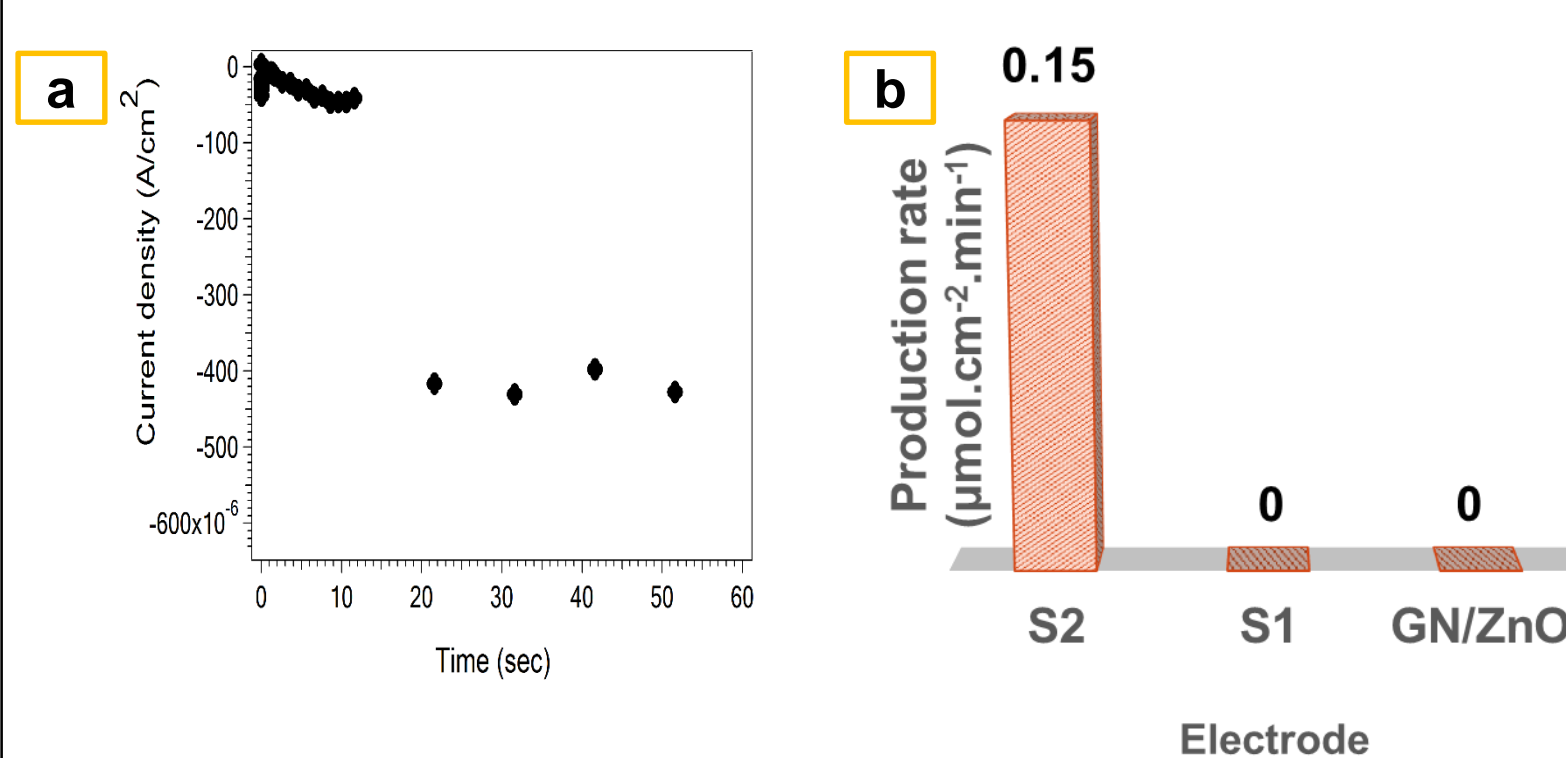


Fig. 6. (a) Current responses for S2 electrode at -1.2 V in CO₂-saturated electrolyte for 1 min reduction. (b) Concentrations of isopropyl alcohol obtained.

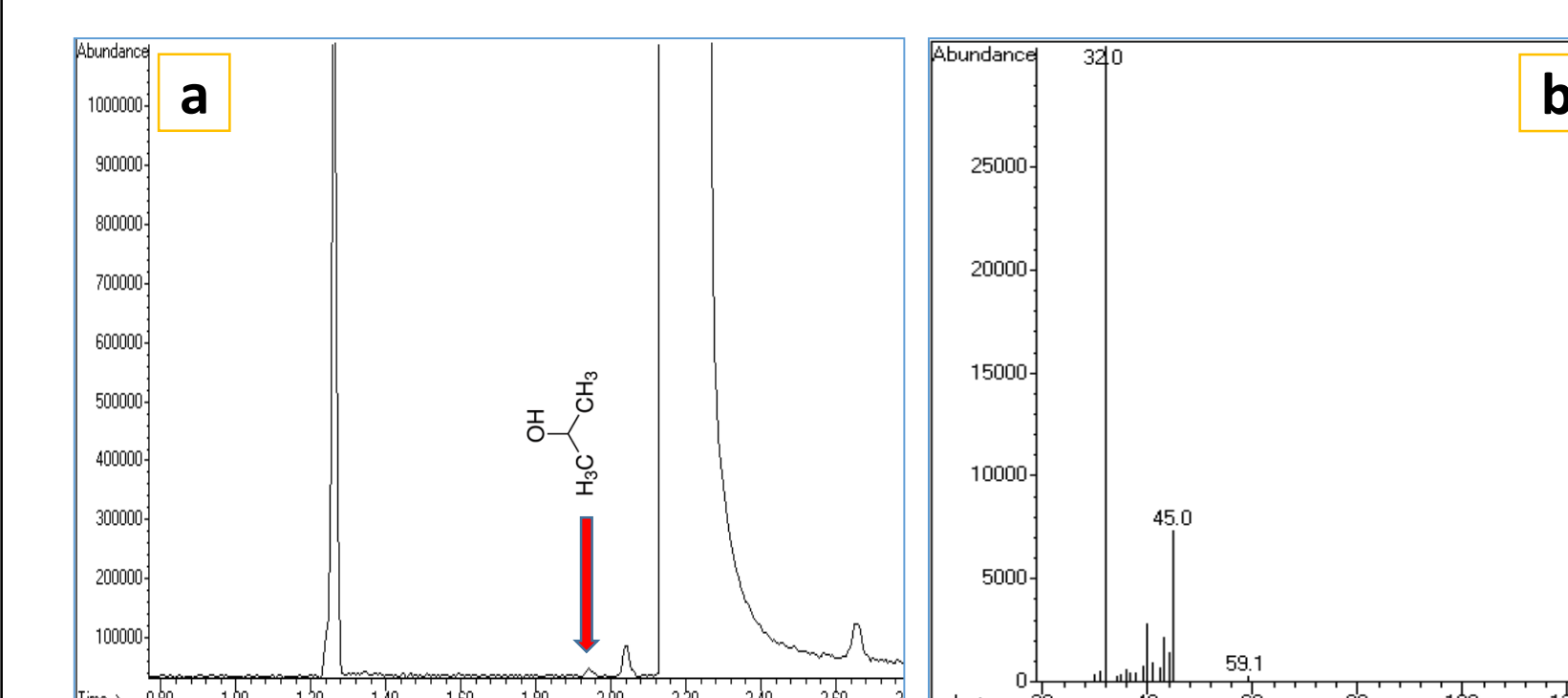


Fig. 7. (a) GC-MS chromatogram shows isopropyl alc. (red arrow) at RT= 1.94 min after 1 min reduction at -1.2 V vs. Ag/AgCl over S2 surface. (b) Mass spectra show defragments of isopropyl alc.

- Cu (I) stabilized by ZnO and stabilizing the link between active sites and CO⁻, and thus result in coupling reactions of C₁ species.⁶
- Graphene increases the high surface area and enhance the electron mobility causing more reduction of CO⁻ adsorbed species, leads to C₃ product.

Conclusion

- Linear sweep voltammetry indicates that, the current increase upon increasing Cu₂O/ZnO weight ratio
- Graphene/ZnO/Cu₂O (Cu₂O/ZnO weight ratio of 2:1) electrode showed excellent catalytic activity and selectivity towards CO₂ reduction to isopropyl alcohol.
- These results suggest that graphene-based catalyst can be efficiently used for CO₂ reduction.

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