

Synthesis of Copper Ferrite (CuFe_2O_4) doped 3D Reduced Graphene Oxide-Based Solar Absorber for Solar Desalination of Saline Water

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Water scarcity is the current global challenge that is expected to worsen due to rapidly advancing industrialization, urbanization, and resource-intensive economic development. To tackle this issue, it is essential to produce and deploy sustainable, cost-effective solar-powered desalination technologies utilizing advanced materials. One particularly promising technology for sustainable freshwater supply is solar-driven interfacial desalination, which utilizes photothermal materials to transform solar energy into heat at the air-water interface, minimizing heat loss to the surrounding water and improving overall efficiency. Reduced graphene oxide (rGO)-based hybrid photothermal materials have proven to be effective for a range of solar-driven applications, including water desalination and energy storage, owing to their remarkable conductivity, broadband solar absorption capabilities, and adjustable bandgap. When combined with copper ferrite (CuFe_2O_4), the 3D rGO-based hybrid material harnesses distinct strengths of both components, synergistically enhancing its solar-to-thermal energy conversion potential. CuFe_2O_4 is a notable p-type semiconductor metal oxide with a relatively narrow band gap (~ 1.4 eV), able to effectively absorb a broadband range of sunlight and convert it into heat, making it well-suited for solar-to-thermal energy conversion applications.

In this study, CuFe_2O_4 -doped 3D reduced graphene oxide (rGO) was synthesized via a two-step process involving coprecipitation followed by hydrothermal reduction. The resulting 3D rGO-based composite demonstrated outstanding efficiency in freshwater generation, achieving up to $1.51 \text{ kg m}^{-2} \cdot \text{h}^{-1}$ with a remarkable photothermal conversion efficiency of $\sim 110\%$ under 1 sun solar illumination. The SEM, FTIR, and UV VIS NIR characterization techniques confirmed a highly porous structure, with a uniform distribution of CuFe_2O_4 within the matrix and strong solar absorption in both the near-infrared (NIR) and mid-infrared (MIR) regions. The 3D macroporous structure facilitates multiple light reflections, leading to superior light absorption, while also increasing the surface area and providing more active sites for water evaporation and heat absorption. These findings highlight the 3D rGO based material's potential for high efficiency photothermal applications and its promising role in sustainable freshwater generation.

Key words: Solar desalination, CuFe_2O_4 -doped 3D rGO, solar driven interfacial desalination

1. Introduction

Water scarcity is one of the greatest global challenges, likely to surpass supply by more than 40% by 2030 and by more than 50% in the developing countries, exacerbated by rapid population growth, economic advancement, and mechanised farming. Although water is abundant on Earth, covering 71% of the planet's surface, its high salinity makes seawater unsuitable for direct use without treatment (Mulwa and Fangninou, 2021; Dolan et al., 2021). As a result, desalination has emerged as a vital solution to tackle freshwater shortages. However, conventional desalination methods, including membrane-based and thermal based desalination technologies, that are commonly employed are both energy- and cost-intensive. These methods often depend on fossil fuels, leading to environmental concerns and increasing overall energy consumption (Al-Obaidi et al., 2024). Although

desalination technologies appear to be mature enough to provide a stable source of freshwater from the sea, intensive research and development have been conducted in order to continuously improve these technologies by reducing their cost of desalination and making them more reliable, efficient, and sustainable.

Conventional solar-driven desalination technologies have been implemented in various parts of the world; however, they suffer from low efficiency and poor performance due to the heating of the entire non-evaporative water body, which results in low energy efficiency and productivity. In recent years, solar-driven interfacial desalination has garnered increasing attention as a promising alternative to conventional methods. This technology uses solar energy for interfacial heating, localized heating at the air-water interface thus decreasing the loss of heat and enabling efficient and sustainable freshwater generation potential (Thoai et al., 2021). Solar driven interfacial desalination stands out for its high efficiency and eco-friendly approach, offering a viable solution to reduce the environmental footprint and energy demands associated with traditional desalination processes. This method improves photothermal performance by up to 100% and beyond owing to the efficient energy management and energy recycle (Liang et al., 2024).

Interfacial desalination technology consists of three key components: a photothermal material designed for efficient solar energy absorption and conversion, which then heats the evaporative water; a substrate or insulator that ensures effective water transfer to the evaporative body while preventing heat loss to the non-evaporative water body; and an enclosure around the evaporative body to minimize convective and radiative heat loss to the environment (Wang et al., 2023; Bezza et al., 2024). The photothermal material, or solar absorber, plays a central role in the interfacial desalination process. Various types of photothermal materials have been developed, including carbon-based materials, metallic or nanometallic substances, and plasmonic nanoparticles that utilize the plasmonic heating effect. Solar irradiation is divided into three regions based on wavelength: the ultraviolet region (300–400 nm, 7%), the visible region (400–700 nm, 43%), and the near-infrared region (700–2500 nm, 50%) (Gueymard, 2004). To fully harness sunlight, one of the primary challenges is designing solar absorbers with strong broadband absorbance that can span the entire solar spectrum (Nawaz et al., 2021).

Copper-based transition metal oxides, particularly the p-type copper ferrite, CuFe_2O_4 , have garnered significant attention for their efficient photocatalytic and photothermal properties. Their excellent solar absorption is attributed to a small band gap of 1.5 eV, enabling superior solar absorption and photothermal performance (Ibrahim et al., 2021). Additionally, $\text{Cu}_x\text{Fe}_{3-x}\text{O}_4$ is notable for its n-type semiconducting properties and its capacity to form nanocomposite thin films with CuO. By varying the Cu and Fe content, the material's conductivity can be extensively tuned, transitioning from n- to p-type behavior (Chapelle et al., 2011). Graphene, a highly conductive material, is widely used in solar desalination due to its excellent electrical conductivity and remarkable ability to absorb solar energy. Composed of a single layer of carbon atoms arranged in a honeycomb lattice, graphene boasts a large specific surface area, superior thermal conductivity, outstanding chemical stability, and exceptional mechanical strength. However, its hydrophobic nature and tendency to restack limit its practical applications. A promising derivative, reduced graphene oxide (rGO), overcomes these limitations by enhancing hydrophilicity and functionality. Reduced graphene oxide (rGO) is produced by oxidizing graphite followed by reduction, introducing oxygen-containing groups that improve its hydrophilic properties while retaining the core characteristics of graphene, making it suitable for a variety of applications (Othman et al., 2019). Furthermore, the development of three-dimensional solar absorbers capable of efficiently capturing solar irradiation across a broad spectrum and effectively utilizing the generated heat through 3D morphology-assisted multiple reflection represents a crucial innovation to overcome current challenges (Thoai et al., 2021; Wang et al., 2023; Liang et al., 2024). In this study, 3D CuFe_2O_4 -doped reduced graphene oxide (rGO) was synthesized, and its potential application for interfacial desalination was investigated.

2. Materials and Methods

2.1 Synthesis of CuFe_2O_4 doped 3D rGO

In this study, 3D CuFe_2O_4 -rGO nanocomposites, comprising 10% CuFe_2O_4 and 90% GO by weight, was synthesized using a hydrothermal reduction technique. The preparation process involved two main steps. First, graphene oxide (GO) was prepared using Tour's method (Bezza et al., 2024). Second, CuFe_2O_4 nanoparticles were synthesized through a sonochemical-coprecipitation technique in a basic medium, utilizing CuSO_4 (4.2 mmol) and FeCl_3 (9.3 mmol) as described by (Rajput et al., 2015). The synthesized GO and CuFe_2O_4 nanoparticles were then mixed, ultrasonicated, and subjected to hydrothermal reduction for 16 hours. The resulting product was freeze-dried and used for the desalination experiment as previously explained elsewhere (Bezza et al., 2024).

2.2 Photothermal solar driven interfacial desalination test

Solar-driven interfacial desalination experiments were performed by placing the 3D CuFe_2O_4 @rGO evaporator on top of cellulose sponge, effectively separating the evaporator from the bulk saline water (3.5% wt salinity) and reducing heat loss as shown in Figure 1a. Owing to the high hydrophilicity of cellulose sponge there was adequate water transfer from the bulk water to the 3D CuFe_2O_4 @rGO evaporator. A solar simulator (Xe lamp, PL-X300) was used to irradiate the evaporator with a light intensity of 1 sun. The evaporation rate was determined by monitoring the mass loss from the vessel using a digital balance. The incident solar irradiation intensity on the evaporator surface was measured using an irradiatometer, while a FLIR TG165 infrared camera was used to capture detailed thermal images, allowing for real-time monitoring of the temperature rise on the evaporator's surface.

3. Results and Discussion

3.1 Characterization of the 3D CuFe_2O_4 @rGO evaporator

Fourier transform infrared (FT-IR) analysis (Figure 1b) showed absorption peaks around 532 cm^{-1} , corresponding to the metal-oxygen (M–O) stretching vibrations, specifically Cu–O and Fe–O bonds within the ferrite structure of CuFe_2O_4 (El-Masry & Ramadan, 2022). These transmittance bands in the $400\text{--}600\text{ cm}^{-1}$ range confirm the presence of copper ferrites. Additionally, a stretching vibration peak at approximately 3250 cm^{-1} indicates –OH vibrations, while peaks at 1820 , 1633 , and 1075 cm^{-1} are associated with the C=O, C=C, and C–O–C components of reduced graphene oxide (rGO), respectively (Bin et al., 2020). Scanning electron microscopy (SEM) revealed a highly wrinkled and porous surface morphology of the solar absorber (Figure 1c and d), which facilitates rapid and continuous water transport during solar evaporation.

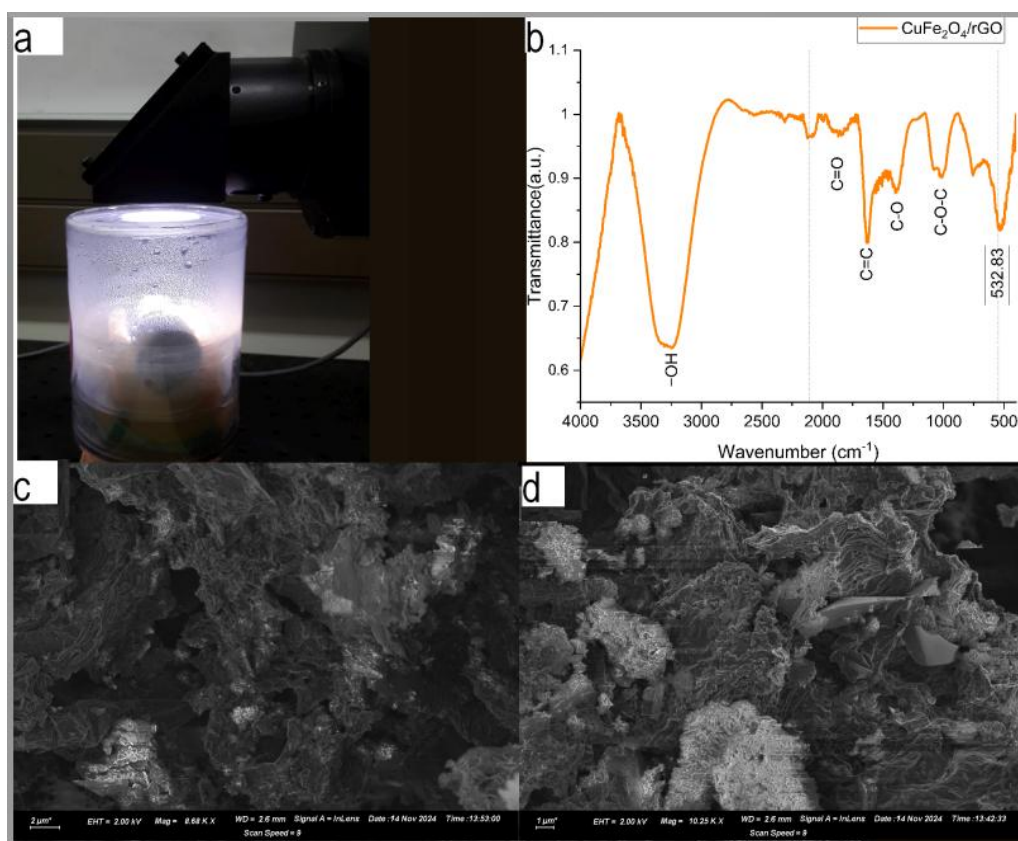


Figure 1: Interfacial desalination setup (a), FTIR spectrum of the material (b), the SEM image of the solar absorber at magnifications corresponding to $2\text{ }\mu\text{m}$ (c) and $1\text{ }\mu\text{m}$ (d) scale bars.

3.2 Solar-Driven interfacial desalination study

The solar-driven desalination performance of the evaporator was evaluated by monitoring the in-situ water mass change in the vessel containing saline water and monitoring the surface temperature rise of the solar absorber

at specified time intervals. The mass change per unit time and area of the irradiated solar absorber was calculated to be $1.51 \text{ kg m}^{-2} \cdot \text{h}^{-1}$. The solar absorber exhibited excellent solar absorption across the UV-VIS-NIR spectrum, as illustrated in Figure 2a. Surface temperature measurements of the solar absorber, recorded every 15 minutes, showed a rapid increase from $26.6 \text{ }^\circ\text{C}$ to $54.9 \text{ }^\circ\text{C}$ within an hour, stabilizing at approximately $54 \pm 1 \text{ }^\circ\text{C}$ as depicted in Figure 2b.

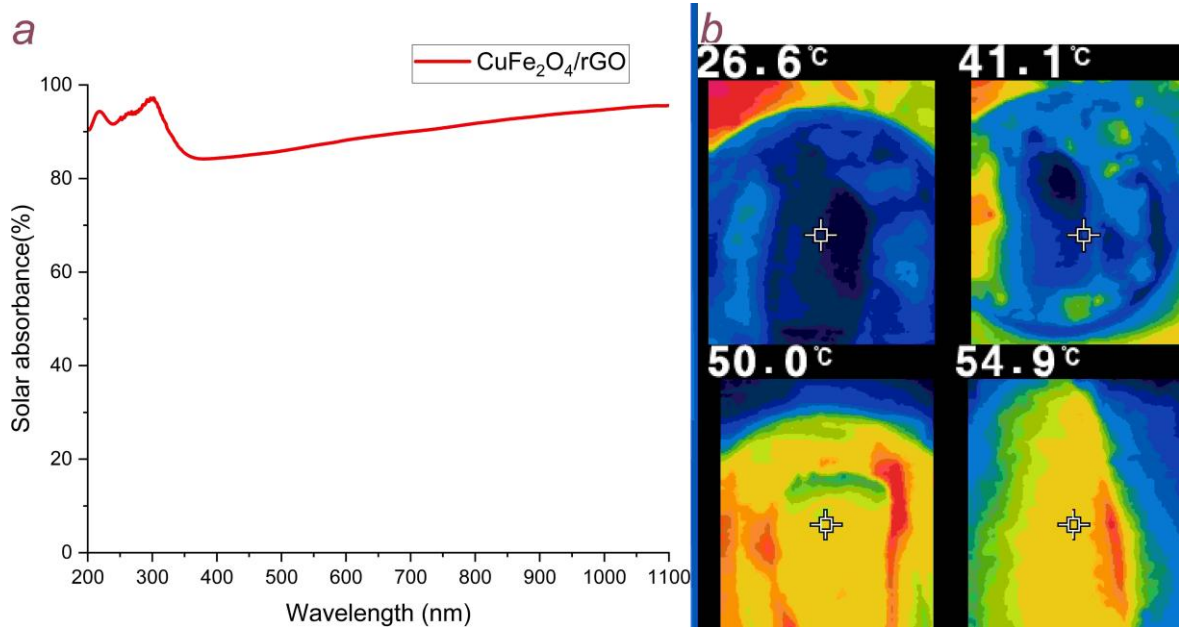


Figure 2: Ultraviolet, visible, and near-infrared (UV-VIS-NIR) broadband solar absorption performance (a) and thermal images showing the heat response of the 3D solar absorber, captured every 15 minutes (b).

As observed in the SEM images, the CuFe_2O_4 -doped 3D rGO composite consists of rGO nanosheets embedded with CuFe_2O_4 nanoparticles. This uniform dispersion preserves the high surface area of the CuFe_2O_4 nanoparticles, preventing agglomeration that could compromise the photothermal performance of the material. In addition to being highly electron conductive, due to its free electrons and high electrical conductivity, the rGO nanosheets serve as a matrix for the dispersed nucleation of CuFe_2O_4 nanoparticles. This synergistic combination enhances electrical conductivity and solar absorption, making the material highly suitable for applications in electronics, energy storage, and other fields where superior electrical conductivity is essential. Similar findings regarding the enhanced solar absorption, photocatalytic activity, and electrical performance of CuFe_2O_4 -doped rGO have been reported in previous studies (Othman et al., 2019; Singh et al., 2022).

The photothermal conversion efficiency (η) is determined using relationship shown in equation 1 (Thoai et al., 2021).

$$\eta = \frac{\dot{m}h_{LV}}{q_i} \times 100\% \quad \text{Equation (1)}$$

Where \dot{m} refers to the evaporation rate of water, h_{LV} refers to the total liquid-vapor phase-change enthalpy (sensible heat and latent heat), q_i is incident solar power density, value of $1 \text{ kW} \cdot \text{m}^{-2}$.

$$h_{LV} = C\Delta T + h_{vap} \quad \text{Equation (2)}$$

Where C is the specific heat capacity of simulated seawater ($3.993 \text{ J g}^{-1} \cdot \text{K}^{-1}$),

The 3D rGO-based composite exhibited a high freshwater generation rate and an impressive photothermal conversion efficiency of $\sim 110\%$ under 1-sun solar illumination. The observed performance can be attributed to the synergistic merits of its components. Copper ferrite (CuFe_2O_4) contributes a high electron concentration, significantly enhancing the light-harvesting capability of rGO. Synergistically, rGO's excellent electrical

conductivity and broadband solar absorption improve the overall performance of the 3D CuFe₂O₄@rGO evaporator (Yang et al., 2020; Wang et al., 2023). The photothermal conversion efficiency surpassing 100% arises from additional evaporation surfaces provided by the 3D structure, which are not directly exposed to solar irradiation but effectively draw heat from the surroundings. This additional energy input enhances the evaporation process. Furthermore, energy recycled from the condensing water vapor also contributes to the system's overall energy input, enabling the remarkable super-photothermal efficiency observed (Li et al., 2019).

4. Conclusions

In this study, CuFe₂O₄-doped reduced graphene oxide (rGO) was successfully synthesized, demonstrating broad solar absorption across the UV-VIS-NIR spectrum. The material achieved a photothermal conversion efficiency of up to 110% and a freshwater generation rate of 1.51 kg m⁻².h⁻¹. The innovative 3D solar absorber design effectively captured solar energy over a wide spectrum while minimizing heat loss. The high photothermal conversion efficiency was attributed to the combined effects of CuFe₂O₄-doped rGO and an advanced heat management system. Additionally, the three-dimensional structure provided extra evaporative surfaces, further enhancing environmental energy absorption. Overall, the 3D solar absorber holds significant potential for large-scale real-world applications, offering an efficient and sustainable solution for solar-driven processes.

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References

- Al-Obaidi, M., Alsarayreh, A.A., Rashid, F.L., Sowgath, M.T., Alsadaie, S., Ruiz-García, A., Khayet, M., Ghaffour, N. and Mujtaba, I.M., 2024. Hybrid membrane and thermal seawater desalination processes powered by fossil fuels: A comprehensive review, future challenges and prospects. *Desalination*, 117694.
- Bezza, F.A., Iwarere, S.A., Brink, H.G. and Chirwa, E.M., 2024. Design and fabrication of porous three-dimensional Ag-doped reduced graphene oxide (3D Ag@rGO) composite for interfacial solar desalination. *Scientific Reports*, 14(1), 13793.
- Bin, Q., Lin, B., Zhu, K., Shen, Y., Man, Y., Wang, B., Lai, C. and Chen, W., 2020. Superior trichloroethylene removal from water by sulfide-modified nanoscale zero-valent iron/graphene aerogel composite. *Journal of Environmental Sciences*, 88, 90-102.
- Chapelle, A., Yaacob, M.H., Pasquet, I., Presmanes, L., Barnabé, A., Tailhades, P., Du Plessis, J. and Kalantar-Zadeh, K., 2011. Structural and gas-sensing properties of CuO-Cu_xFe_{3-x}O₄ nanostructured thin films. *Sensors and Actuators B: Chemical*, 153(1), 117-124.
- Dolan, F., Lamontagne, J., Link, R., Hejazi, M., Reed, P. and Edmonds, J., 2021. Evaluating the economic impact of water scarcity in a changing world. *Nature communications*, 12(1), 1-10.
- El-Masry, M.M. and Ramadan, R., 2022. The effect of CoFe₂O₄, CuFe₂O₄ and Cu/CoFe₂O₄ nanoparticles on the optical properties and piezoelectric response of the PVDF polymer. *Applied Physics A*, 128(2), 110.
- Gueymard, C.A., 2004. The sun's total and spectral irradiance for solar energy applications and solar radiation models. *Solar energy*, 76(4), 423-453.
- Ibrahim, I., Seo, D.H., McDonagh, A.M., Shon, H.K. and Tijing, L., 2021. Semiconductor photothermal materials enabling efficient solar steam generation toward desalination and wastewater treatment. *Desalination*, 500, 114853.
- Li, X., Ni, G., Cooper, T., Xu, N., Li, J., Zhou, L., Hu, X., Zhu, B., Yao, P. and Zhu, J., 2019. Measuring conversion efficiency of solar vapor generation. *Joule*, 3(8), 1798-1803.
- Liang, Y., Wang, D., Yu, H., Wu, X., Lu, Y., Yang, X., Owens, G. and Xu, H., 2024. Recent innovations in 3D solar evaporators and their functionalities. *Science Bulletin*.

- Mulwa, F., Li, Z. and Fangninou, F.F., 2021. Water scarcity in Kenya: current status, challenges and future solutions. *Open Access Library Journal*, 8(1), 1-15.;
- Nawaz, F., Yang, Y., Zhao, S., Sheng, M., Pan, C. and Que, W., 2021. Innovative salt-blocking technologies of photothermal materials in solar-driven interfacial desalination. *Journal of Materials Chemistry A*, 9(30), 16233-16254.
- Othman, I., Haija, M.A., Ismail, I., Zain, J.H. and Banat, F., 2019. Preparation and catalytic performance of CuFe₂O₄ nanoparticles supported on reduced graphene oxide (CuFe₂O₄/rGO) for phenol degradation. *Materials Chemistry and Physics*, 238, 121931.
- Rajput, J.K., Arora, P., Kaur, G. and Kaur, M., 2015. CuFe₂O₄ magnetic heterogeneous nanocatalyst: Low power sonochemical-coprecipitation preparation and applications in synthesis of 4H-chromene-3-carbonitrile scaffolds. *Ultrasonics sonochemistry*, 26, 229-240.
- Singh, S.K., Penke, Y.K., Ramkumar, J., Akhtar, M.J. and Kar, K.K., 2022. Facile synthesis of Al substituted Cu-ferrite infused reduced graphene oxide (rGO) nanohybrid for improving microwave absorption at gigahertz frequencies. *Journal of Alloys and Compounds*, 901, p.163659.
- Thoai, D.N., Ta, Q.T.H., Truong, T.T., Van Nam, H. and Van Vo, G., 2021. Review on the recent development and applications of three dimensional (3D) photothermal materials for solar evaporators. *Journal of Cleaner Production*, 293, 126122;
- Wang, J., Kong, Y., Liu, Z. and Wang, H., 2023. Solar-driven interfacial evaporation: design and application progress of structural evaporators and functional distillers. *Nano Energy*, 108, 108115. ;
- Yang, J., Chen, Y., Jia, X., Li, Y., Wang, S. and Song, H., 2020. Wood-based solar interface evaporation device with self-desalting and high antibacterial activity for efficient solar steam generation. *ACS Applied Materials & Interfaces*, 12(41), 47029-47037;