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Copper Nanoparticle Doped Reduced Graphene Oxide (CuNP@rGO) Coated Poplar Wood for Solar-driven Interfacial Desalination of Saline Water

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Global freshwater scarcity is one of the most pressing problems of the modern society. Solar driven interfacial desalination technology, which concentrates heat at the air-water interface and decreases thermal losses has gained an increasing attention owing to its high photothermal conversion efficiency and transformative environmental applications. However, there are still challenges of producing efficient and scalable photothermal materials with high evaporation rate, photothermal conversion efficiency and low cost. Graphene and its derivatives are ideal photothermal materials owing to their stability, excellent thermal and electrical conductivity, efficient broadband light absorption potential, lightweight and low cost. Conversion of graphene to reduced graphene oxide /plasmonic hybrid nanocomposites increases its performance and photothermal conversion efficiency. In the currents study copper nanoparticle doped reduced graphene oxide (CuNP@rGO) layered 3D poplar wood based interfacial desalination system was setup by depositing CuNP@rGO photothermal layer on porous hydrophilic poplar wood substrate and used for interfacial desalination of hypersaline water. The photothermal material displayed strong broadband solar absorption of ~95%, high evaporation rate of 1.39 $kg.m^{-2}.h^{-1}$, corresponding to photothermal conversion efficiency of ~96%, under 1-Sun solar irradiation, demonstrating the high energy efficiency and water generation potential. The results of the study demonstrated promising potential of the cost effective, environmentally sound, and scalable photothermal material for large scale real world saline water desalination and brackish water purification applications.

1. Introduction

Freshwater scarcity is the pressing global challenge of the 21st century, posing a significant challenge in achieving sustainable socioeconomic growth and achieving the Sustainable Development Goals. The limited amount of freshwater that is accessible faces additional confronts due to the increasing levels of pollution and salinization (He et al., 2021). As a result, there is an increasing need for the generation of additional freshwater sources to cater to the growing population size and socioeconomic development. Therefore, in the face of the growing shortage of freshwater resources, desalination is considered to be one of the most promising solutions to the growing demand for fresh water (Sun et al., 2023). Solar energy is one of the most abundant renewable resources and does not produce secondary pollution during use, making it an environmentally friendly, economically efficient, and clean energy source at present. Recently solar driven interfacial desalination has become an efficient and most promising desalination technology to solve the current water shortage problem, owing to its inherent ability to localize heat generated and high solar to thermal energy conversion efficiency (Wang et al., 2023). The overall structure of solar-driven interfacial desalination can be categorized into two distinct layers. The upper layer, known as the photothermal conversion layer, is responsible for effectively capturing sunlight and converting it into thermal energy. On the other hand, the lower layer functions as both a water transfer and thermal insulation layer. The photothermal conversion layer is able to convert the absorbed sunlight into thermal energy to provide an energy source for the subsequent evaporation process and is the engine of solar-driven interfacial desalination system (Sun et al., 2023).

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Hence the design and fabrication of novel and efficient photothermal materials that possess high solar absorption and photothermal conversion efficiency, while also being sustainable and economically viable, is crucial for the advancement of the interfacial desalination technology. Additionally, the choice and preparation of the bottom substrate layer to serve as a supportive and insulating layer play a pivotal role in the interfacial desalination technology. The recent progress and evolution of interfacial desalination technology has primarily been facilitated by optimization of energy management and rational structural design of photothermal materials (Wang et al., 2023).

Photothermal conversion materials are broadly divided into the following four categories: 1) metallic nanostructures, 2) inorganic semiconductor materials, 3) carbon-based light absorbing materials and 4) polymeric material (Wu et al., 2019). Graphene and its reduced graphene oxide derivative are narrow bandgap semiconductors exhibiting significant photothermal effects and are among the prominent candidates for the utilization of solar energy. The large number of conjugated π bonds in graphene facilitates the excitation of electrons, making it an excellent material for absorption in broadband solar spectrum and an efficient photothermal material (Li et al., 2021). Copper nanoparticles are known for their remarkable photothermal properties due to their localized surface plasmon resonance (LSPR) effect. They exhibit a range of unique characteristics such as superior electric and thermal conductivity, photocatalytic behaviour, superior plasmonic resonance, and nonmagnetic nature (Cui et al., 2023).

Combination of the graphene derivative rGO with Cu NPs has been reported to be outstanding photothermal materials due to their strong light-absorbing and photon-to-heat conversion abilities through the combined surface plasmon resonance and lattice vibration mechanisms (Gai et al., 2023). Various substrates, including carbon foam, polystyrene foam, and polymeric compounds, have been utilized in interfacial solar steam generation devices due to their hydrophilic, porous, and thermal insulation properties (Mehrkhah et al., 2023). However, the practical applications of these substrates are limited due to their high cost, complex manufacturing processes, and toxicity.

In addition, a bilayer photothermal evaporator has been developed to enhance evaporation by separating the evaporative surface from the bulk water, thereby minimizing heat loss through conduction to the bulk water. (Gnanasekaran and Rajaram, 2024). Wood, being a renewable resource abundantly available on Earth, has gained popularity in solar steam generation due to its low thermal conductivity, inherent microchannels for water transport, low density allowing it to float on water, and ease of processing (Mehrkhah et al., 2023). Herein, a bilayer wood-based evaporator coated with CuNP-doped rGO photothermal material is developed and utilized for solar-driven interfacial desalination. The photothermal conversion efficiency and solar desalination performance of the system were evaluated.

2. Method

2.1 synthesis of substrate

The poplar wood substrate was produced by cutting down a tree trunk into rectangular blocks of 7 cm length by 4 cm width and by 2 cm height. The block was treated with 2.5 M NaOH and 0.4 M Na_2SO_3 at 95 °C for 24 h to remove lignin and increase its hydrophilicity for efficient water transfer to the photothermal material as previously described by Li et al (2022).

2.2 Synthesis of copper nanoparticles doped reduced graphene oxide (CuNP@rGO)

Graphene oxide was synthesized from graphite using Tours method aa previously described elsewhere (Bezza et al., 2023). A wet-chemical reduction strategy was employed to synthesize CuNP@rGO as previously described by Sekhar et al (2023). Briefly 11g $CuSO_45H_2O$ was homogenous dispersed in GO solution (10 wt. %) and subjected to ultrasonication for 30 min to ensure homogeneity. Subsequently the pH was tuned to 12 using NaOH and, l-ascorbic acid (2 g) was added, and the mixture was heated at 150 °C for three 3 h, resulting in the concurrent reduction of Cu^{2+} along with GO. The product was collected by centrifugation, dried at 100 °C and calcined at 500°C for 2 h, resulting in the and production of CuNP@rGO powder. The CuNP@rGO was characterized and used for the bilayered substrate coating and interfacial desalinations study.

2.4 Characterization

The CuNP@rGO was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) spectroscopy. SEM analysis was carried out using (JEOL JSM-7800F) to examine the morphology of the photothermal material, X-ray diffraction (XRD) measurements were conducted with a Bruker D8 Discover X-ray diffractometer employing Cu Kα radiation. Ultraviolet-Visible-Near Infrared (UV-Vis-NIR) spectroscopy measurements have been performed using a UV-2600 series (Shimadzu, Japan) spectrophotometer.

2.5 Solar powered interfacial desalination test using solar simulator.

The freshwater generation performance test of the solar evaporator was carried out in an enclosed transparent plexiglass device with a simulated seawater contained in a 50 ml smaller container. A solar simulator was used as a light source under 1 -Sun solar illumination. The CuNP@rGO coated wood was placed on a 50 mL water container inside the transparent plastic bottle, as schematically represented in Figure 1 and the mass change in the water during evaporation was measured using an electronic balance. The surface temperature of the photothermal material was monitored using an IR camera (FLIR TG 165, FLIR Systems, Inc., USA).

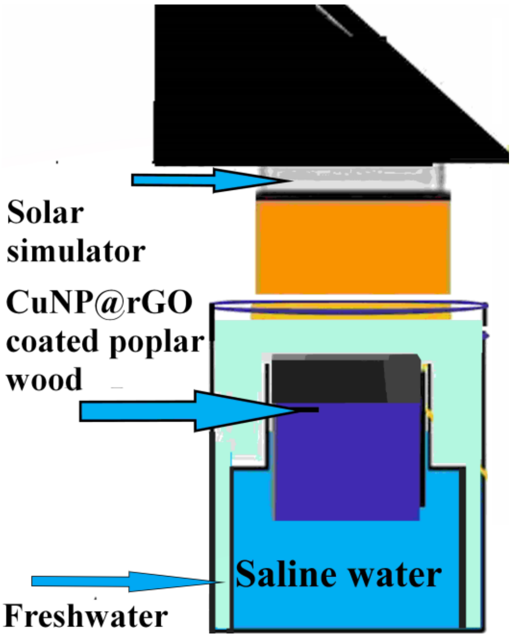

Figure 1: Schematic illustration of CuNP@rGO coated poplar wood based solar driven interfacial desalination system.

3. Results and discussion

3.1 Characterization of CuNP@rGO

The as-synthesized CuNP@rGO was characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), and ultraviolet-visible near-infrared (UV-Vis NIR) spectroscopy. Figure 2a, b shows the SEM micrographs of the CuNP@rGO. The SEM micrographs of the composite material reveal a highly porous morphology at different magnifications, which indicates the potential of the composite to accommodate efficient steam release and adequate water transfer. The CuNPs embedded are uniformly dispersed throughout the porous rGO sheets. Fig.2 c displays the XRD patterns of CuNP@rGO photothermal material. The diffraction peaks observed at 2θ values of 43.31°, 50.40° and 74.62° correspond to (111), (200) and (220) planes of face-centered cubic (fcc) structured Cu phase (JCPDS card no. 85-1326), and the diffraction peak at 2θ value of 25.4° corresponds to the 002 plane of rGO (Zhang et al., 2016). Figure 2d, shows the CuNP@rGO photothermal material coated wood block floating on the saline water containing vessel and placed in a plexiglass plastic with transparent lid subjected to simulated solar irradiation. The wood substrate consists of plenty of micro-nano channels that pump water through the capillary force.

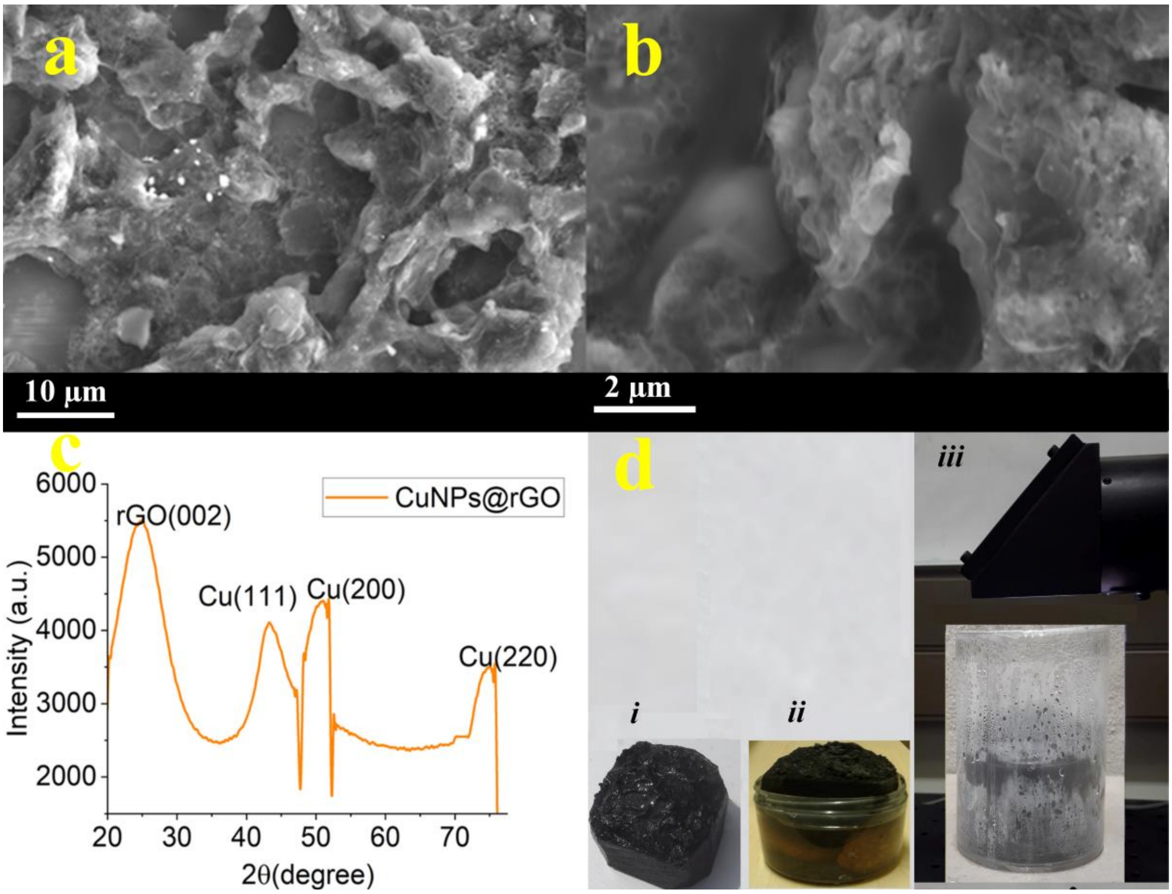

Figure 2: SEM images of the CuNP@rGO at different magnification (a,b); XRD pattern of the CuNP@rGO (c); interface desalination set up (d)with wood block coated with CuBPs@rGO (i); woodblock coated with CuNP@rGO bilayer floated on saline water filled contained(ii), the bilayer subjected to 1 sun solar simulation (iii)

3.2 Photothermal performance

The photothermal performance of a material is characterized by studying its ability to absorb solar radiation and convert it into heat. As shown in Figure 3a, the CuNP@rGO shows a nearly perfect absorption in the broadband UV-Vis-NIR region with an average absorption of about ~ 95 %. The IR imaging of the solar evaporation system in Figure 3b, shows that the surface temperature of the solar absorber rises sharply form 27.2 °C reaches up to 54.0 °C within an hour, while the temperature of the bulk water is barely changed under 1 sun irradiation. This proves its efficient photothermal performance owing to higher solar absorption capacity. The tuneable and strong localized surface plasmon resonance (LSPRs) effect of copper nanoparticles (CuNPs) in the range of 500–600 nm and associated plasmonic heating offer it a high photothermal conversion potential through the LSPR effect (Zhao et al., 2021). Reduced graphene oxide is an excellent photothermal material with strong light-to-heat conversion abilities through thermal vibrations within the atomic lattices. The superior photothermal conversion efficiency and stream generation performance is attributed to the synergistically broadband solar absorption of the rGO and localized surface plasmonic heating of CuNPs offering the CuNP@rGO the high photothermal performance (Patel et al., 2019).

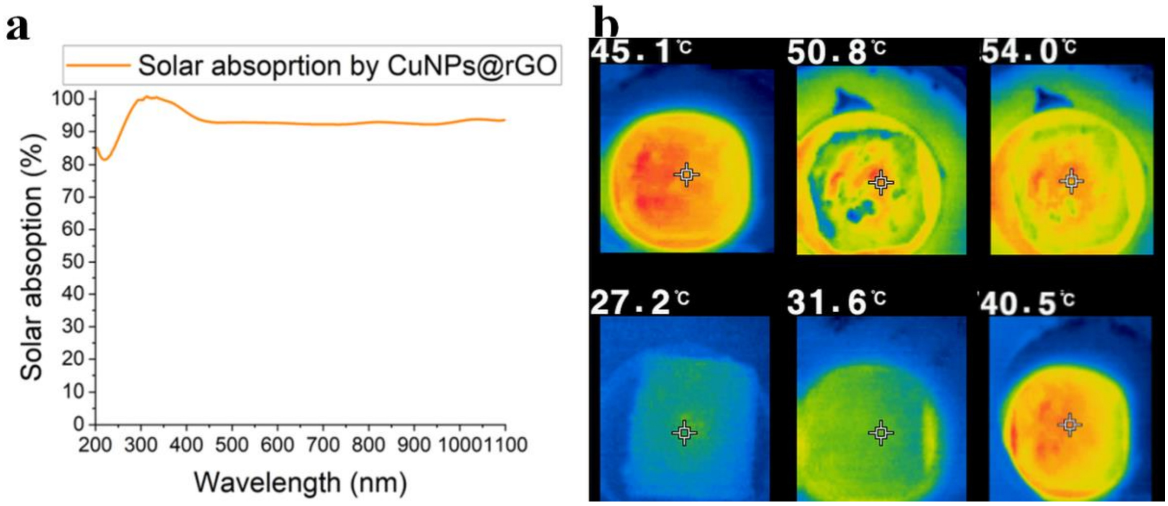

Figure 3: Photothermal performance of CuNP@rGO. a) Light absorption spectra of CuNP@rGO in the range of solar spectrum (200–1100 nm), b) Temperature rises (ΔT, relative to the environmental temperature) of the CuNP@rGO under 1 sun solar illumination (1 kW m^{-2}).

As shown in Figure 2d(iii), when CuNP@rGO coated wood is floated on the simulated seawater with salinities (3.5 wt% salinity), the vapor generated subsequent to solar irradiation is condensed and collected as freshwater. The evaporation rate of the photothermal evaporator was evaluated by measuring the mass change of the water in the contained per hour per evaporative surface area. The solar driven evaporation rate of water using CuNP@rGO evaporator under 1 sun illumination was determined to be 1.39 kg m^{-2} hr^{-1} compared to the plain water evaporation rate of 0.24 kg m^{-2} hr^{-1}.

The solar to heat conversion efficiency of the solar absorber is analysed using the relation (Zhang et al., 2020).

$$\mathbf{h} = \frac{\dot{m}(C\Delta T + \Delta h_{vap})}{P_i} \qquad (1)$$

Where $\dot{m}$ is the evaporation rate (kg m^{-2} hr^{-1}), C is the specific heat capacity of water, 4.18 J g^{-1} K. ΔT is the temperature increase of the water, Δh_{vap} is the enthalpy of vaporization of water at the evaporative temperature, and P_i represents the solar illumination intensity (1 kW m^{-2}). The photothermal conversion efficiency is determined to be ~96%.

The high photothermal conversion efficiency attained is attributed to the outstanding solar light trapping of the photothermal material, as well as the efficient heat management, which avoided heat loss to the bulk water and to the environment. The substrate made of wood blocks effectively provides insulation against conductive heat loss and offers fast transfer of water to the evaporative surface. The vertically aligned tubular structures found in wood blocks offer three-dimensional microchannels that enable continuous water supply. The abundant hydrophilic hydroxyl groups found in wood substrate contributes towards efficient steam generation via reduction of the enthalpy of evaporation of wate, by disrupting a portion of the bulk water's hydrogen bond network, by creating hydrogen bonds with water molecules to lower the enthalpy of water evaporation (Liu et al., 2022). Similar observations have been reported by Sun et al. (2020), wherein a portion of the water molecules establish hydrogen bonds with the hydrophilic groups of a corn stalk evaporator, diminishing the van der Waals force between the water molecules and resulting in a significant reduction in the water evaporation enthalpy. Furthermore, the CuNP@rGO top layer efficiently heats the area between water and air serving as driving force for enhanced capillary flow of water and evaporation, enabling a high photothermal conversion efficiency achieved.

4. Conclusions

A novel bilayered photothermal material composed of CuNP@rGO, which exhibited high light trapping potential and wood block substrate possessing low thermal conductivity, and hydrophilicity was produced. The CuNP@rGO showed broadband light trapping ability covering up to ~95% and the wooden block substrate provided efficient water transfer and insulation against conductive heat loss. In the the solar-driven interfacial evaporation experiments carried out under 1 Sun, the bilayered photothermal material demonstrated efficient photothermal conversion and outstanding evaporation rate. The energy efficient broadband solar absorptive bilayered CuNP@rGO shows a promising potential for solar driven interfacial desalination of saline water for sustainable freshwater generation.

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