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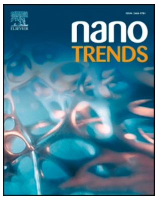

Enhancing the thermal conductivity and stability of cuprous oxide nanofluids: Ribose-mediated single step chemical synthesis for solar energy applications

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ABSTRACT

The efficiency of photovoltaic (PV) panels can be compromised by rising temperatures, prompting extensive research into thermal management strategies aimed at maximizing power output. Recently, there has been growing interest in using nanofluids to enhance the cooling efficiency of photovoltaic thermoelectric generator (PV-TEG) systems compared to conventional water cooling. This underscores the potential of investigating innovative synthetic methods to improve the thermal conductivity and stability of nanofluids. We employed a simple straightforward method to synthesize cuprous oxide nanofluid. This solution-based technique constrains formation of cuprous oxide particles to the nanoscale dimensions using cetylammonium bromide as capping agent. Our investigation delved into the impact of various parameters on the formation and dispersion of nanoparticles within a base fluid comprised of a 1:1 mixture of water and ethylene glycol. The resulting nanofluid exhibited Newtonian behaviour and demonstrated remarkable stability of 9 months, accompanied by a notable increase in thermal conductivity upto 3.59 W m^{-1} K^{-1}. This meticulous approach has proven to be not only straightforward and dependable but also efficient for the rapid synthesis of highly stable Newtonian nanofluids overcoming the complexities associated with traditional two-step processes and could be extended to other metal oxide nanofluids. Beyond its economic appeal, the nanofluid's improved thermal properties and stability position it for diverse applications requiring efficient heat transfer.

1. Introduction

The exponential growth of population and industrialization has led to overexploitation of fossil fuel resource. With an intention to meet the energy demands while mitigating environmental impacts, clean and renewable energy sources like solar energy and thermoelectric energy generation are sought after [1–3]. Whether directly through photovoltaic (PV) or thermal technologies, solar energy derived from the sun's abundant and renewable radiation offers an inexhaustible, clean and sustainable solution for future energy needs [4]. PV technology, which converts sunlight directly into electricity, has experienced significant advancements in recent years, leading to increased adoption and deployment of solar PV systems worldwide. However, PV panels are susceptible to performance degradation due to elevated operating temperatures, which reduce their efficiency and output power. Dissipation of heat generated during absorption of solar energy by the photovoltaic panels is a critical aspect to improve the efficiency [5]. This absorption of excess heat can be done either by using cooling fluid or by using thermoelectric materials [6–8]. Thermoelectric materials scavenge this waste heat and convert it into electricity [9,10]. Incorporation of a thermoelectric generator along with a solar unit will remarkably improve the performance of the photovoltaic system [11]. In contrast, solar thermal collectors which is also employed to harness solar energy utilize a heat transfer medium to transform solar energy into heat energy [12]. This process involves a fluid absorbing and subsequently transferring heat directly or indirectly to another fluid or location, often opting for water as the preferred medium. However, it has been noted that only 13 % of incident solar energy is absorbed by water, leading to a significant decrease in collector thermal efficiency. While structural redesigns of solar collectors have been explored, such changes often

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come with high economic costs, making it imperative to find practical solutions that improve efficiency without significant investment. Therefore, enhancing the thermophysical properties of the working fluid emerges as a viable, cost-effective strategy [13].

Nanofluids, consisting of nanoparticles dispersed in conventional heat transfer fluids have emerged as a revolutionary class of fluids with remarkable potential across various fields, including solar energy applications [14,15]. The integration of nanofluids into solar energy systems represents a promising approach to overcome existing limitations and enhance the efficiency and performance of these systems [16]. One of the key advantages of nanofluids in solar applications is their ability to improve heat dissipation and thermal management in PV panels. By incorporating nanofluids as the heat transfer fluid, these systems can benefit from increased thermal conductivity and heat transfer coefficients, leading to higher thermal efficiencies and improved overall performance, minimizing losses [17]. With continued advancements in nanotechnology and materials science, nanofluids hold the potential to play a significant role in solar energy technologies, contributing to a more sustainable and renewable energy future [18–22].

Numerous researchers have explored how the photothermal properties of nanofluids are affected by both the base fluid and the properties of nanoparticles [23]. Investigations have delved into various base liquids and nanoparticles, employing experimental and simulation techniques to understand their influence on photothermal behaviour [20–22,24,25]. Despite their potential, a major challenge facing nanofluids is the instability caused by nanoparticle agglomeration, which adversely affects their performance [26]. While much research has focused on minimizing agglomeration during nanofluid preparation, the precise mechanisms by which agglomeration impacts the properties remain poorly understood. Agglomeration not only decreases the thermal conductivity it also destabilizes the nanofluids and leads to sedimentation, which reduces their long-term performance and necessitates frequent replacements. This problem is compounded in industrial settings where increased apparent viscosity due to high nanoparticle concentrations elevates pumping costs and affects the efficiency of heat exchange equipment. Consequently, the performance of nanofluid-based heat exchangers can vary significantly depending on flow regimes, presenting both opportunities and challenges when compared to traditional single-phase coolants [27].

Developing effective and scalable synthesis methods for nanofluids tailored for solar applications is therefore crucial [28,29]. An eco-friendly approach that ensures stable nanoparticle dispersion, reduced viscosity, and enhanced thermal conductivity at low particle loading could significantly improve the thermal management of solar energy systems [30]. The potential to fine-tune nanofluid properties through innovative synthesis techniques offers a promising pathway to overcome current limitations, ultimately enhancing the overall efficiency and sustainability of solar energy conversion and storage. Single-step synthesis is particularly valuable for solar applications because it directly produces nanofluids with tailored properties that can significantly enhance the heat transfer efficiency of solar collectors and PV cooling systems [31]. The importance of single-step nanofluid synthesis extends beyond performance improvements; it also offers economic and environmental benefits. The streamlined production process is more cost-effective and environmentally friendly compared to traditional multi-step methods. As solar energy continues to evolve as a key component of the global energy mix, the development and deployment of advanced nanofluids synthesized via single-step methods will play a critical role in pushing the boundaries of solar technology [32].

This study aims to address these challenges by presenting a novel one-step synthesis method for cuprous oxide nanofluids, designed to offer superior stability and thermal properties, thereby providing a viable solution for optimizing thermal management in solar energy applications. Our approach employs a one-step chemical reduction process of copper sulphate using ribose in presence of cetylammonium bromide (CTAB) as a stabilizing agent. Focusing on the cooling requirements of solar systems, we comprehensively assessed the thermal conductivity, viscosity, and sedimentation behaviour of the synthesized nanofluids. Our simple and environmentally friendly approach addresses the challenges associated with traditional two-step methods [33]. The resulting nanofluids demonstrate a uniform distribution of nanoparticles, exhibit Newtonian behaviour, and offer record high thermal conductivity value of 3.59 W m^{-1} K^{-1} and stability of 9 months, making them highly suitable for improving heat transfer and temperature regulation in solar energy systems. Furthermore, the ability to fine-tune the thermal properties of nanofluids through this method allows for the development of customized solutions for specific solar applications, enhancing their adaptability and effectiveness in real-world scenarios.

Fig. 1. Depiction of colour changes during nanofluid synthesis.

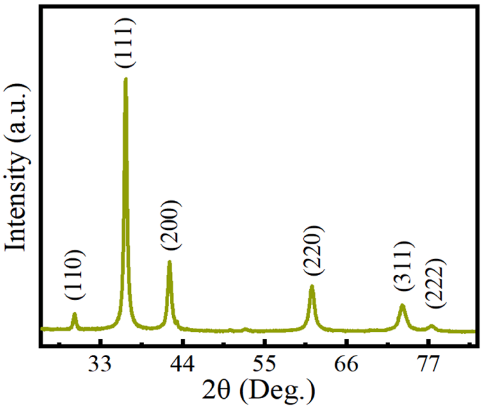

Fig. 2. XRD pattern of the synthesized cuprous oxide nanoparticles.

2. Experimental

2.1. Preparation of cuprous oxide nanofluid

Cuprous oxide nanofluid synthesis involves the reduction of 30 mL (0.1 M) copper sulphate solution in ethylene glycol. Initially, the copper sulphate solution was ammoniated by adding ammonium hydroxide. Then 20 mL (0.01 M) CTAB solution in ethylene glycol and 50 mL of distilled water was added and stirred for 10 min. To this, 2.5 g of ribose was added and stirred continuously at 70 °C until the solution color transitioned from blue to golden brown. At this point, acid is introduced to adjust the pH as desired, followed by further heating to generate a reddish-brown nanofluid (Fig. 1). Different reaction parameters like variations in the concentration of reducing agent, amount of CTAB, dilutions, power and irradiation duration of microwave were methodically altered to assess their effects on nanofluid synthesis. The characterization of the synthesized nanofluids and study of its thermal and rheological properties were carried out as established in previous literature [13,34].

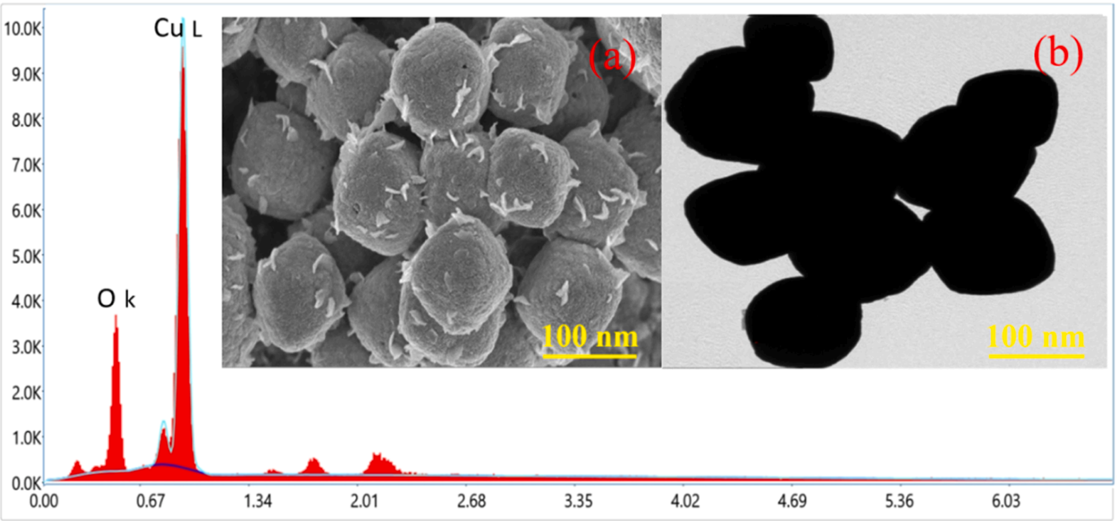

Fig. 3. EDX spectrum. Inset shows (a) FESEM image and (b) TEM image of the synthesized cuprous oxide nanoparticles.

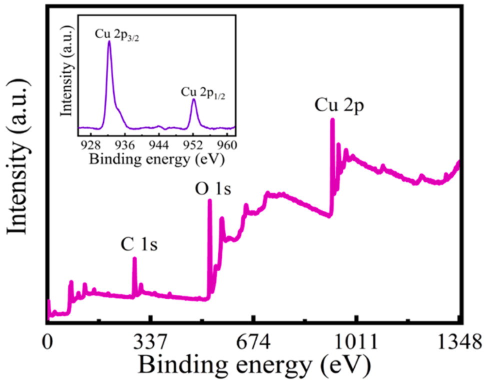

Fig. 4. XPS survey spectrum of Cu_2O. Inset shows the high-resolution spectrum of Cu 2p.

3. Results and discussion

3.1. Diffraction and morphology studies

X-ray diffraction (XRD) and elemental diffraction X-ray (EDX) analysis techniques were employed to confirm the phase and purity of the synthesized cuprous oxide nanoparticles. The XRD pattern recorded using PAN analytical X-ray diffractometer (Fig. 2) displays the cubic structure of cuprous oxide, exhibiting six prominent peaks matching the (110), (111), (200), (220), (311), and (222) planes [JCPDS Card No 05–0667, with lattice parameter $a = 4.2696$ Å, and space group: Pn3 m (224)] [34,35]. No impurity peaks, such as copper or cupric oxide, were detected. Scherrer's formula [$D = K\lambda/\beta\cos\theta$] was used to determine the average size of the synthesized nanoparticle using the data from XRD analysis [36].

The nanoparticles' EDX spectrum (Fig. 3) exhibits copper and oxygen peaks, affirming their high purity. The Cu to O ratio was approximately 2:1, indicating that the nanoparticles comprise of Cu_2O. The field emission scanning electron microscopy (FESEM, 7610F PLUS JEOL, JAPAN) and transmission electron microscopy (TEM, JOEL JEM 2100 PLUS) images unveiled that the Cu_2O nanoparticles were slightly faceted but with smoothened edges (Fig. 3a and 3b). The flagella like protrusions shown in the FESEM image further improves the surface area and thus thermal conduction of the nanofluid.

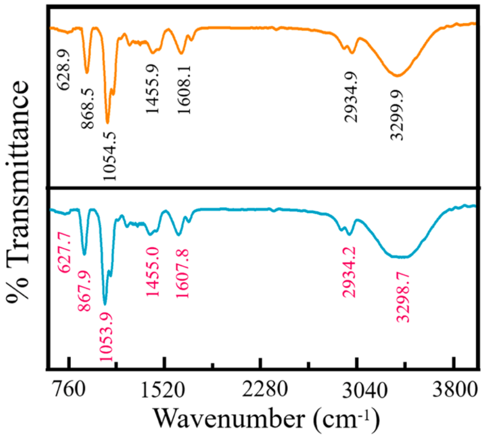

Fig. 5. FTIR spectra of ethylene glycol and cuprous oxide nanofluid in upper and lower panel, respectively.

3.2. Results of spectroscopy studies

Fig. 4 illustrates the X-ray photoelectron spectroscopy (XPS) survey spectrum recorded using Kratos XSAM800 spectrometer to identify the chemical state of the element within a material. It confirms the presence of copper (Cu) and oxygen (O). The Cu 2p high-resolution spectrum displays two peaks at 932.9 eV and 952.9 eV, corresponding to the Cu $2p_{3/2}$ and Cu $2p_{1/2}$ states, respectively [37,38]. This observation suggests that the oxidation state of Cu is +1, rather than +2 [39]. The peak observed at 531.1 eV in the O 1 s spectrum indicates the existence of Cu-O bonds within the Cu_2O structure [40].

Fourier transform infrared (FTIR) spectra recorded using Nicolet Bruker instrument was used to determine ethylene glycol's role in reducing copper sulphate. Fig. 5 displays the resemblance of FTIR spectra of pure ethylene glycol (upper panel) and cuprous oxide nanofluid (lower panel). The slightly broader peak around 3298.7 cm^{-1} is due to the presence of water in the nanofluid. This indicates that ethylene glycol did not undergo oxidation in this process [41]. From this, it can be inferred that ribose functioned as the reducing agent, while ethylene glycol primarily acted as the base fluid along with water. Therefore, it could be said that this method amalgamates the advantages of the polyol process and aqueous chemical reduction technique [30].

Table 1
Effect of volume of water on size of nanoparticles.

Volume of water (mL)	Particle size (nm)
50	35
100	26
150	16
200	9

Table 2
Effect of concentration of CTAB on the particle size.

Concentration of CTAB (M)	Particle size (nm)
0	40
0.01	35
0.05	18
0.1	11

3.3. *Effect of synthetic conditions*

3.3.1. *Effect of amount of reducing agent*

The impact of the concentration of reducing agent on particle size during the synthesis was studied by adding 2.5 g to 10 g of ribose to the reaction mixture. For the reaction to undergo completion, a minimum of 2.5 g of ribose was essential. When the amount of ribose was increased from 2.5 g to 10 g with increment of 2.5 g each time, a decrease in particle size was observed from 35 nm to 28 nm to 22 nm to 11 nm. Previous research revealed that at the early stages of the reaction the presence of higher amount of reducing agent increases the nucleation rate [24]. Subsequently, particles formed during advanced stages of the reaction adhere to existing nuclei [31]. With an abundance of nuclei, the number of particles available for growth diminishes, resulting in smaller size particles at higher concentration of reducing agent. At low concentrations of the reducing agent, fewer nuclei are formed [24]. As the reaction progresses, particles produced are deposited onto the existing nuclei instead of generating new particles [30]. Therefore, we see a decrease in the particle size with increase in the amount of ribose added.

3.3.2. *Effect of total reactant concentration*

Some of the reactions were carried out, by decreasing the total concentration of the reactants by adding various volumes of water while maintaining a constant ratio between the copper salt and reducing agent. The findings shown in Table 1, distinctly illustrate an inverse relationship between the size of the particles and the volume of water added. This phenomenon can be explained by previous research findings [42]. The distance between the produced nuclei increases as the total concentration decreases, resulting in a reduction in interatomic collisions. As a result, smaller-sized particles were obtained as growth through deposition is hindered at higher dilutions [31,42].

3.3.3. *Microwave irradiation*

The same experiments were replicated under microwave irradiation at microwave powers of 30 %, 50 %, 70 %, and 90 % for 7 min respectively. At 30 % power, the reaction was incomplete, and particles measured 22 nm. On the other hand, at 50 %, 70 %, and 90 % power, the reaction was fully completed and the obtained particles were 27 nm, 13 nm, and 5 nm in size. Higher microwave power levels accelerated the reaction rate by enhancing molecular friction and collisions, thus fostering nucleation, and leading to a higher yield of smaller particles [15]. However, when prolonging the irradiation duration at 50 % power from 7 min to 9 min and 11 min, an escalation in particle sizes from 27 nm to 33 nm, and 36 nm, is observed. The formation of larger particles is attributed to sustained particle interactions during prolonged exposure, facilitating continued growth [42].

Table 3
Comparison of thermal conductivity and stability values of cuprous nanofluids synthesized using single step chemical method with ethylene glycol and water (1:1) mixture as base fluid.

Reducing Agent	Copper Precursor	Stabilizing Agent	Thermal Conductivity ($W m^{-1} K^{-1}$)	Stability (in weeks)	Reference
Ribose	Copper sulphate	CTAB	3.590	36	Present work
Ribose	Copper sulphate	SLS	3.052	16	[34]
Glucose	Copper acetate	SLS	2.948	12	[36]
Glucose	Copper nitrate	PVP	2.852	09	[43]

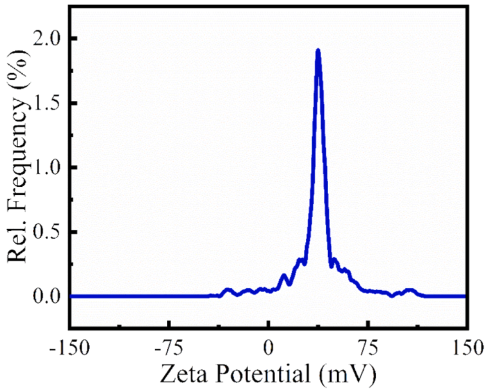

Fig. 6. Zeta potential plot of cuprous oxide nanofluid.

3.4. *Role of surfactant*

In general, the stability of nanofluids is a critical factor for practical applications. Here, we employed CTAB as a stabilizing and capping agent. The study systematically investigated the influence of surfactant concentration on both particle size and stability, with particular relevance to solar applications. We noticed that the particle sizes decreased with increased surfactant concentration due to the capping effect of CTAB (Table 2).

Rapid settling of nanoparticles is observed in the absence of surfactant due to a lack of internal mechanisms for stabilization. However, in the presence of CTAB, particles remained suspended within the base fluid for an extended duration. CTAB, a cationic surfactant capped the nanoparticles post-formation, thus enabling electrostatic stabilization. Here the repulsive columbic forces counterbalance the attractive Vander Waals forces, allowing them to remain stably suspended in the base fluid without undergoing agglomeration. Under stationary conditions at room temperature, a dispersion stability of nine months was observed, attributed to the stabilizing effect of CTAB. The attained dispersion stability exceeded previous reports where SLS and PVP were employed as stabilizing agents as shown in Table 3 [34,36,43]. The stability of the cuprous oxide nanofluid also exceeded that exhibited by copper nanofluids obtained using copper sulphate precursor with PVP (3 weeks) and SLS (6 weeks) as stabilizing agents [24,31]. This indicates CTAB can act as a better capping and stabilizing agent for cuprous oxide nanofluids than other chemicals which is also the case with copper nanofluids [13].

Zeta potential measurements carried out using Litesizer TM 500 instrument were used to evaluate the stability of the synthesized nanofluid. Potential developed at the interface of a particle enveloped by a liquid layer, comprising an inner firmly bound region (stern layer) and outer diffuse region is known as zeta potential [18]. A higher magnitude of zeta potential signifies that the particles influence their charge to a greater distance, resulting in stronger repulsive forces between them

Fig. 7. Nanofluids with different particle weight fractions (0.215 %, 0.107 %, 0.054 %, 0.027 %, 0.013 %, 0.007 %, 0.003 % and 0.000 % from left to right, respectively).

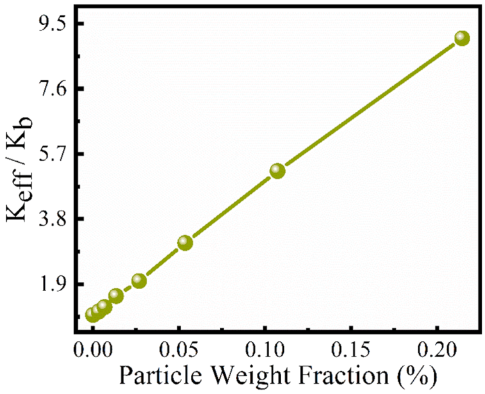

Fig. 8. Variations of thermal conductivity ratio (K_{eff}/K_b where, K_{eff} and K_b are the thermal conductivities of nanofluid and base fluid, respectively) with cuprous oxide nanoparticle weight fractions at 30 °C.

[13]. Consequently, these repulsive forces hinder clustering and agglomeration of nanoparticles, ensuring the nanofluid remains well-dispersed and stable over an extended period. This characteristic is particularly crucial for solar applications, where stability is essential for consistent performance and long-term reliability [44]. Fig. 6 depicts the zeta potential peak at +38 mV, indicating the prepared nanofluid containing cuprous oxide nanoparticles was highly stable. This greater value of zeta potential compared to previous report of +30 mV supports the higher stability obtained in the present case [34].

3.5. Thermal conductivity measurements

Nanofluids play a vital role in heat transfer applications, necessitating fluids of exceptional stability with enhanced thermal conductivity. The synthesized nanofluid exhibited a remarkable thermal conductivity of 3.59 W m^{-1} K^{-1} for a particle loading fraction of 0.215 % at 30 °C as determined by KD2 Pro thermal property analyser using KS 1 sensor. This number notably surpassed thermal conductivity values of cuprous oxide nanofluids synthesized using stabilizing agents like SLS and PVP as indicated in Table 3 [34,36,43]. It also surpassed thermal conductivity values of 0.827 W m^{-1} K^{-1} and 0.979 W m^{-1} K^{-1} obtained for copper nanofluids with copper sulphate as precursor and PVP and SLS as stabilizing agents, respectively [24,31]. The effect of particle weight fraction on thermal conductivity was elucidated by serially diluting the obtained nanofluid. Fig. 7 visually illustrates the different particle weight fractions of 0.215 %, 0.107 %, 0.054 %, 0.027 %, 0.013 %, 0.007 %, 0.003 % and 0.000 % from left to right, respectively, achieved through serial dilution. With an increase in particle weight fraction, the thermal conductivity of nanofluid also increases due to nano-scale particle interactions, and uniform dispersion throughout the base fluid (Fig. 8). The high thermal conductivity and improved dispersion of these nanofluids enable more efficient heat absorption and dissipation, which are crucial for maintaining optimal operating temperatures in solar panels. This not only maximizes energy conversion efficiency but also prolongs the lifespan of solar devices by preventing overheating.

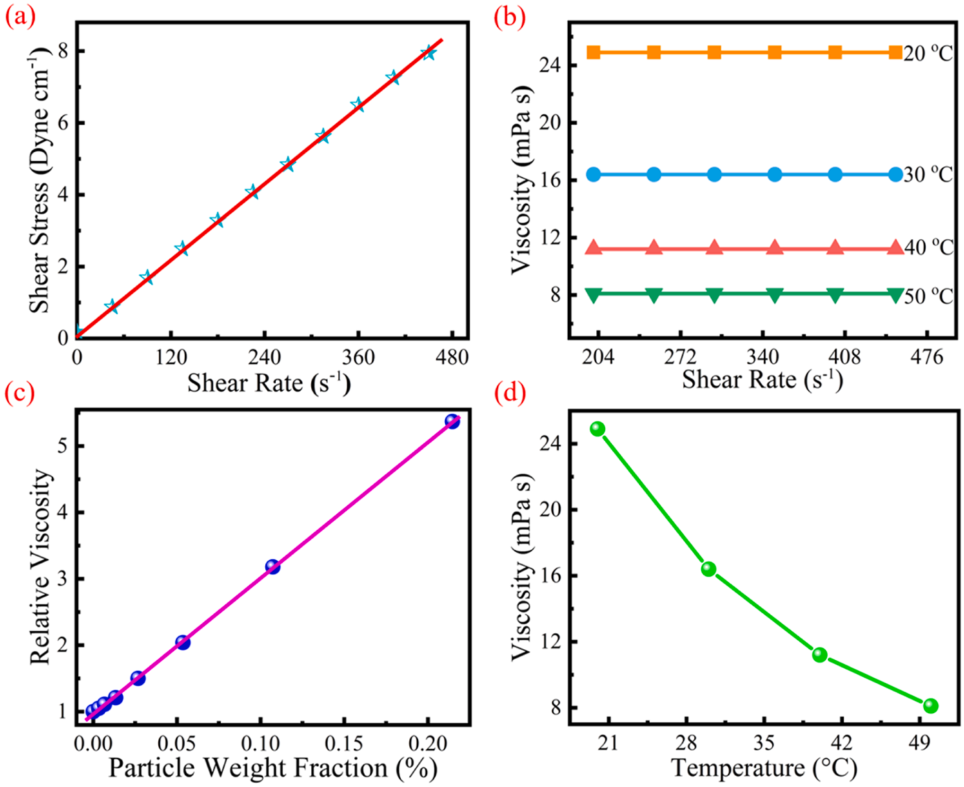

Fig. 9. Rheological measurements. (a) Shear stress versus shear rate at 30 °C; (b) Viscosity as a function of shear rate for particle loading of 0.215 %; (c) Variation of relative viscosity of the nanofluid with particle weight fraction at 30 °C and (d) Viscosity as a function of temperature for particle loading of 0.215 %.

3.6. *Rheological studies*

Understanding the rheological properties of nanofluids becomes pivotal before it is applied in thermal and mechanical applications [45]. Hence, MCR 702 multidrive rotational rheometer from Anton Paar (Austria) was used for determination of rheological properties of the nanofluid. The synthesized nanofluid displays Newtonian behaviour, analogous to water and ethylene glycol which is evident from the linear correlation between shear stress and shear rate, as illustrated in Fig. 9 [34]. At a given temperature, the viscosity of the nanofluid was not impacted by variations in the shear rate. However, we noted a linear rise in viscosity values with increasing particle loading, due to interactive forces between the particles and between the particles and the base fluid within the nanofluid [30]. Additionally, a drop in viscosity is observed as the temperature increases, suggesting that the increase in kinetic energy aided in overcoming the intermolecular forces of attractions [18]. This observation concludes that the current synthetic method facilitates the synthesis of nanofluid exhibiting Newtonian behaviour, even at low particle loading, while concurrently delivering high thermal conductivity and notable stability. These nanofluids hold the potential to advance solar energy utilization by improving heat transfer efficiency, thereby contributing to the global transition towards sustainable renewable energy solutions.

4. Conclusions

To capitalize on the advantage of a one-step chemical method for nanofluid synthesis, we opted for a solution-phase approach to synthesize cuprous oxide nanofluid using ribose. The resulting nanofluid displayed Newtonian behaviour and showed remarkable stability over 9 months. The size of particles was notably affected by different factors, including the concentration of reactants, surfactants, degree of dilution, microwave power and duration of microwave irradiation. Even with a low particle loading fraction of 0.215 %, the nanofluid exhibited significantly improved thermal conductivity (3.59 $W\ m^{-1}\ K^{-1}$). Thus, this method presents a simple and environmentally friendly technique to boost the thermal conductivity of the base fluid (1:1 water and ethylene glycol), offering a fresh and easily obtainable technique for synthesizing cuprous oxide nanofluid in large scale. The study's findings hold significant implications for solar energy systems, offering a viable solution to enhance thermal management and overall efficiency. The eco-friendly synthesis method, coupled with the exceptional thermal properties and stability of the nanofluid, positions it as promising candidate for addressing future critical thermal management challenges in solar energy conversion and storage systems.

CRediT authorship contribution statement

D. Krishna Bhat: Writing – review & editing, Supervision, Resources, Project administration, Conceptualization. **S. Pavan Kumar:** Investigation. **U. Sandhya Shenoy:** Writing – review & editing, Writing – original draft, Investigation, Funding acquisition, Formal analysis.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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