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Research paper

Fabrication of $Zn_{1-X}Cu_XO$ nanoparticles and investigation of their effect on the thermal conductivity of nanofluids

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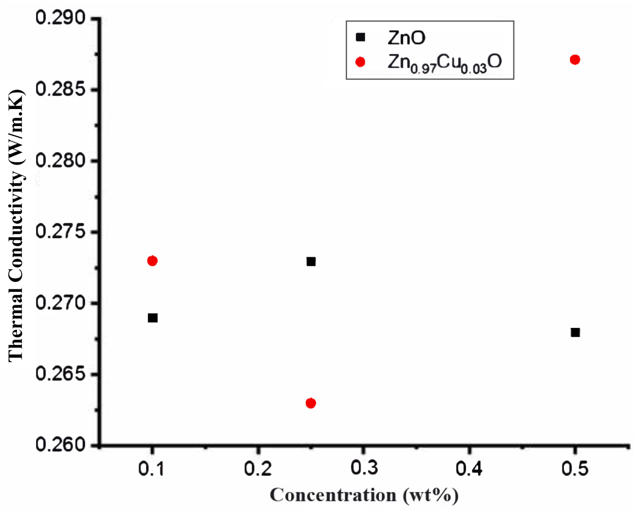
HIGHLIGHTS

- There are few reports on the use of doped nanoparticles to prepare nanofluids. So in this study, $Zn_{0.97}Cu_{0.03}O$ doped nanoparticles were used as an additive to prepare ethylene glycol-based nanofluids.
- The results showed that the thermal conductivity of nanofluids containing $Zn_{0.97}Cu_{0.03}O$ nanoparticles was improved.
- The highest observed thermal conductivity enhancement was 12.5 %.
- An advantage of using doped nanoparticles as additives in the preparation of nanofluids is enhanced nanofluid stability.

GRAPHICAL ABSTRACT



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ABSTRACT

The main purpose of this research is to investigate the effect of doped nanoparticles on the thermal conductivity of nanofluids. ZnO, CuO, and $Zn_{1-X}Cu_XO$ doped nanoparticles were first fabricated by the sol-gel auto-combustion method using glycine as fuel with different molar ratios of glycine/metal ions. Different values of X = 0.02, 0.03, 0.04, 0.06, 0.07, and 0.08 were used to fabricate the $Zn_{1-X}Cu_XO$ doped nanoparticles. The X-ray diffraction patterns showed that the substitution of Zn atoms with Cu atoms was completed for X = 0.02 and 0.03, so X = 0.03 was obtained as the solubility limit for fabricating $Zn_{1-X}Cu_XO$ doped nanoparticles. The ZnO, CuO, and $Zn_{0.97}Cu_{0.03}O$ doped nanoparticles were then used as an additive to prepare ethylene glycol-based nanofluids with different nanoparticle concentrations. The results showed the highest observed thermal conductivity enhancement was 12.5 % and related to the nanofluid containing $Zn_{0.97}Cu_{0.03}O$ doped nanoparticles at a concentration of 0.5 wt%. Moreover, adding Cu to the ZnO structure increased the thermal conductivity of the ethylene glycol-based nanofluid containing $Zn_{0.97}Cu_{0.03}O$ doped nanoparticles due to its high thermal conductivity.

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1. Introduction

Nanotechnology can fabricate, control, and use materials in nanometer dimensions and has been used to create more effective systems in many fields of application [1-2]. Some fields in which nanotechnology has been able to find special applications are cooling engines in electronic, mechanical and nuclear systems, heating and cooling systems, heat storage, and so on [3-4]. One particular material that has made progress in these areas is nanofluids. Nanofluids include a base fluid with suspended nanoparticles that increases the efficiency of heat transfer fluids. The term nanofluid was invented by Choi in 1995. Base fluids have low thermal conductivity and low efficiency in heat transfer systems. Therefore, if the nanoparticles have high thermal conductivity, one can increase the heat transfer coefficient of fluids by dispersing them in the base fluid [5-6]. For example, various additives, such as metal and metal oxide nanoparticles or carbon nanotubes, have been dispersed in base fluids to improve the thermal conductivity of nanofluids [6]. If more than one type of nanoadditive is used to prepare a nanofluid, the suspension is called a hybrid nanofluid [7-9]. Zinc oxide and copper oxide nanoparticles are among the various metal oxides used in the preparation of nanofluids. The thermal conductivity of ZnO and CuO is 21 and 32.9 $W.m^{-1}.K^{-1}$, which are much higher than the thermal conductivity of base fluids (water, ethylene glycol, and oil) [4, 10-11]. ZnO, one of the most widely used metal oxides, is n-type semiconductor that is chemically and thermally stable with a band gap of 3.37 eV. CuO, another attractive metal oxide, is a P-type semiconductor with a band gap of 1.85 eV [12]. One way to improve the properties of metal oxides is to substitute one metal atom with another. For example, the Zn atoms in ZnO can be substituted with Cu atoms, changing the properties of the matter [13-14]. Many articles have used ZnO and CuO nanoparticles and their combinations to prepare hybrid nanofluids [15]. However, no articles were found about the doped nanoparticles used to prepare nanofluids. Therefore, the main goal of this research is to dope a nanoparticle (ZnO) with another nanoparticle that has higher thermal conductivity (CuO) and then investigate the thermal conductivity of nanofluids containing the doped nanoparticles ($Zn_{1-X}Cu_XO$) compared to its mono nanofluid. In this study, $Zn_{1-X}Cu_XO$ doped nanoparticles were first prepared and then used as an additive to prepare ethylene glycol-based nanofluids with different concentrations to investigate the effect of the doped nanoparticle on the thermal conductivity of nanofluids.

2. Experimental

In this study, the sol-gel auto-combustion method was used to synthesize ZnO, CuO, and $Zn_{1-X}Cu_XO$ nanoparticles. Hexahydrate Zinc nitrate ($Zn(NO_3)_2.6H_2O$) and trihydrate copper (II) nitrate ($Cu(NO_3)_2.3H_2O$) were used as precursors, and glycine ($C_2H_5NO_2$) was used as fuel for combustion. First, different molar ratios of glycine/metal ions (1:1, 1:2, 1:4, and 1:6) were used to synthesize ZnO and CuO nanoparticles. To prepare each of the nanoparticles, a specific amount of metallic nitrate was weighed, and the corresponding amount of glycine was obtained using stoichiometric equations. Then, they were mixed in water using a magnetic stirrer for 30 min. with no heat in order to obtain a uniform solution (Sol). Next, the solution was heated at 100 ^oC and stirred with a magnetic stirrer at a constant speed until a gel was formed. Heating was continued until the combustion process took place and a powdery matter was obtained. Next, the resulting powder was grounded thoroughly and reheated at 500 ^oC for 4 h. Results showed that the average size of the obtained nanoparticles was smaller in the 1:1 ratio, and the particle size distribution was more uniform than in the other ratios. So, the 1:1 ratio was chosen to synthesize $Zn_{1-X}Cu_XO$ doped nanoparticles. Afterward, different values of X = 0.02, 0.03, 0.04, 0.06, 0.07, and 0.08 were used to find the solubility limit of copper in the zinc oxide nanoparticles. The results showed that X = 0.03 was the solubility limit, after which traces of copper oxide were observed in the XRD patterns. The $Zn_{0.97}Cu_{0.03}O$ nanoparticles were then used to prepare nanofluids with concentrations of 0.1, 0.25, and 0.5 (wt%). To prepare nanofluids, a specific mass of nanoparticles was placed in a container, a specific volume of ethylene glycol was added to it, and the mixture was sonicated for 2 h. Lastly, the thermal conductivity of the nanofluids was measured using a KD2-Pro thermal analyzer (Decagon Devices, USA).

3. Results and discussion

X-ray diffraction pattern (XRD) was used to study the structure and crystallinity of the samples. Fig. 1 shows the X-ray diffraction patterns of ZnO nanoparticles with different molar ratios of glycine/zinc ions. It was observed that for all samples, the X-ray diffraction patterns showed a wurtzite hexagonal structure of zinc oxide corresponding to the standard JCPDS card No. 05-0664, and no additional peaks were observed. Fig. 2 shows the X-ray diffraction pattern of CuO nanoparticles with different molar ratios of glycine/copper ions. In this figure, it was also observed that for all samples, the X-ray diffraction pattern corresponds to the standard JCPDS card No. 45-0937 card, and no additional peaks were observed.

Field emission scanning electron microscopy (FE-SEM) was used to study the morphology of the nanoparticles. Fig. 3 shows the FE-SEM images of zinc oxide nanoparticles, and Fig. 4 shows the FE-SEM images of copper oxide nanoparticles with different glycine/metal ion ratios of 1:1, 1:2, 1:4, and 1:6. For both types of nanoparticles, the results showed that as the amount of the fuel increased, the morphology of the particles became more spherical and uniform, and the average particle size became smaller. Since the smaller particles are more suitable for preparing stable nanofluids, the sample with the highest amount of fuel (1:1 ratio) was considered the optimal sample.

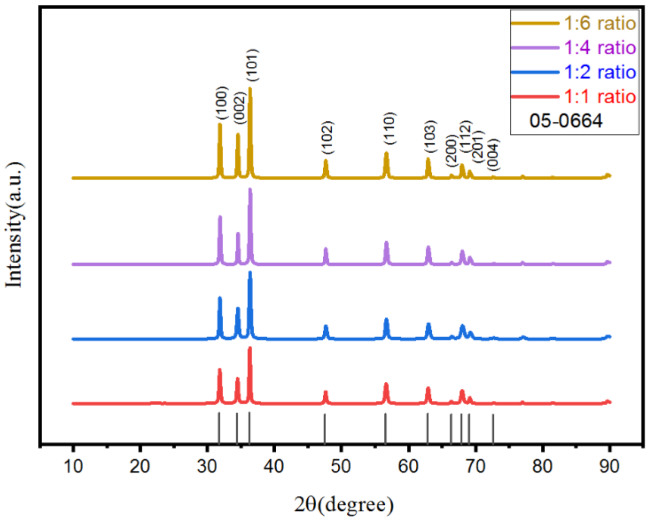

Fig. 1. X-ray diffraction pattern of ZnO nanoparticles with different molar ratios of glycine/zinc ions.

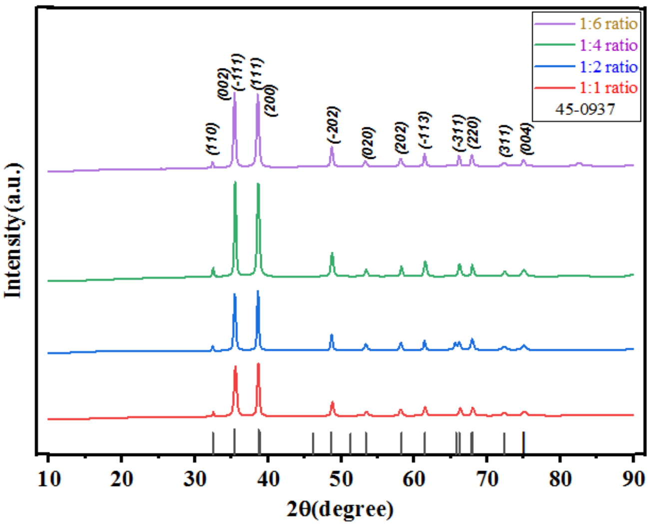

Fig. 2. X-ray diffraction pattern of CuO nanoparticles with different molar ratios of glycine/copper ions.

The average particle size of the samples was measured using Digimizer software. Table 1 shows the average particle size of ZnO nanoparticles with different molar ratios of glycine/zinc ions, and Table 2 shows the average particle size of CuO nanoparticles with different molar ratios of glycine/copper ions. As can be seen, the average particle size decreased for both types of nanoparticles as the amount of fuel increased.

In order to fabricate $Zn_{1-X}Cu_XO$ doped nanoparticles, a 1:1 ratio for the molar ratio of glycine/metal ions was chosen. In addition, different values of X = 0.02, 0.03, 0.04, 0.06, 0.07, and 0.08 were investigated to find the solubility limit for doping zinc oxide nanoparticles with copper atoms. Fig. 5 shows the X-ray diffraction pattern of the different samples. As seen, for X = 0.02 and 0.03, no additional peaks were observed in XRD patterns, indicating a complete substitution of Cu atoms. While for X = 0.04, a small peak appeared around $2\theta = 38°$,

Table 1. The average particle size for zinc oxide samples with different molar ratios of glycine/zinc ions.

Molar ratio of glycine/zinc ions	Average particle size (nm)	Range of particle size (nm)
1:1	58	10-95
1:2	76	10-130
1:4	185	36-690
1:6	150	51-900

Table 2. The average particle size for copper oxide samples with different molar ratios of glycine/copper ions.

Molar ratio of glycine/copper ions	Average particle size (nm)	Range of particle size (nm)
1:1	95	15-360
1:2	130	28-335
1:4	180	10-760
1:6	170	10-1000

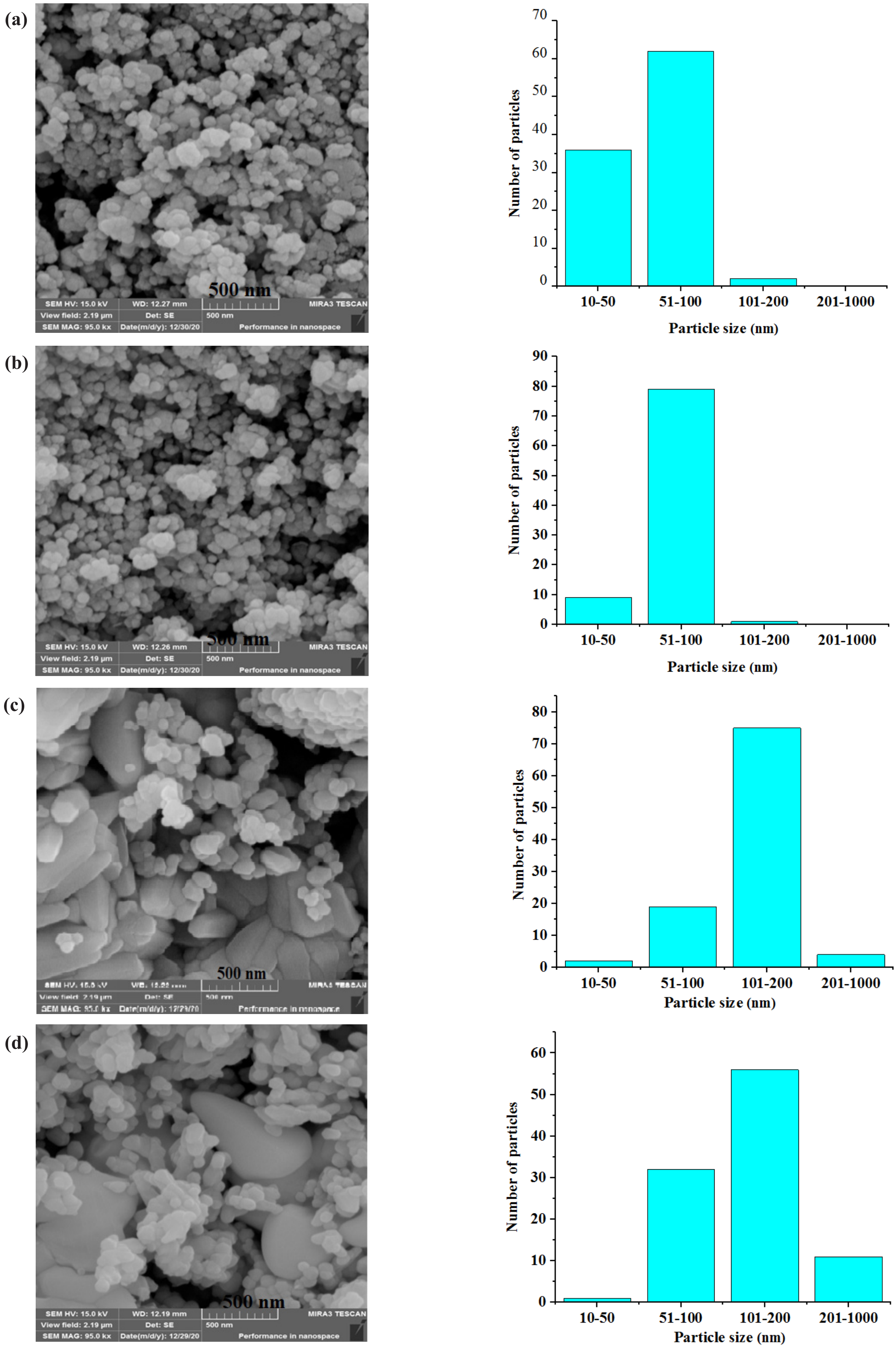

Fig. 3. FE-SEM images and frequency distribution diagrams of ZnO nanoparticles with different ratios of glycine/zinc ions, (a) 1:1, (b) 1:2, (c) 1:4, and (d) 1:6.

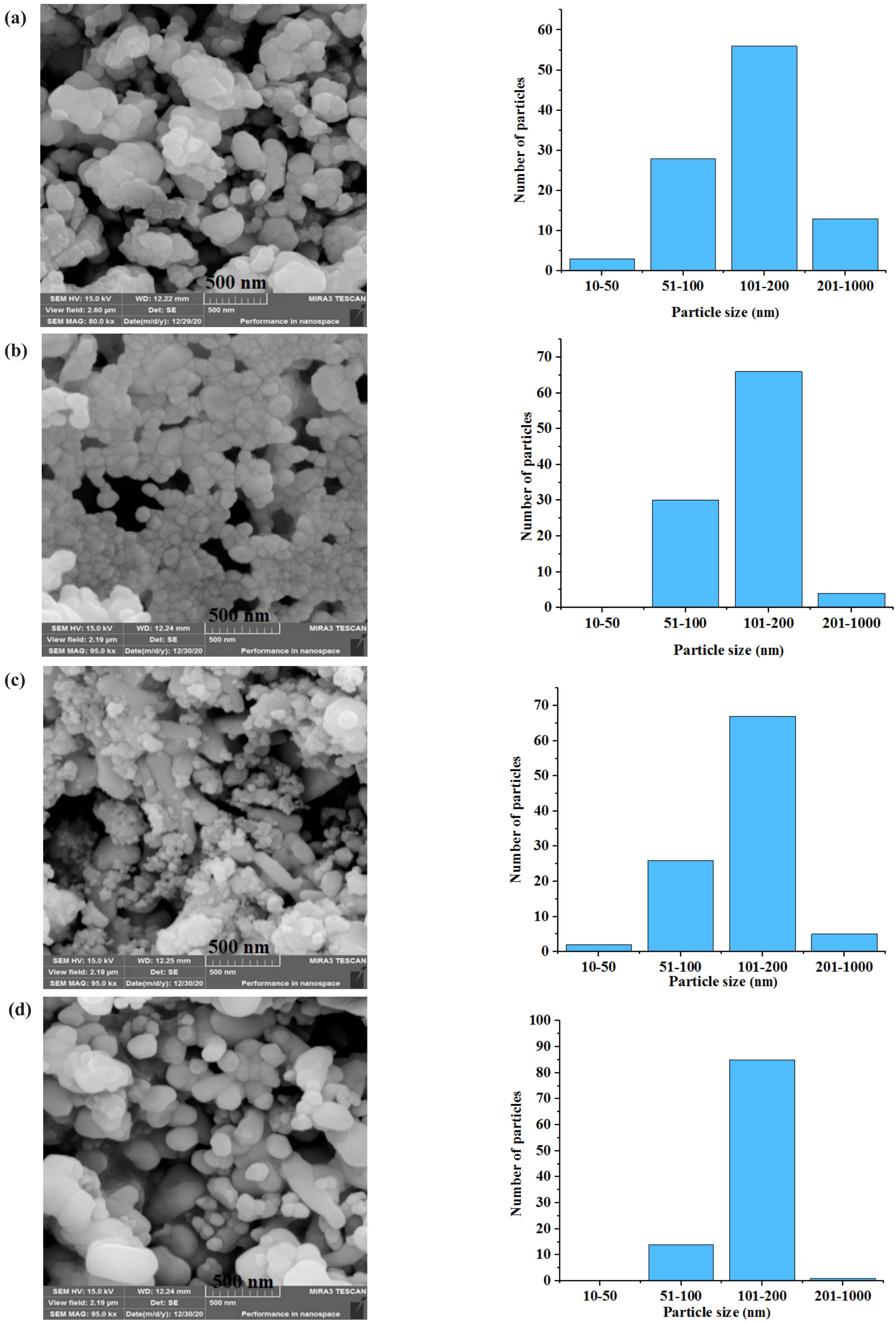

Fig. 4. FE-SEM images and frequency distribution diagrams of CuO nanoparticles with different ratios of glycine/copper ions, (a) 1:1, (b) 1:2, (c) 1:4, and (d) 1:6.

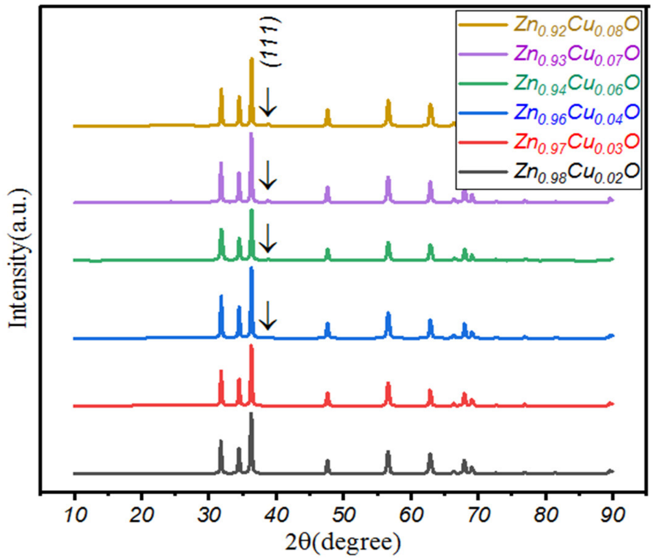

Fig. 5. X-ray diffraction pattern of $Zn_{1-X}Cu_XO$ doped nanoparticles (X= 0.02, 0.03, 0.04, 0.06, 0.07, and 0.08).

which is related to the crystal plane (111) of copper oxide, which grows as the X value increases in the following samples.

The presence of additional peaks around 2θ = 38° indicates that for samples with values of X = 0.04 and above, the copper atoms could not completely substitute. Therefore, X = 0.03 was considered the solubility limit for the fabrication of $Zn_{1-X}Cu_XO$n noparticles. Fig. 6 shows the FE-SEM images of $Zn_{1-X}Cu_XO$ nanoparticles. The average particle size of doped samples with different values of X was calculated using Digimizer software, shown in Table 3.

In order to investigate the effect of nanoparticles' doping on the thermal conductivity of nanofluids, ZnO, CuO, and $Zn_{0.97}Cu_{0.03}O$ nanoparticles were used as an additive to prepare ethylene glycol-based nanofluids at different concentrations of 0.1, 0.25 and 0.5 (wt%). The thermal conductivity of the samples was measured using the standard transient hot-wire method by a KD2-Probe thermal analyser (Decagon Devices, Inc., USA) using a KS-1 probe. It is necessary to observe some important points to avoid convection effects and accurately measure with a KD2-Probe, such as dipping the probe vertically into the middle of the suspension and preparing a thermally and acoustically stable environment around the sample. It is important to note that the KD2-Pro has the ability to show if the quality of the conditions is suitable for measuring thermal conductivity by an error factor. The thermal conductivity value is reliable if the error is less than 0.01. To ensure the precise thermal conductivity measurement, all measurements were done ten times, and the average value was reported. The maximum measurement error was ±5 %.

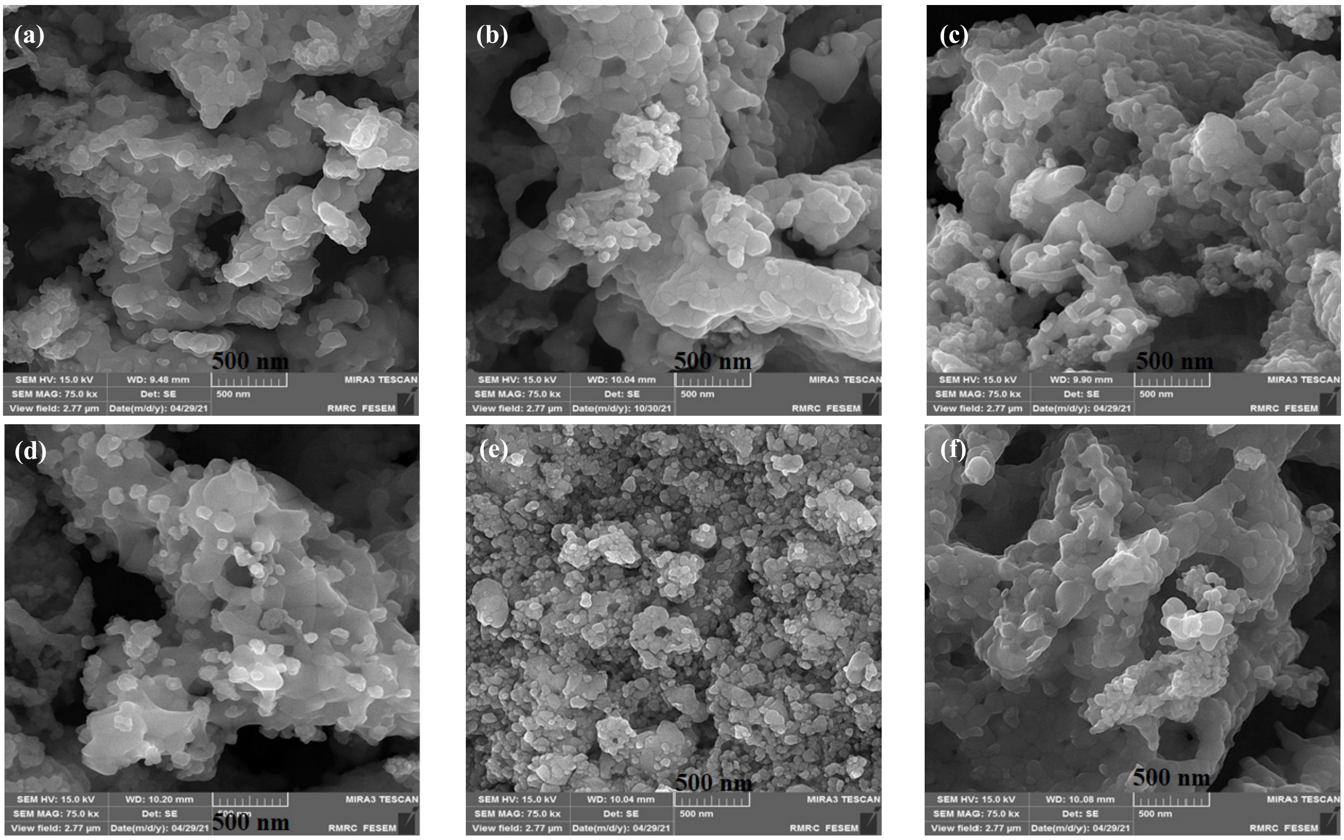

Fig. 6. FESEM images of $Zn_{1-X}Cu_XO$ doped nanoparticles, (a) X= 0.02, (b) X= 0.03, (c) X= 0.04, (d) X= 0.06, (e) X= 0.07, and (f) X= 0.08.

Table 3. The average particle size of $Zn_{1-X}Cu_XO$ doped nanoparticles (X= 0.02, 0.03, 0.04, 0.06, 0.07, and 0.08).

Doped samples	Average particle size (nm)	Range of particle size (nm)
$Zn_{0.98}Cu_{0.02}O$	57	15-140
$Zn_{0.97}Cu_{0.03}O$	61	17-130
$Zn_{0.96}Cu_{0.04}O$	66	20-150
$Zn_{0.94}Cu_{0.06}O$	74	20-305
$Zn_{0.93}Cu_{0.07}O$	81	30-260
$Zn_{0.92}Cu_{0.08}O$	97	22-245

Fig. 7 shows the thermal conductivity of nanofluids containing ZnO, CuO, and $Zn_{0.97}Cu_{0.03}O$ nanoparticles, and Table 4 shows the thermal conductivity enhancement for the nanofluids with different concentrations of 0.1, 0.25, and 0.5 (wt%). As can be seen, nanofluids containing $Zn_{0.97}Cu_{0.03}O$ nanoparticles have a higher thermal conductivity than nanofluids containing ZnO nanoparticles. The highest observed thermal conductivity enhancement was 12.5%, related to the nanofluid containing $Zn_{0.97}Cu_{0.03}O$ nanoparticles at a concentration of 0.5 wt%. As can be seen in Fig.7, nanofluids containing CuO nanoparticles have higher thermal conductivity than the other samples. So, by doping the ZnO nanoparticles with CuO nanoparticles, the thermal conductivity of doped nanoparticles ($Zn_{0.97}Cu_{0.03}O$) was increased compared to the ZnO nanoparticles.

The advantage of using doped nanoparticles as additives in the preparation of nanofluids includes

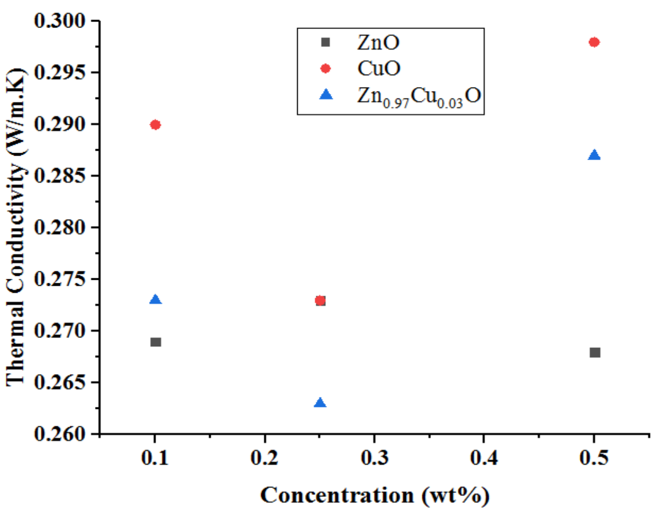

Fig. 7. Thermal conductivity of nanofluids containing ZnO, CuO, and $Zn_{0.97}Cu_{0.03}O$ nanoparticles at different concentrations.

Table 4. Thermal conductivity enhancement for nanofluids containing ZnO, CuO, and $Zn_{0.97}Cu_{0.03}O$ nanoparticles in different concentrations.

Nanoparticles concentrations (wt%)	ZnO	CuO	$Zn_{0.97}Cu_{0.03}O$
0.1	6.69	13.45	8.05
0.25	8.39	8.06	4.56
0.5	6.34	15.78	12.5

enhancing the nanofluids' stability. Many researchers have investigated the thermal conductivity of hybrid nanofluids in recent years to increase the thermal conductivity of nanofluids. However, the stability of nanofluids has always been its main challenge. It seems that using elements with higher thermal conductivity to synthesize doped nanoparticles should increase the thermal conductivity of the resulting material. So, when doped nanoparticles are used to synthesize nanofluids instead of two separated nanoparticles, it should be possible to achieve better stability more easily. This hypothesis will be investigated in future research.

4. Conclusions

In this study, ZnO, CuO, and $Zn_{1-X}Cu_XO$ nanoparticles were fabricated using the sol-gel auto-combustion method, and the effect of fuel on their size was investigated. In this study, the amount of fuel (glycine) relative to metal ions was systematically increased, and it was observed that as the amount of glycine relative to metal ions increased, the size of nanoparticles decreased. Also, in order to find the solubility limit of copper in zinc oxide nanoparticles, different values of X = 0.02, 0.03, 0.04, 0.06, 0.07, and 0.08 were used, and the value of X = 0.03 was found to be the solubility limit for the fabrication of $Zn_{1-X}Cu_XO$ doped nanoparticles. ZnO and $Zn_{0.97}Cu_{0.03}O$ nanoparticles were used as an additive to prepare ethylene glycol-based nanofluids with different concentrations of 0.1, 0.25, and 0.5 (wt%). It was observed that nanofluids containing $Zn_{0.97}Cu_{0.03}O$ nanoparticles have a higher thermal conductivity than nanofluids containing ZnO nanoparticles. The highest observed thermal conductivity enhancement was 12.5 %, related to the nanofluid containing $Zn_{0.97}Cu_{0.03}O$ nanoparticles at a concentration of 0.5 wt%.

Conflict of interest

No potential conflict of interest was reported by the authors.

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Additional information

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