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Original Research Article

Alcohol assisted synthesis and photothermal studies of ZnO nanostructures

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ABSTRACT

In this paper, we experimentally investigated the thermal diffusivity of ZnO nanostructures synthesized by solution method using methanol, 1-butanol, 1-hexanol, and 1-decanol as solvents. The dual beam thermal lens technique was utilized for measuring thermal diffusivity. The results reveal the morphology-dependent thermal properties of ZnO nanoparticles. Thermal diffusivity variations dependence the ZnO emission mechanism.

1. Introduction

The solution method is a simple and low-cost chemical method. Ostwald ripening, nucleation, aggregation, and coarsening are different types of growth mechanisms involved in the solution method. The choice of solvent is a prime factor in the growth mechanism. The solvent properties such as dielectric constant, viscosity, dipole moment, polarity, coordination ability, and solubility are the dependent parameter for the growth kinetics of nanoparticles [1, 2]. Alcohols are organic solvents used in the nanoparticle synthesis process that can help to control size and morphology properly. The ZnO nanoparticles growth process in the alcohol phase is relatively small than in an aqueous solution [2, 3].

The thermal lens technique is a simple, precise, less time-consuming, and sensitive technique for measuring thermal diffusivity carried out at room temperature. Thermal diffusivity (α) is related to thermal conductivity (k), specific heat capacity (C_p) and density of the fluid (ρ) by the equation $\alpha = k/\rho C_p$. So, the determination of thermal diffusivity leads to an accurate measurement of thermal conductivity. The thermal

diffusivity of colloids depends on the size, shape, and concentration of particles suspended in them. Conventional fluids contain micro-sized particles, and the chance of agglomeration is more, preventing heat transfer. Fluids consist of nanoparticles (sizes 1-100 nm) that enhance the heat transfer mechanism. These fluids are named nanofluids, considered next-generation heat transfer fluids [4-6].

In this paper, we discussed the structural dependence on the thermal diffusivity of ZnO nanofluid.

2. Experimental

2.1 Synthesis of ZnO nanostructures

A simple solution method was used for the synthesis of ZnO nanostructures. The synthesis procedure was carried out in the presence of various primary alcohols. A detailed description of the synthesis, characterizations, and growth mechanisms has been described in the previously published paper [2]. A schematic representation of the synthesis procedure is shown in Figure 1.

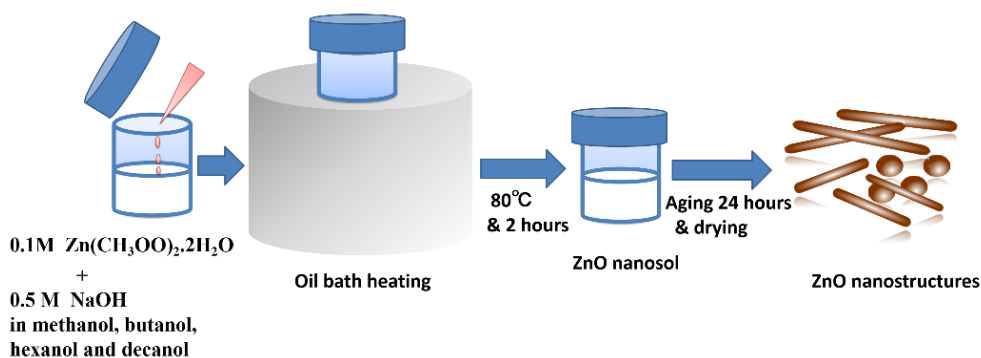


Figure 1: Schematic of ZnO nanostructure synthesis.



The synthesized ZnO nanostructures are dispersed in water at a concentration of 0.1 mg/ml under 1 hour of ultrasonication. This ultrasonication results in the formation of stable ZnO nanofluids. Using this nanofluid thermal studies are carried out.

2.2 Thermal studies

The thermal diffusivity of the prepared nanofluid was estimated using the dual beam thermal lens technique. Schematic representation was shown in Figure 2. In a thermal lens, the sample is irradiated by a DPSS laser (403 nm, 100 mW), which changes the refractive index of the medium to produce a lensing effect. Using the probe, He-Ne laser (632.8 nm, 4 mW), we can detect the thermal lens signals. More experimental and theoretical details are given in our previously published work [4].

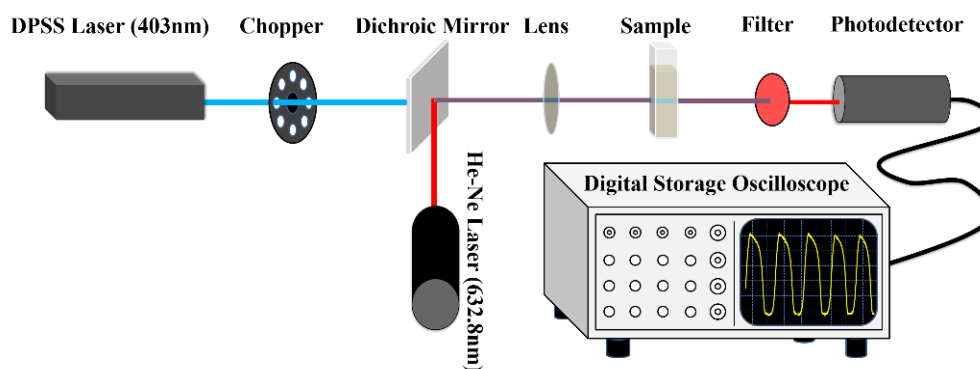


Figure 2: Schematic representation of thermal lens experimental setup.

3. Results and discussion

TEM images of ZnO nanostructures synthesized in primary alcohols are shown in Figure 3. The ZnO nanostructures synthesized in methanol, butanol, hexanol, and decanol were named Sample A, Sample B, Sample C and Sample D. In methanol medium 17 nm sized ZnO nanodots are formed. In butanol (size ~ 2 nm, length ~ 62 nm) and hexanol (size ~ 18 nm, length ~ 90 nm) medium regularly arranged nanorods are formed. In decanol medium larger sized (~ 33 nm) nanodots are formed. These results show that morphological tuning was observed with respect to the alkyl group length.

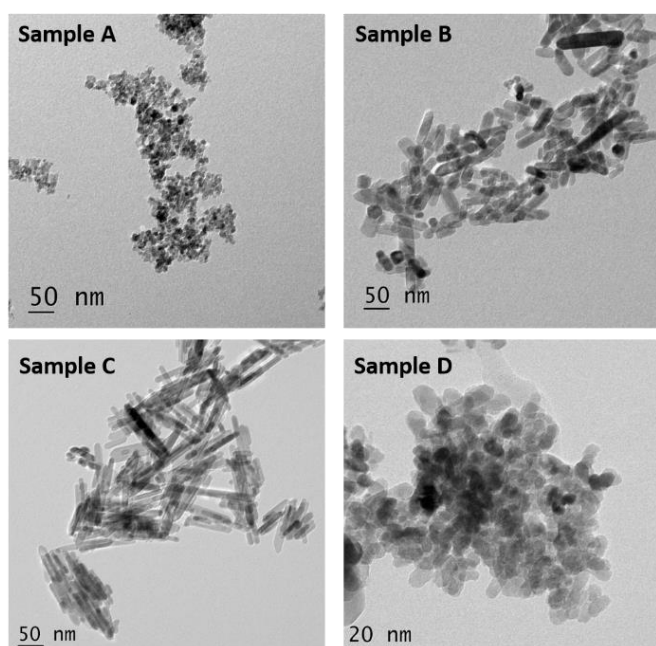


Figure 3: TEM image of synthesized ZnO nanostructures.

The morphology-dependent thermal diffusivity was studied. Figure 4 shows the thermal response of water-based ZnO nanofluid consisting of different shaped and sized nanoparticles. The time-dependent probe beam intensity was given by

$$I(t) = I(0) \left[1 - \frac{\theta}{1 + \frac{t_c}{2(t-t_0)}} + \frac{\theta^2}{2(1 + \frac{t_c}{2(t-t_0)})^2} \right]^{-1}$$

where θ and t_c are fitting parameters. Thermal diffusivity, $\alpha = \omega^2/4t_c$, where ω is the beam waist radius and t_c is the time constant. Table 1 shows the thermal diffusivity values of the ZnO nanofluid. From the table, we realized that the structure of dispersed nanoparticles has a greater role in thermal diffusivity.

Table 1: Morphology-dependent thermal diffusivity of ZnO nanofluid.

Sample	Solvent	Thermal diffusivity (α) $\times 10^{-4}$ cm ² /sec
A	Methanol	2.184
B	Butanol	5.922
C	Hexanol	3.866
D	Decanol	2.528

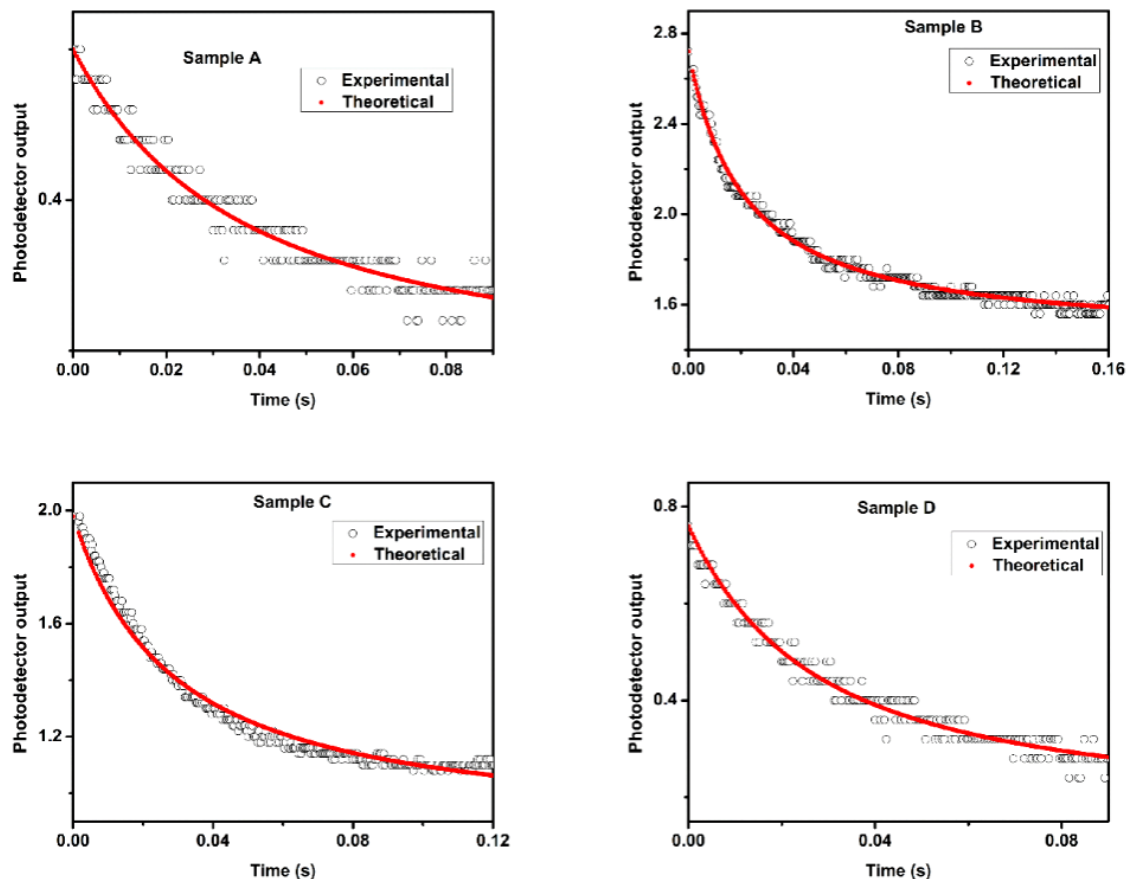


Figure 4: Thermal lensing plot of ZnO nanofluid.

ZnO nanorods prepared in a butanol medium show enhanced thermal diffusivity compared to other structures. The larger nanorods prepared in hexanol medium show the second highest thermal diffusivity value. The dot like structure shows a lower thermal diffusivity value. The size of nanodots increases thermal diffusivity. This is due to reduce the phonon scattering and increasing the thermal diffusivity value. Also, with increases in particle size, interfacial thermal resistance decreases which increase the heat transfer mechanism. In the case of smaller-sized nanoparticles contact with the surrounding liquid is low, which leads to a decrease in thermal diffusivity [4].

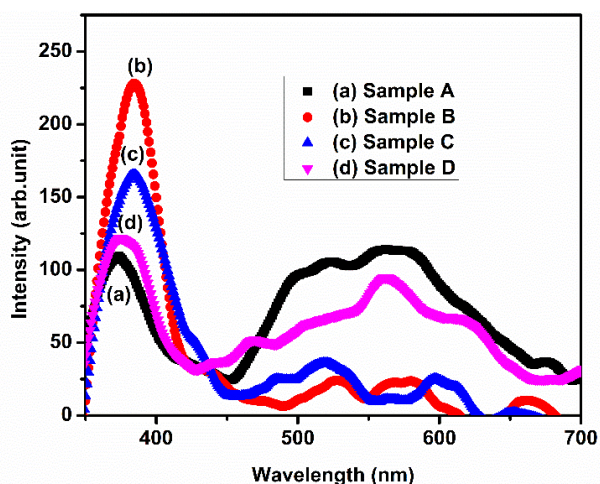


Figure 5: Emission spectra of ZnO nanostructures.

The thermal diffusivity variations were explained using emission intensity variation shown in Figure 5. ZnO shows near band emission (UV emission) and defect state (visible) emission [7]. From emission spectra, it is clear that defect state (visible) emission is maximum for dot-like structures. This is the reason for decreasing the thermal diffusivity [7].

4. Conclusions

The present work explored the structural dependence on the thermal properties of ZnO nanocolloids. It was observed that ZnO nanorod-based nanocolloids showed higher thermal diffusivity value than nanodot structures. The emission mechanism played a critical role in thermal diffusivity. ZnO lattice defect state emission increases in turn decrease the thermal diffusivity of nanofluid.

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