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Thermal diffusivity of silver metallic nanoparticles in clay matrix

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In this work, we have applied thermal lens (TL) technique to measure thermal diffusivity of clay suspensions containing metallic silver nanoparticles (Ag-NPs) prepared by chemical reduction method in different concentration. This study carried out with diode laser (wavelength 514 nm, power 80mW) as the excitation source and intensity stabilized He-Ne laser as a probe beam. The results show that thermal diffusivity of fluid increases when Ag-NPs concentrations increase.

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Keywords: Silver nanoparticle, Nanofluids, Thermal lens, Thermal diffusivity

1. Introduction

Nanoparticles (NPs) are important materials with new physical and chemical properties which are totally different from those observed in bulk materials [1]. They have applications in vast area such as heat transfer fluids in automotive and electronic cooling [2] and as targeted thermal agents for use in medical therapies and drug delivery [3] and many others that have been approved and studied during this year's. But when pure metallic NPs are used alone, they present some common problems, e.g. agglomeration between together [4]. To overcome the agglomeration, one of the most effective solutions is to prepare NPs based in clay matrices, in which NPs are supported within the interlamellar spaces of clay and on its external surfaces [5-7]. Montmorillonite (MMT) as a lamellar clay has intercalation, swelling and ion exchange properties. Its interlayer space has been used for the synthesis of material and biomaterial NPs, as support for anchoring transition-metal complex catalysts and as adsorbents for cationic ions [8]. Thermal lens (TL) technique is one of the photothermal techniques is very sensitive and accurate methods that can be apply to measure thermal diffusivity of sample. This technique is result of temperature gradient which is following to absorption of radiation and nonradiative relaxation of the excited molecules. The laser excitation beam profile is Gaussian so the temperature gradient produces a refractive index gradient which behaves like a converging or diverging lens depending on whether dn/dT is positive or negative [9], therefore when the probe beam propagate inside the sample can focused or defocused by this lens. Measuring of this change in intensity of probe beam has relation with thermo optical parameters of sample.

In this work, we used this technique to investigate thermal diffusivity of clay suspensions containing metallic Ag-NPs with different concentration.

2. Experiment

2.1 Materials

All reagents were of analytical grades and were used as received without further purification. $AgNO_3$ (99.98%), used as silver precursor, was supplied from Merck, Germany. MMT, used as a solid support for Ag-NPs, was purchased from Kunipia-F, Japan. $NaBH_4$ (98.5%, Sigma-Aldrich, USA) was used as a reducing agent. All aqueous solutions were prepared with double distilled water (DD-water).

2.2 Synthesis of Ag/MMT nanocomposites

For preparation of Ag/MMT nanocomposites we applied, the silver contents of the samples were synthesized in 0.5%, 1.0%, 2.0% and 5.0% Ag/MMT. Constant amounts of MMT were suspended in different volumes of 1×10^{-3} M $AgNO_3$ solution and stirred for 24 hr. Freshly prepared $NaBH_4$ (4×10^{-2} M) solution was then added to the suspensions under continuous stirring to reach a constant $AgNO_3/NaBH_4$ molar ratio (1:4). After the addition of the reducing agent stirring was continued for another one hour. The suspensions were finally centrifuged, washed with Double-distilled water twice and dried under vacuum overnight. All experiments were conducted at ambient temperature. The prepared Ag/MMT

nanocomposites were characterized by using ultraviolet-visible (UV-vis) spectroscopy and transmission electron microscopy (TEM). The UV-vis spectra were recorded over the range of 300-700 nm by a Lambda 25-Perkin Elmer UV-vis spectrophotometer. TEM observations were carried out on a Hitachi H-7100 electron microscopy, and the particle size distributions were determined using the UTHSCSA Image Tool software, Version 3.00 program. After reactions the samples were centrifuged by using high speed centrifuge machine (Avanti J25, Beckman).

2.3 Experimental setup

The thermal lens (TL) experimental setup is shown in Fig. 1. Measurements were carried out using a diode laser (532 nm and 80 mW) as an excitation light and a He-Ne laser (632.8 nm and 0.5mW) as a probe beam. The excitation beam was focused by a lens with 21 cm focal length and the sample was positioned at its focal plane. A chopper with variable frequency controls the exposure of the sample to the excitation beam. The probe beam was focused by a lens with 5 cm focal length and aligned at an angle smaller than 1.5° with respect to the excitation beam. The focused probe beam waist is positioned around $\sqrt{3}\, z_c$ to the cuvette. A bandpass filter was placed over the pinhole to prevent stray light entering the photodiode (PD). The output of the PD was sent to the storage oscilloscope for further analysis. The LabVIEW software was used to capture the time history data from oscilloscope and to normalized it with respect to signal at time t=0.

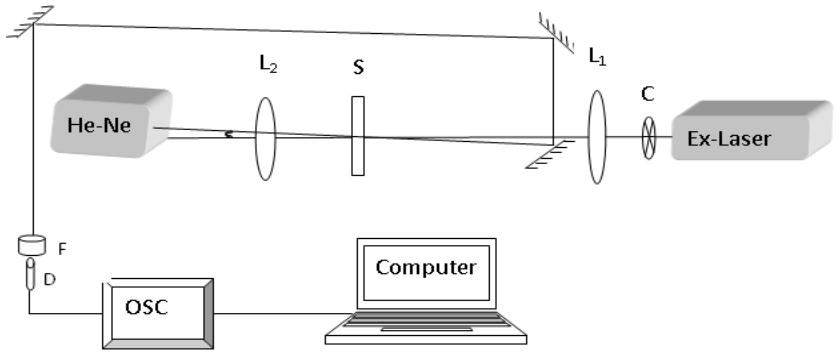

Fig.1. experimental set up of thermal lens.

3. Results and discussions

The probe beam intensity at the detector plane can be given by [10]:

$$I(t) = I(0)\left[1-\frac{\theta}{2}\tan^{-1}\left(\frac{2mV}{[(1+2m)^2+V^2]\frac{t_c}{2t}+1+2m+V^2}\right)\right]^2 \quad (1)$$

Where

$$V=\frac{z_1}{z_c};\ \theta=-\frac{p_e A_e L}{\kappa\lambda}\left(\frac{dn}{dT}\right);\quad m=\left(\frac{w_p}{w_e}\right)^2;$$

$$and \quad D=\frac{w_e^2}{4t_c} \quad (2)$$

Here, $I(0)$ is the initial intensity when t is zero, p_e is the excitation beam power (80 mW), A_e is the absorption coefficient (cm^{-1}), L is the sample thickness, λ is the laser wavelength (632.8 nm).

The dn/dT is the change refractive index of the sample, $z_c = w_0^2/\lambda$ is the confocal distance (cm), Z_1 is the distance of the laser beam waist to sample, D is the thermal diffusivity of the sample (cm^2/s), t_c is the characteristic thermal time constant. The parameter, θ and t_c can be determined by fitting the experimentally measured intensity to Eq. (1). This thermal diffusivity D can be calculated by using Eq. (2).

Fig. 2 shows the UV-vis absorption spectra of the prepared Ag-NPs. The characteristic silver surface plasmon resonance (SPR) bands were detected around 400 nm. These absorption bands were assumed to correspond to the Ag-NPs smaller than 10 nm [11, 12]. TEM images and size distributions of Ag-NPs also confirmed this phenomenon (Fig. 2). While there is no characteristic UV-vis absorption of Ag-NPs before addition of $NaBH_4$ (Fig. 3e), growth of the Plasmon peak at 396 nm indicates the formation of Ag-NPs in Figure. 3a Gradual increase in $AgNO_3$ concentration, from Fig. 3a-d, increases the corresponding peak intensities due to increases in Ag-NPs concentrations [13].

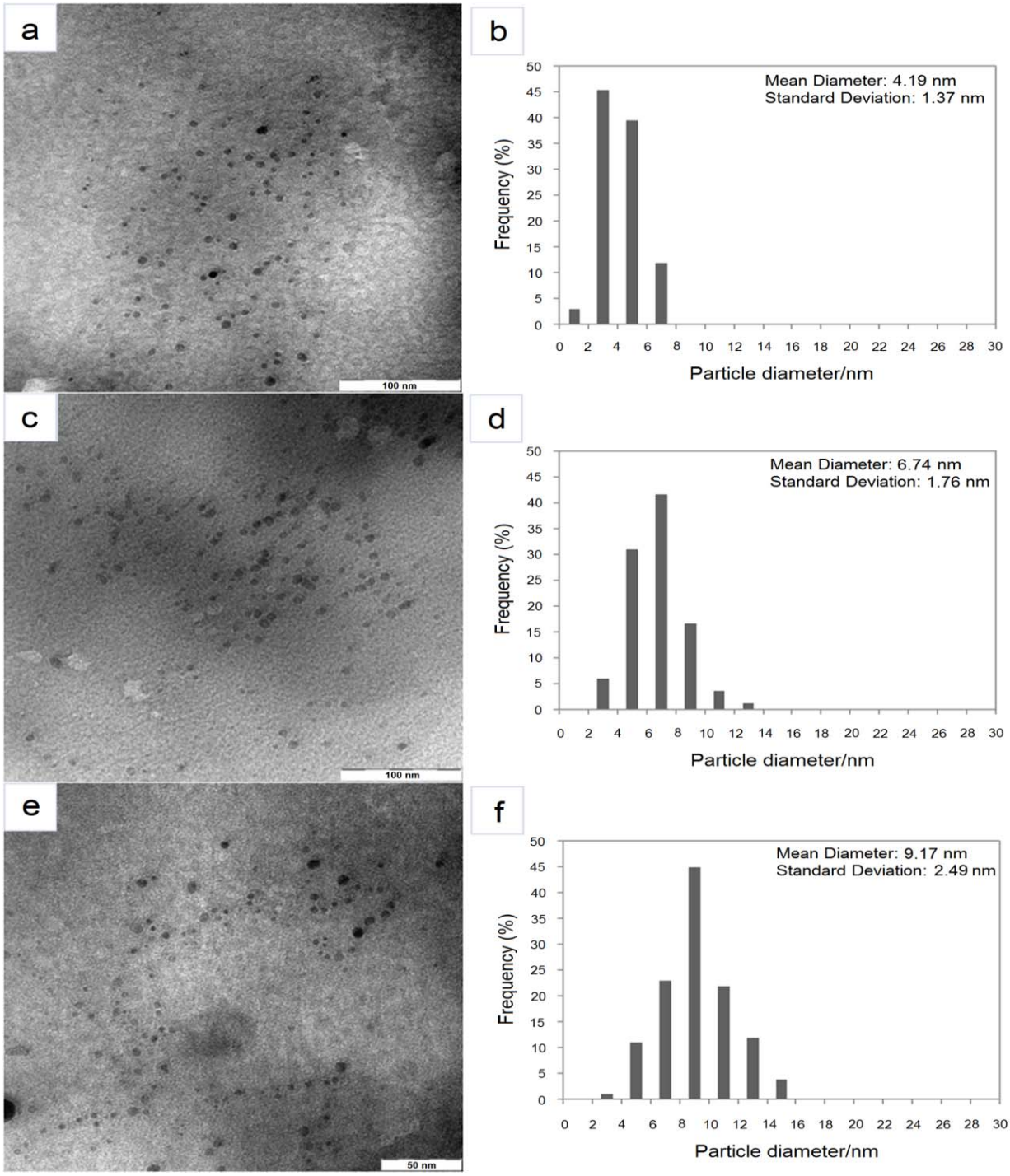

Fig.2 TEM images and the corresponding particle size distributions of prepared Ag-NPs in MMT suspension at different of $AgNO_3$ concentration [1.0% (a-b), 2.0% (c-d) and 5.0% (e-f)].

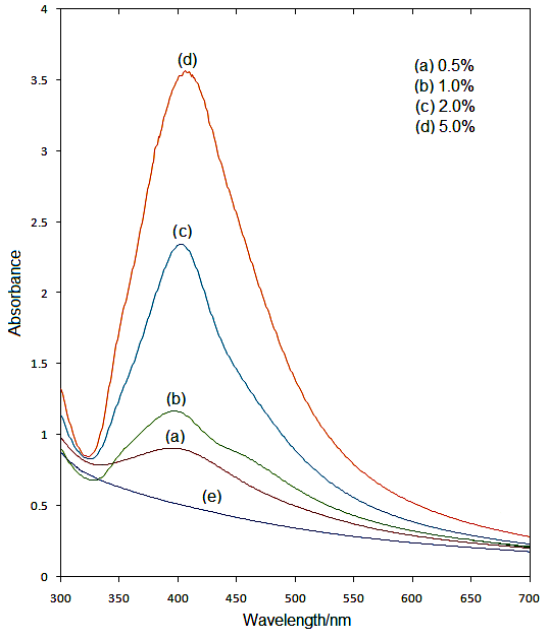

Fig.3 UV-vis absorption spectra of Ag/MMT suspension for different $AgNO_3$ concentrations; 0.5%, 1.0%, 2.0%, 5.0% (a, b, c, d) and (e) $AgNO_3$/MMT suspension.

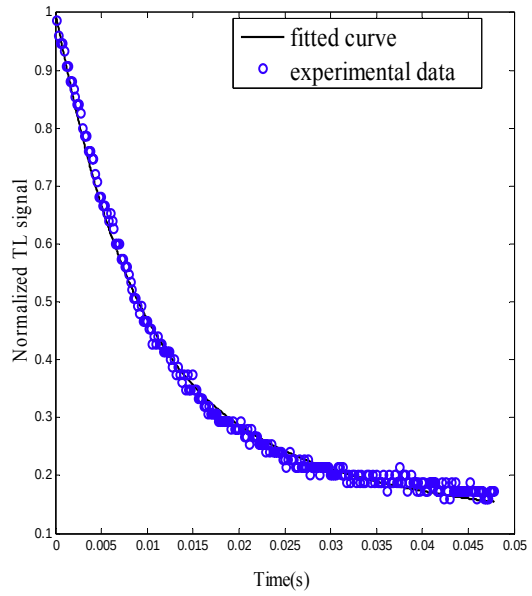

Fig. 4. Time evolution of the thermal lens (TL) signal for sample with 2%concentration. Solid line corresponds to the best fit of Eq. (1) to the TL experimental data.

Fig. 4 shows the normalized TL signal for sample 2% , where symbols represent the experimental points and the solid lines correspond to their best fitting to Eq.(1) to the TL experimental data with θ and t_c as adjustable parameters. After finding θ and t_c from this fitting we use Eq. (2) to calculate thermal diffusivity for corresponding sample. From this fit we obtained the values of θ=1.086±0.010and t_c =(0.004±0.002)s which are corresponds to the thermal diffusivity D=(25.91±0.51)×10^{-4} cm^2/s. Similar TL signals evolution was obtained for other concentration of Ag-NPs and their corresponding thermal diffusivities are listed in Table1.

Table.1 Experimental θ and t_c and calculated D for solvents with Ag-NPs with different sizes.

sample	t_c(s)	θ	D(10^{-4} cm^2/s)
Clay	0.1907±0.0017	1.625±0.006	9.00±0.04
0.5%	0.0077±0.0001	1.049±0.012	15.13±0.42
1%	0.0059±0.0002	1.394±0.019	19.45±0.82
2%	0.0045±0.0001	1.086±0.023	25.91±0.51
5%	0.0034±0.0001	1.234±0.011	33.54±1.67

Fig. 5 shows the normalized TL signal for clay sample without nanoparticle where the solid lines corresponding to their best fitting to Eq. (1). From this fitting the adjustable parameter values θ (1.625 ± 0.006) and t_c (0.190 ± 0.001) s are obtained and the calculated value of thermal diffusivity D is (9.00 ± 0.04) ×10^{-4} cm^2/s.

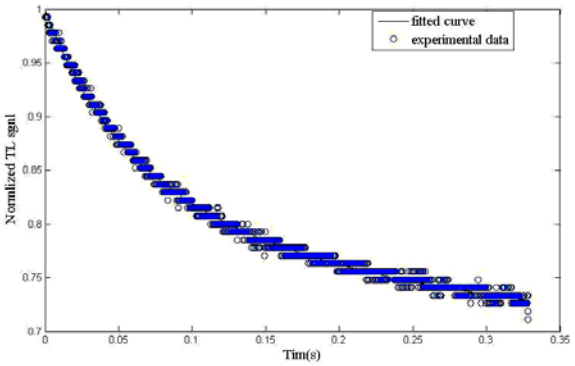

Fig. 5. The normalized TL time evolution signal for Clay. Solid line corresponds to the best fit of Eq. (1) to the TL experimental data

Form the obtained results can be seen that there is an increase in the clay thermal diffusivity when Ag-NPs concentration increases. A possible reason for this increment is, when fine metal particles are irradiated with light, the electrons go into a state called hot electrons, in which the electron temperature is high. Generally, the hot electrons and lattices gradually go into a thermal equilibrium state, due to electron-lattice interactions, and then, the thermal energy transfers to the medium around the particles [14]. Therefore when the NPs concentration is increased in MMT matrix, the optical absorption intensity and in following thermal diffusivity of fluid is increased.

4. Conclusion

In summary, the thermal diffusivity of MMT suspensions with different Ag-NPs concentrations and also without nanoparticles was measured by using TL technique. The obtained results show that the solution thermal diffusivity increase with the increase of silver nanoparticle concentration.

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