JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS, Vol. 12, No. 5, May 2010, p. 1083 - 1086

Determination of thermal diffusivity of montmorillonite containing silver nanoparticles

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The thermal lens (TL) technique is used to study thermal diffusivity of silver nano-fluid containing silver nanoparticles (Ag-NPs) of a particular size from about 30.5 to 4.2 nm at Montmorillonite (MMT) as an inorganic matrix in aqueous solution. In this technique a diode laser (wavelength 514 nm, power 80mW) and intensity stabilized He-Ne laser were used as the excitation source and probe beam, respectively. Experimental results showed that the thermal diffusivity values of nano-fluids decreases when the particle size of Ag-NPs decreases.

(Received March 20, 2010; accepted May 26, 2010)

Keywords: Thermal diffusivity, Nano-fluids, Thermal lens, Montmorillonite, Silver nanoparticles

1. Introduction

Metal nanoparticles are very important because of various unique applications primarily in microelectronics [1], sensors [2] and their potential specific applications in nonlinear optics, photoelectrochemical cells, heterogenerous photocatalysis, optical switching, and single electron transistors [3-6]. Thermal diffusivity of nanoparticle can be important in determining the performance of many engineering systems. The application of nanoparticles for increasing the efficiency of thermoelectric energy conversion enhances heat conduction in heat transfer fluids [7]. Therefore, it is important to determine the thermal diffusivity of the nano-fluid.

Thermal lens spectrometry (TLS) is one of precise photo-thermal techniques based on temperature gradient which is caused by absorption of optical radiation and non-radiative relaxation of the excited molecules. In general in this technique the excitation laser must have Gaussian profile, so when sample absorb the beam with Gaussian distributed intensity the temperature distribution has radially dependence. This gradient of temperature can create a refractive index gradient which behaves similarly to a converging or diverging lens depending on whether the change rate of refractive index with respect to temperature, is positive or negative [8,9].

This technique has very important properties such as "high sensitivity" that makes it appropriate for measuring the thermal diffusivity of samples rely on physical changes that arise in the sample. In this work, we have reported the thermal diffusivity measurements of Ag/MMT nanocomposites as nanofluids with various sizes of Ag-NPs for explain the effect of particle size on thermal diffusivity using TLS technique.

2. Material and method

Silver nitrate (99.98%, Merck, Germany) and Montmorillonite (Kunipia-F, Japan) were used as silver precursor and solid support for Ag-NPs. The Ag/MMT nanocomposites were prepared according to our previous work [10]. Briefly, for the prepare of Ag-NPs, 5.0 g of MMT was dispersed in 500 ml double distilled water and vigorously stirred for 1hr. Five hundred ml aqueous solution of $AgNO_3$ (0.02 M) was added into the MMT aqueous suspension, and the mixture was further stirred for 1hr. The dispersion was irradiated using the UV reactor with UV lamp at λ=365 nm while it was stirred at constant speed. Irradiation times of 3hr (S1), 48hrs (S2) and 96hrs (S3) were applied for different vessels, respectively. Then the suspensions of Ag/MMT were separated, washed with double distilled water twice and dried under vacuum overnight. The UV-irradiation process was carried out on a UV reactor (UV-A, 6W). The prepared Ag/MMT nanocomposites were characterized using ultraviolet-visible spectroscopy (UV-vis, Lambda 35-Perkin Elmer) and transmission electron microscopy (TEM).

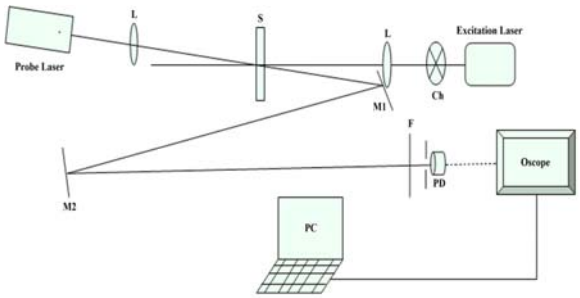

Fig. 1. Schematic diagram of TLS experimental set-up.

Schematic diagram of the TLS experimental set up is shown in Fig. 1. Measurements were carried out using a diode laser (532 nm at 80 mW) as an excitation light and a He-Ne laser (632.8 nm and 0.5 mW) as a probe beam. In the setup the excitation light beam modulated at 10 Hz frequency is focused by a lens of 21 cm focal length onto the sample positioned at its focal plane. The probe beam is focused by a lens of 5 cm focal length onto a quartz sample cuvette and is adjusted at an angle smaller than 1.5° with respect to the excitation beam. An optical bandpass filter was placed in the front of pinhole to remove the stray light from excitation beam entering the photodiode (PD). The PD output signal was coupled to the digital storage oscilloscope (Tektronix TDS 210) to record the time history of thermal lens (TL) change signal.

3. Theory

The intensity of probe beam at the detector can be written by [9]:

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

where;

$$V = \frac{z_1}{z_c}; \theta = -\frac{p_e A_e L}{\kappa \lambda_p}\left(\frac{dn}{dt}\right)$$

$$; m = \left(\frac{w_p}{w_e}\right)^2; \quad D = \frac{w_e^2}{4t_c}, \quad (2)$$

here, $I(0)$ is the initial intensity when time t=0, p_e is the excitation beam power, A_e is the absorption coefficient (cm^{-1}), L is the sample thickness, λ_p is the probe laser wavelength, dn/dT is the refractive index change of sample, $z_c = w_o^2/\lambda$ is the confocal distance (cm), w_o is the probe beam radius it's waist, w_p is the probe beam radius at sample, w_e is the excitation beam radius at sample, κ is the thermal conductivity of sample, z_1 is the distance of laser beam waist to sample, D is the thermal diffusivity of the sample (cm^2/s), t_c is the characteristic thermal time constant. After obtaining θ, and t_c by fitting Eq. (1) to the experimental data we can calculated thermal diffusivity from Eq. (2).

4. Results and discussion

The colour of solutions during the UV-irradiation gradually changed from colourless to light brown, then to brown and finally to green, indicating the formation Ag-NPs in MMT suspension. The synthesis of Ag-NPs into MMT matrix by UV-irradiation was observed by TEM. Fig. 2 shows the TEM image and corresponding size distribution of produced Ag-NPs under UV light for selected irradiation time. When the MMT/$AgNO_3$ suspension was irradiated by UV light for 3hr, photo-reduced Ag-NPs are formed with a mean particle size of about 30.53 ± 11.39 nm and when the irradiation time was increased to 48 and 96hr, the mean particles size of Ag-NPs were decreased considerably to 6.01 ± 1.37 and 4.24 ± 1.31 nm, respectively. It can be seen that the larger Ag-NPs was obtained under shorter irradiation time and they was disintegrate under further irradiation of UV light [11]. As shown in Fig. 3, the silver surface plasmon resonance (SPR) bands occurred about from 350 to 360 nm. The absorption peak due to SPR of obtained Ag-NPs at 48hr shows the blue-shift with decreasing in the particle size and it is in a good agreement with TEM results.

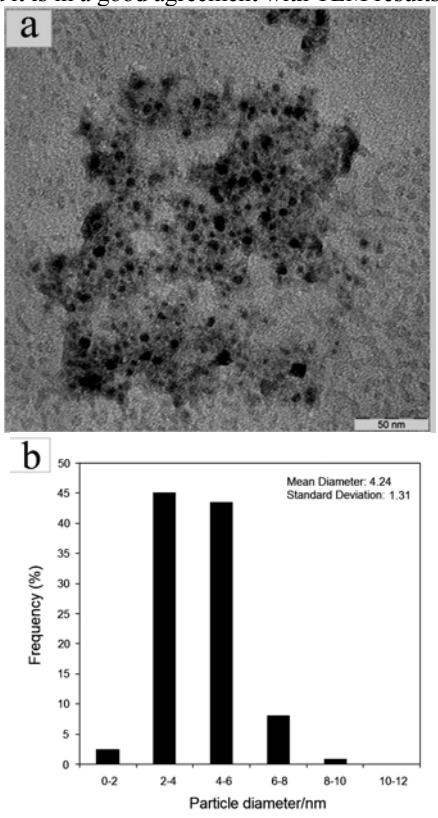

Fig. 2. TEM image (a) and corresponding particle size distribution (b) of synthesized Ag-NPs under UV-irradiation for 96hr.

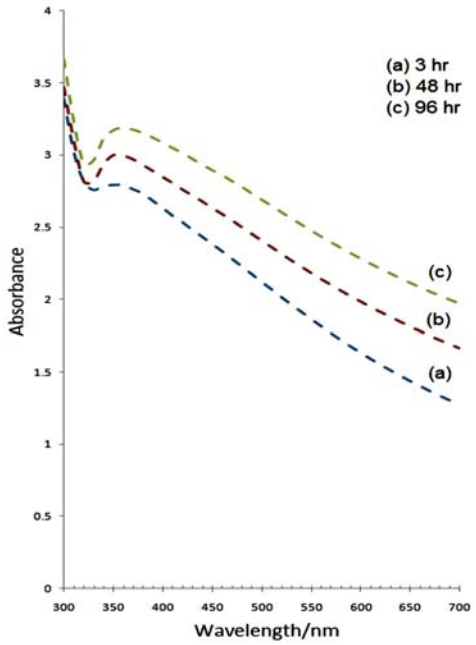

Fig. 3. UV-vis absorption spectra of synthesized Ag/MMT nanocomposites in different irradiation times: 3hr (a), 48hr (b) and 96hr (c).

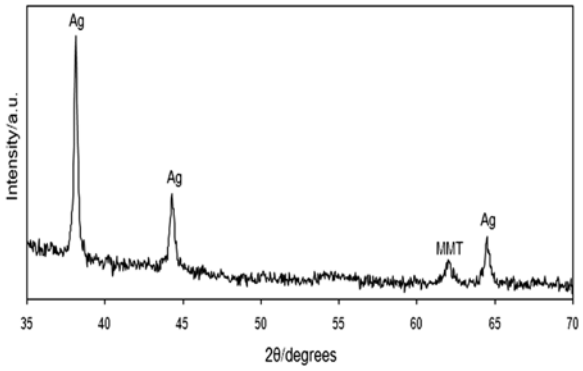

Fig. 4. PXRD Pattern of synthesized Ag/MMT nanocomposites under UV-irradiation for 96hr.

The comparison of PXRD patterns of MMT and Ag/MMT nanocomposite (96hr) indicate the formation of the intercalated structure. The original d-spacing of MMT, 1.24 nm is increased to 1.41 nm at smaller 2θ angles (2θ=6.26˚ for 96hr UV irradiation) by silver intercalation. The PXRD pattern was also employed to determine the crystalline structure of the photo-reduced Ag-NPs. As shown in Fig. 4, the PXRD peaks at 2θ of 38.2º, 44.3º and 64.5º can be attributed to the (111), (200) and (220) crystallographic planes of face-centered cubic (fcc) silver crystals, respectively [12]. In addition there is a characteristic peak in about 2θ = 62.1° that related to MMT clay (PXRD Ref. No. 00-003-0010) as a stable substrate.

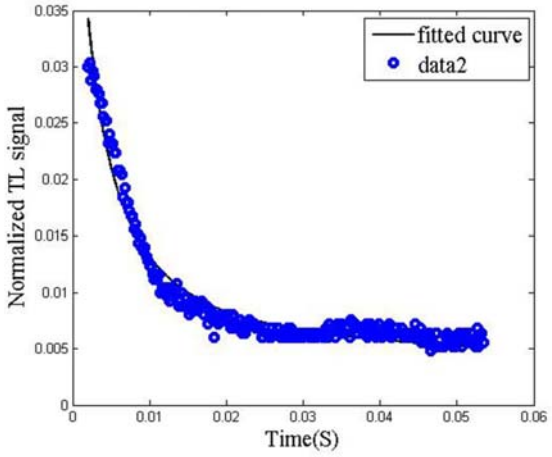

Fig. 5. The time evolution of the thermal lens (TL) signal for sample 3h, Solid line corresponds to the best fit of Eq. (1) to the TL experimental data.

Fig. 5 shows the thermal lens signal for 3h sample and from fitting the values of θ (2.599±0.025) and t_c (0.0072±0.0004s) are obtained the thermal diffusivity: (29.22±1.94) $\times 10^4$ cm^2/s. Similar TL signals evolution were obtained for other Ag-NPs and their corresponding θ's, t_c's and D's were also obtained and are tabulated in Table 1.

Table 1. The fitting parameters; θ, t_c and the calculated D for MMT/Ag-NPs nanocomposites.

Sample	Particle size of Ag-NPs (nm)	t_c (s)	θ	$D(10^{-4}\ cm^2/s)$
MMT/Ag-NPs (3h)	30.53±11.39	0.0072 ± 0.0004	2.599 ± 0.025	29.22 ± 1.94
MMT/Ag-NPs (48h)	6.01±1.37	0.0082 ± 0.0006	2.780 ± 0.039	26.08 ± 1.95
MMT/Ag-NPs (96h)	4.24±1.31	0.0097 ± 0.0004	2.226 ± 0.038	24.59 ± 1.13
MMT	-	0.1907 ± 0.0017	1.625 ± 0.006	9.00 ± 0.04

We also measured thermal diffusivity of clay, the parameter and thermal diffusivity that has been found are θ (1.625±0.006), t_c (0.190±0.001 s) and D (9.00±0.04) $\times 10^4$ cm^2/s. It can be seen that, there is an increase in thermal diffusivity of clay after formation Ag-NPs in MMT suspension but we have decrease in the thermal diffusivity of nanofluid when the size of Ag-NPs decreases. A proper interpretation for the decrement in thermal diffusivity with decrement of particle size is due to different transportation rate of phonon in two media can produced thermal assistance [13], and nanoparticles can take affect during the phonon scattering at interface when the particle sizes become small and therefore the thermal diffusivity decreases.

5. Conclusion

In summary, we successfully prepared Ag-NPs into MMT and measured thermal diffusivity of MMT and MMT suspension containing Ag-NPs with different particle size using thermal lens technique. The obtained results show that with decrease in particle size of Ag-NPs, the thermal diffusivity of nanofluid decreases.

Acknowledgement

The authors are grateful to the Ministry of Higher Education of Malaysia for supporting this work under Research University Grant No. 05-01-09-0754RU.

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