Stability Assessment Through Dynamic Light Scattering and Rheological Study of Hexanoic Acid-Surface-Modified Cerium Oxide Nanoparticles in Cyclohexane at Low Concentration

Research Article

Muhammad Zamir Hossain

Department of Chemistry, Jagannath University, Dhaka-1100, Bangladesh

ABSTRACT

The stability of 1wt% cerium oxide (CeO_2) nanoparticles in cyclohexane is assessed in this paper. To do so, first, *n*-hexanoic acid (C6-) surface-modified CeO_2 nanoparticles were synthesized by heating the aqueous $Ce(OH)_4$ suspension at 400 °C and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), high regulation transmission electron microscopy (HRTEM), Fourier transform infrared (FTIR) spectroscopy and thermogravimetric analysis (TGA). XRD pattern indicated the crystalline structure and TEM showed the cubic shape of the synthesized CeO_2 nanoparticles with an average size of 4.5 nm. Next, 1 wt% CeO_2–cyclohexane dispersion (nanofluids) was prepared simply by dispersing the required amounts of CeO_2 nanoparticles in cyclohexane. Finally, the stability of CeO_2–cyclohexane was assessed by dynamic light scattering (DLS) and rheological study. DLS measurement revealed that the 1wt% CeO_2–cyclohexane nanofluid has good dispersibility with a small DLS diameter (~6 nm) comparable to that of the pristine particle diameter measured by TEM. Also, the rheology study depicted the Newtonian behavior of prepared nanofluids which indicated its excellent stability.

1. Introduction

The dispersion of solid nanoparticles (NPs; 1–100 nm in diameter) in a solvent is known as nanofluid (Choi, 1995). Nanofluids exhibit enhanced properties related to heat transfer, mass transfer, and many more (Babita et al., 2016)(Pang et al., 2015). Nanofluids show potential properties to be

---

Corresponding author: Muhammad Zamir Hossain
E-mail: zamir@chem.jnu.ac.bd

used in the preparation of high thermal conductive films, printed electronics, and coolants for industrial heat management, high voltage transformers and electronics, and power generation by solar, nuclear, and electrical energy and nano drug delivery (Dey & Sahu, 2021)(Wahab et al., 2019). In other words, the liquid state of CeO_2 nanoparticles has many important usage. However, dispersion/nanofluid stability is important for flow-related applications (Urmi et al., 2020). Therefore, verification of nanofluid's stability is needed before their real applications.

Generally, nanoparticles tend to aggregate/agglomerate in solvents. Many efforts have been made to make a stable dispersion of nanoparticles by preventing such kind of aggregation/agglomeration. Ultrasonication and surfactant addition are the common techniques applied to get stable dispersion of nanoparticles (Fuskele & Sarviya, 2017). Often, the greatest requirement for good dispersion of nanoparticles is its controlled size and morphology.

Synthesizing nanoparticles with desired size and morphology has significant importance, and various methods via wet or dry have developed in the progress related to these fields. Surface capping/modifying of nanoparticles is one of the effective techniques to make the nanoparticles with the desired size and shape which makes them dispersible in suitable solvents (Alivisatos, 2010). Surface treatment of nanoparticles by surface-modifying molecules is generally done via post-synthesis treatment or *in-situ* modification. These techniques allowed many researchers to succeed in the preparation of non-aggregated nanoparticles using some methods like vapor pressure deposition and liquid phase crystallization or precipitation. Development of *in-situ* surface modification of nanoparticles by supercritical water, water at or above 400 °C and 22.1 MPa, allows the formation of metal oxide nanoparticles from a metal salt aqueous solution is a benchmark in this way (Adschiri, 2007). *In*-situ surface modification in supercritical water using *n*-hexanoic acids (C6-) as surfactants provides strongly chemically bound surfactant layered cubic CeO_2

nanoparticles (Hossain et al., 2018).

Good dispersion of any nanoparticles in solvents is a prerequisite to handling them in a liquid state. Dispersibility assessment of high-concentration nanofluid is demonstrated by the ultraviolet-visible spectroscopic method (Hossain et al., 2019). For low-concentration nanofluid, DLS measurements allow us to assess their stability as DLS directly measures the diameter of nanoparticles in liquid (Lee et al., 2014). The dispersion stability of CeO_2 in cyclohexane depends on the size and size distribution of nanoparticles (Arita et al., 2010). Additionally, the dispersion dispersibility of decanoic acid (C10-) surface-modified CeO_2 in cyclohexane is more than that of dodecanoic acid (C12-) surface-modified CeO_2 in cyclohexane which indicates that the chain length of surface aping agent also affects the stability of dispersion (Arita et al., 2010). However, no data is available on the dispersion stability of hexanoic acid (C6-) modified CeO_2 in cyclohexane. As the chain length of the surface modifying fatty acid affects the stability of CeO_2 nanoparticles in cyclohexane, assessing the stability of hexanoic acid (C6-) modified CeO_2 in cyclohexane would be worthwhile.

Another means of stability testing is the rheological behavior evaluation of nanofluids (Hossain et al., 2019). Rheology is the flow behavior of fluids. The flow behavior of fluids can be either Newtonian or non-Newtonian. Newtonian behavior means i.e. plot of shear stress vs shear state is linear going through the origin. In other words, the viscosity of nanofluids remains constant at different shear rates. That means viscosity is independent of the shear rate. On the contrary, non-Newtonian behavior is dependent on shear rate. Non-Newtonian behavior can be shear thinning (decrease of viscosity with an increase in shear rate) and shear thickening (increase of viscosity with increased shear). Both shear thinning and thickening indicate the instability of nanofluids. Viscosity is the measure of the friction of the different layers of fluids. Viscosity can be measured by either a viscometer or rheometer. But for the shear-dependent viscosity, which is called rheology, a rheometer is required.

Often, low viscosity ultimately indicates the stability of nanofluids, and favorable for flow-related applications.

In this paper, we aimed to assess the stability of low concentration of 1wt% CeO_2–cyclohexane nanofluid by DLS measurement and rheology study in addition to the synthesis and characterization of hexanoic acid (C6-) modified CeO_2 nanoparticles.

2.   Materials and Methods

2.   1 Materials

Cerium (IV) hydroxide ($Ce(OH)_4$) was purchased from Aldrich Chemistry, USA and used as received. *n*-Hexanoic acid (99%) as a surface modifier and organic solvents such as ethanol (99%), cyclohexane (99.5%), *n*-hexane (96%), and acetone (99%) were purchased from Wako Pure Chemical Industries, Ltd. Purified water obtained from Daiwa Pharmaceutical Co., Ltd. was filtered before the use for hydrothermal synthesis.

2.2 Methods

2.2.1 Synthesis of hexanoic acid-surface-modified CeO₂ nanoparticles

Synthesis of CeO_2 nanoparticles by a supercritical water method is described in detail elsewhere (Hossain et al., 2018). Hexanoic acid-surface-modified CeO_2 nanoparticles were synthesized from the precursor of 0.1 M $Ce(OH)_4$ aqueous suspension; it was prepared by adding 0.229 g of $Ce(OH)_4$ in 11 mL of deionized water and ultrasonication for ~10 s. The precursor (2.5 mL) was loaded into a pressure-resistant Hastelloy C reactor (5.0 mL inner volume), and the required amount of hexanoic acid was added (to make the molar ratio of 1: 3 as a precursor to modifier) for *in-situ* surface modification to obtain hexanoic acid-surface- modified CeO_2 nanoparticles. Hydrothermal reactions were done in two steps by using two electric furnaces with pre-set temperatures. The first step was a pre-treatment at 150 °C for 20 minutes, and the second step was a reaction conducted at 400 °C for 10 minutes. The reaction was terminated by submerging the reactor into a room-temperature water bath, and the products were collected with 5 mL of *n*-hexane. CeO_2 nanoparticles were obtained as a dispersion in a mixture of water, *n*-hexane, unreacted fatty acids, and the precursor. The organic phase was separated, and the unreacted hexanoic acid molecules were removed by centrifugation at 9600 rpm for 20 min with ethanol. The particles were dispersed in cyclohexane to protect the bond formation with remaining water, and freeze-dried under vacuum. For further purification, products were re-dispersed in cyclohexane and added drop-wise to acetone with the molar volume of cyclohexane: acetone = 1:20 and a magnetic stirring followed by centrifugation at 9600 rpm for 20 min. This step was repeated three times to remove all unreacted modifiers. Centrifuged particles were dispersed in cyclohexane and kept overnight to ensure their dispersion. Next, supernatant, the upper layer of dispersion that contains well-dispersed nanoparticles, was collected and carefully freeze-dried under vacuum until all the cyclohexane was removed. Then the product was stored inside a moisture-free box for characterization.

2.3 Characterization methods of nanoparticles

The crystallinity of the synthesized nanoparticles was tested using an X-ray diffractometer (XRD, Rigaku Smart Lab.) with Cu Kα radiation in a 2θ–θ setup. The 2θ angle was scanned between 20 and 80° at a scanning rate of 2 degrees/min. Measured data were compared with a standard database [the joint committee for powder diffraction studies (JCPDS)] file for CeO_2 (No. 00-34-0394). The morphology, average size, and structure of nanoparticles were characterized by transmission electron microscopy and high regulation transmission electron microscopy (TEM, H–7650, Hitachi, Japan) with 100 kV acceleration voltage. TEM grid was prepared by placing micro-droplets of the nanoparticles-loaded dispersions onto the carbon-coated copper grid and allowing them to dry at ambient temperature. The average particle size was obtained by using a caliper to measure ~300 particles that appeared in the TEM image. Fourier

transform infrared spectra were acquired using a JASCO FT/IR–680 spectrometer to investigate the existence of chemical bonding and functional groups of the hexanoic acid on the surface of the nanoparticles. Absorption IR spectra were collected from 400 to 4000 cm^{-1}. The samples were prepared in KBr pellets. The number of organic modifiers attached to the surface of nanoparticles was estimated using TGA; this was conducted under constant (100 mL/min) N_2 gas flow in the temperature range of 20–800 °C at a ramp rate of 10 °C/min with Rigaku TG-DTA8120 system. The packing density of modifiers (molecules/nm^2) on the surface of the modified nanoparticles was quantified from the number of modifiers measured by TGA and the average diameter of the nanoparticle core assuming the core has a cubic shape.

2.4 Preparation of 1wt% CeO$_2$–cyclohexane nanofluids

Dispersion of CeO_2 in cyclohexane i.e. nanofluid is prepared by a two-step method; first, the required amounts of nanoparticles are ready, and then dispersed the nanoparticles in cyclohexane (Sidik 2014). 1wt% CeO_2–cyclohexane nanofluid is prepared in 1 mL of cyclohexane by adding 0.0078 g of CeO_2 nanoparticles. Nanoparticles were weighed using a sensitive electronic balance (SHIMAZU AUW120D) with an accuracy of 0.01 mg. Then, weighed nanoparticles were added to 1 mL volume of cyclohexane and gently shaken by hand. Nanofluid preparation requires no any kind of additional mechanical treatments like ultra-sonication. Concentration i.e.; weight percent (wt%) of nanofluid is calculated by using the following equation (1):

$$\text{NP wt\%} = \frac{M}{M + M_{\text{sol}}} \times 100 \qquad (1)$$

Here, M is the nanoparticles' mass percentage (wt%) and M_{sol} is the solvent mass.

2.5 Dispersibility assessment of 1 wt% CeO$_2$–cyclohexane nanofluids

Dispersibility of 1 wt% CeO_2–cyclohexane nanofluid is measured by a DLS machine, (Malvern, UK) using a quartz cell of 10 mm path length.

2.6 Rheology study of 1 wt% CeO$_2$–cyclohexane nanofluids

In the present study, we used a programmable rotational rheometer (LVDV–III Ultra, Brookfield Engineering, USA) to study the rheology and dynamic viscosity. Experiments were done by using spindles CPE-40 and CPE-51 over a wide range of shear rates (10–1200 s^{-1}) following the operating manual's instructions. An isothermal temperature bath was attached during viscosity measurements to maintain the experimental temperature at 20 °C. Each measurement point was taken after 60 s of constant shear rate acting on the sample. Five data points were averaged for each shear rate, and the average values were used for the analysis. All the measurements were repeated. The average uncertainty in viscosity as measured by the rheometer is ±1.0%.

3. Results and Discussion

3.1 Characterization of hexanoic acid-modified CeO$_2$ nanoparticles

Hexanoic acid-surface-modified products were characterized by XRD, TEM, FTIR, and TGA. The obtained XRD pattern of the product was similar to the expected profile for crystalline CeO_2 (JCPDS No. 00-034-0394) as shown in Fig.1.
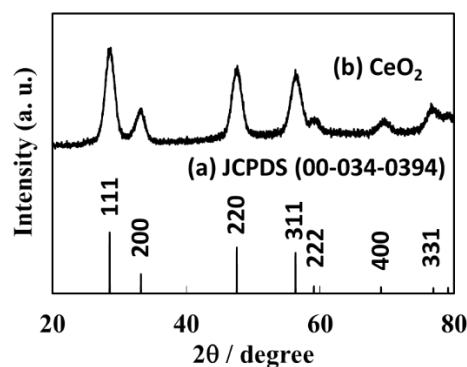

Fig. 1. XRD patterns of samples: (a) JCPDS 00-034-0394 (b) Hexanoic acid-modified CeO_2.

The TEM and HRTEM images and particle size

distribution of the product are shown in Fig. 2. TEM and HRTEM images revealed that the hexanoic acid-modified CeO_2 were cubic shaped with small sizes (Fig. 2(a, b)). The average size of a single CeO_2 was determined to be 4.5±0.6 nm, by averaging ~300 nanoparticles. The average size revealed the small sizes of the synthesized CeO_2 nanoparticles. A narrow size distribution of between 3 and 7 nm was also obtained ((Fig. 2(c)).
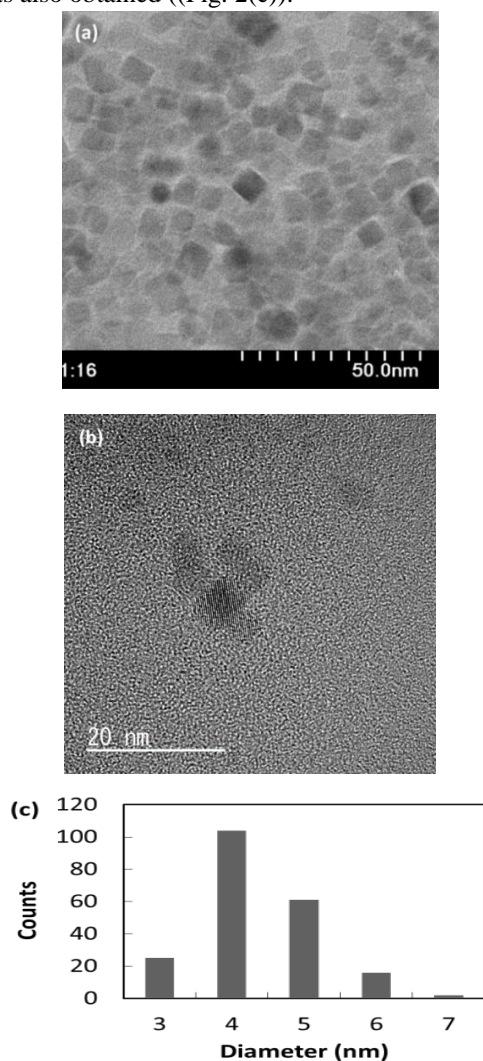

Fig. 2. TEM (a) and HRTEM (b) images and particle size distribution (c) of hexanoic acid-modified CeO_2.

To evident the modifiers present on the surface of the products and to obtain structural information about CeO_2 crystals, FTIR spectroscopy was applied as shown in Fig. 3. Obtained spectra showed a broadband between 600 to 400 cm^{-1} corresponding to the cerium–oxygen (Ce–O) bond in the CeO_2 crystal (Ho et al., 2005). A weak band appears at approximately 2960 cm^{-1}, which is assigned to the asymmetric (v_{as}) stretching mode of $–CH_3$ in the alkyl chain of fatty acids. Additional bands at approximately 2900 and 2850 cm^{-1} are assigned to the asymmetric (v_{as}) and symmetric (v_s) stretching modes of $–CH_2–$ in the alkyl chain of the hexanoic acids. Besides, three peaks, as seen in Fig. 3, corresponding to the symmetric (1,445 and 1,414 cm^{-1}) and asymmetric (1,532 cm^{-1}) stretching of the carboxylate anion (COO^-) were observed in the FTIR spectrum of a sample (Ho et al., 2005), (Taguchi et al., 2014). Moreover, no peak due to the free carboxyl C=O stretching mode (1,700 cm^{-1}) indicates that the nanoparticles were purified perfectly which indicates the surface-modified nanoparticles were well purified and don't have any residual or weakly bound carboxylic acids (Nakanishi 1962).
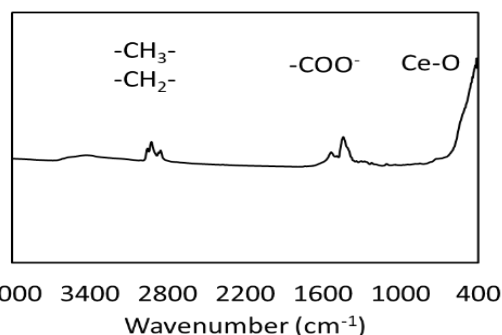

Fig. 3. FTIR spectra of hexanoic acid surface-modified CeO_2 nanoparticles.

To quantify the number of surface modifiers on the products, TGA measurements were performed. Fig. 4 shows the TGA diagram of the product between room temperature and 800 °C. The weight loss is attributed to the combustion of organic molecules in the products and reflects the amount of surface

modifiers present in them. The TGA curves showed a gradual decline in the range of 300–700 °C, indicating that the organic modifiers were not physisorbed on the surfaces of the products but rather chemically attached to them (Taguchi et al., 2014). The curve of weight losses after 700 °C was almost at a steady state. The average TG weight loss was 9%. The average weight loss was calculated from 3 measurements. The weight loss suggests that the hexanoic acid was attached to the surface of the CeO_2 crystal.
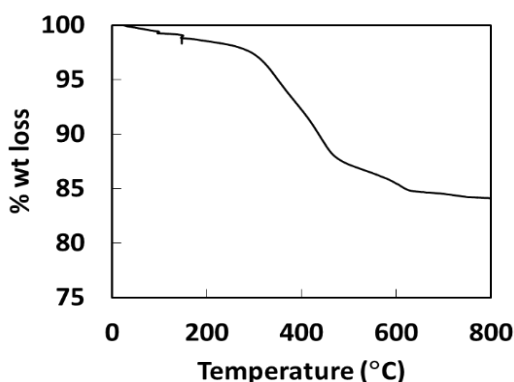

Fig. 4. TG-weight loss of hexanoic acid surface-modified CeO_2 nanoparticles.

Some calculated values of the hexanoic acid-surface modified nanoparticles are summarized in Table 1.

Table 1. Average particle size, TG weight loss, packing density, surface modifiers' chain length, and calculated density of surface modifiers attached on the surface of CeO_2 NPs.

Parameter	Values
TEM size (nm)	4.5±0.67
TG weight loss (%)	9
Packing density (molecule/nm^2)	4.93
Chain length of surface modifiers	0.66
Calculated modifiers' density(g/cm^3) (density at original state, g/cm^3)	1.44 (0.927)

3.2 Dispersibility and stability assessment of 1 wt% CeO_2–cyclohexane nanofluid

Dispersibility of 1wt% CeO_2–cyclohexane nanofluid is evaluated by DLS using a quartz cell of 10 mm path length. Taking hydrodynamic diameter measurements of the nanoparticles in dilute nanofluids by DLS is a good option to know the dispersion state of nanoparticles because DLS provides the nanoparticles/agglomerates diameter directly. DLS measurements of CeO_2–cyclohexane nanofluid at 1 wt% concentration were taken immediately after its preparation. Fig. 5 shows the DLS diameter of 1 wt% CeO_2–cyclohexane nanofluid. Before, DLS measurement, a photograph of the nanofluid was captured using a camera (inset). The appearance of the nanofluid is clear which indicates its good dispersion and stability. Besides, the diameter of the hexanoic acid (C6-) surface-modified nanoparticles was calculated from the modifier length and core of nanoparticles as shown in Table 1. The DLS results for the 1 wt% CeO_2–cyclohexane nanofluid proved that they contained nanoparticles with diameters (6.5 nm) comparable to that measured from the TEM images plus twice the thickness of the surface modifier layers, which can be referred to as good dispersion. Also, the DLS data is consistent with the clear appearance of the nanofluid as shown in the inset of Fig. 5. Comparable DLS and TEM calculation diameter indicates that hexanoic acid (C6-) surface-modified CeO_2 is well dispersible in cyclohexane at 1 wt% concentration.
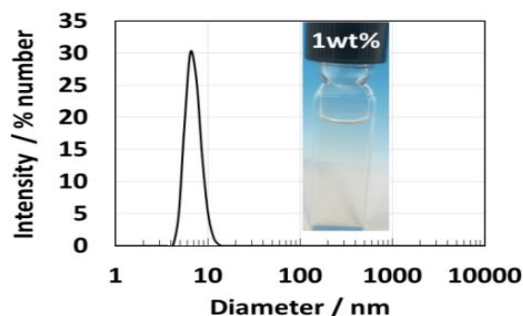

Fig. 5. DLS intensity as a function of particle diameter. The peaks reveal the average size of the hexanoic surface-modified CeO_2–cyclohexane (inset, image of nanofluid).

3.2 Rheological study of 1 wt% CeO$_2$–cyclohexane nanofluid

To know the flow behavior of nanofluid, a rheological study was performed. First, the flow behavior was checked for base fluid cyclohexane as shown in Fig. 6. Fig. 6(a) shows the shear stress as a function of shear rate between 10 and 1200 s^{-1} for cyclohexane. The plot of shear stress vs shear rate gives a line going through the origin. Therefore, viscosity, from the slope, of the cyclohexane is found to be 0.86 mPa.s. Also, Fig. 6(b) depicts the Newtonian behavior of cyclohexane as the viscosity remained unchanged even when the shear rate was increased until 1200 s^{-1}.
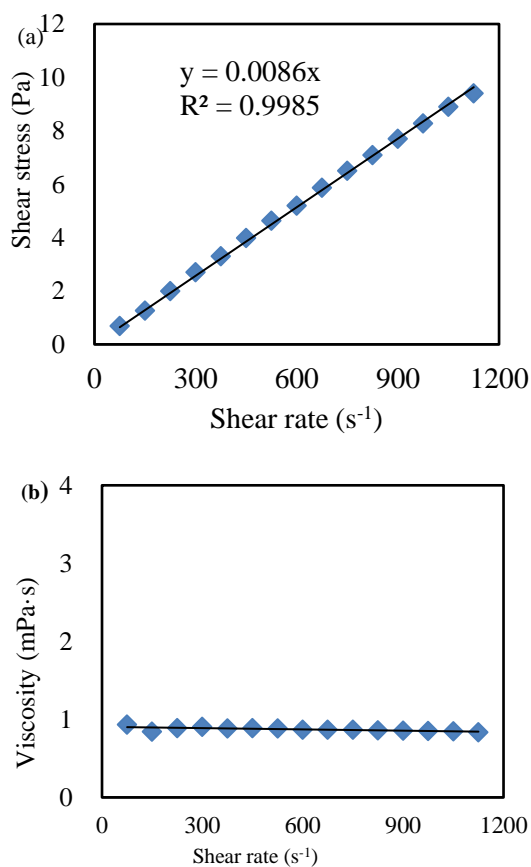
Next, the rheological behavior of 1 wt% CeO$_2$–cyclohexane nanofluid is shown in Fig. 7. Fig. 7(a) shows the shear stress as a function of shear rate between 10 and 1200 s^{-1} for 1 wt% CeO$_2$–cyclohexane nanofluid. The plot of shear stress vs shear rate gives a line going through the origin. Therefore, the viscosity, from the slope, of the 1 wt% CeO$_2$–cyclohexane nanofluid is found to be 0.91 mPa.s. Also, Fig. 6(b) depicts the Newtonian behavior as the viscosity remained unchanged even though the shear rate was increased until 1200 s^{-1}. This phenomenon indicates that the 1 wt% CeO$_2$–cyclohexane nanofluid is stable. Besides, low viscosity is an indirect indication of the stability of the prepared nanofluid.
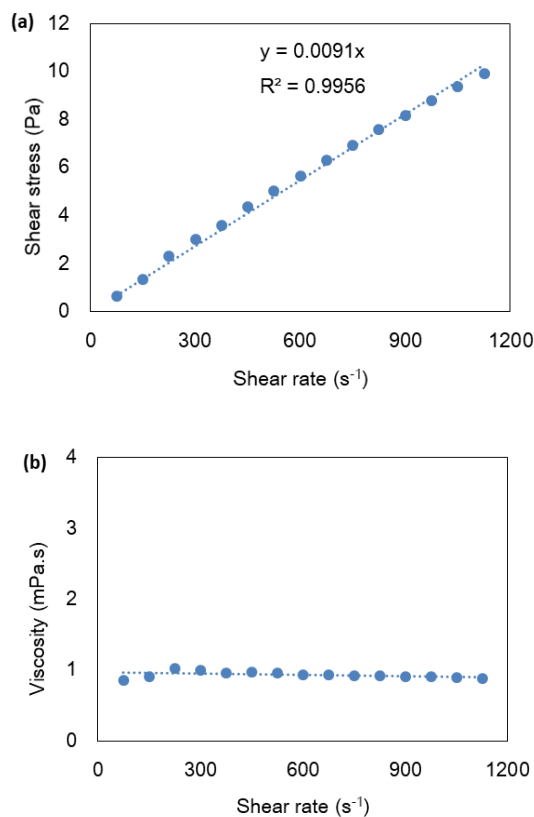

Fig. 6. Rheological study of cyclohexane; (a) Shear stress as a function of shear rate of cyclohexane and (b) Viscosity as a function of shear rate.

Fig. 7. Rheological study of 1 wt% CeO$_2$–cyclohexane nanofluid; (a) Shear stress as a function of shear rate of cyclohexane and (b) Viscosity as a function of shear rate.

4. Conclusions

Hexanoic acid (C6-) surface-modified cubic CeO_2 nanoparticles with 4.5 nm sizes and narrow size distribution were synthesized successfully in supercritical water. XRD, TEM, HRTEM, FTIR, and TGA analysis supported the cubic CeO_2 nanoparticle formation. TEM and DLS analysis suggest that the hexanoic acid-modified CeO_2 has good dispersibility and stability in cyclohexane at 1 wt%. Therefore, in-situ surface capping of nanoparticles would be an effective strategy for designing stable nanofluids for many applications. The rheological study indicates that the prepared 1 wt% CeO_2–cyclohexane nanofluid was stable. Low viscosity (0.91 mP.s) of 1 wt% CeO_2–cyclohexane nanofluid is another sign of good stability. This study concludes that in-situ surface capping of CeO_2 nanoparticles using hexanoic acid (C6-) is a technique to produce well-dispersed and stable nanofluids with low viscosity.

Acknowledgment

References

Adschiri T. 2007. Supercritical hydrothermal synthesis of organic-inorganic hybrid nanoparticles. *Chemistry Letters*, *36*(10), 1188–1193. https://doi.org/10.1246/cl.2007.1188

Alivisatos AP. 2010. Semiconductor Clusters, Quantum Nanocrystals, and. *Advancement of Science*, *271*(5251), 933–937.

Arita T, Yoo J, Ueda Y, Adschiri T. 2010. Size and size distribution balance the dispersion of colloidal CeO_2 nanoparticles in organic solvents. *Nanoscale*, *2*(5), 689–693. https://doi.org/10.1039/b9nr00395a

Babita, Sharma SK, Gupta SM. 2016. Preparation and evaluation of stable nanofluids for heat transfer application: A review. *Experimental Thermal and Fluid Science*, *79*, 202–212. https://doi.org/10.1016/j. expthermflusci.2016.06.029

Choi SUS. 1995. Enhancing thermal conductivity of fluids with nanoparticles. *American Society of Mechanical Engineers, Fluids Engineering Division (Publication) FED*, *231*(January 1995), 99–105.

Dey D, Sahu DS. 2021. A review on the application of the nanofluids. *Heat Transfer*, *50*(2), 1113–1155. https://doi.org/10.1002/ htj.21920

Fuskele V, Sarviya RM. 2017. Recent developments in Nanoparticles Synthesis, Preparation and Stability of Nanofluids. *Materials Today: Proceedings*, *4*(2), 4049–4060. https://doi.org/ 10.1016/ j.matpr. 2017.02.307

Ho C, Yu JC, Kwong T, Mak AC, Lai S. 2005. Morphology-controllable synthesis of mesoporous CeO_2 nano- and microstructures. *Chemistry of Materials*, *17*(17), 4514–4522. https://doi.org/10.1021/ cm0507967

Hossain MZ, Hojo D, Takami, S, Adschiri T. 2018. Synthesis of fatty acid-surface- modified CeO_2 nanoparticles in supercritical water: high modifiers' packing density with controlled shape and size. *Jagannath Univ. J. Sci.*, *5*(II), 45–56. https://jnu.ac.bd/journal/portal/archives/science .jsp

Hossain MZ, Hojo D, Yoko A, Seong G, Aoki N, Tomai T, Takami S, Adschiri T. 2019. Dispersion and rheology of nanofluids with various concentrations of organic modified nanoparticles: Modifier and solvent effects. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, *583*(August), 123876. https://doi.org/10.1016/ j.colsurfa.2019.123876

Lee J, Han K, Koo J. 2014. A novel method to evaluate dispersion stability of nanofluids. *International Journal of Heat and Mass Transfer*, *70*, 421–429. https://doi.org/ 10.1016/ j.ijheatmasstransfer. 2013.11.029

Pang C, Lee JW, Kang YT. 2015. Review on combined heat and mass transfer characteristics in nanofluids. *International Journal of Thermal Sciences*, *87*, 49–67. https://doi.org/10.1016/ j.ijthermalsci.2014.07.017

Taguchi M, Yamamoto N, Hojo D, Takami S, Adschiri T, Funazukuri T, Naka T. 2014. Synthesis of monocarboxylic acid-modified CeO_2 nanoparticles using supercritical water. *RSC Advances*, *4*(91), 49605–49613. https:// doi.org/ 10.1039/c4ra06936f

Urmi WT, Rahman MM, Kadirgama K, Ramasamy D, Maleque MA. 2020. An overview on synthesis, stability, opportunities and challenges of nanofluids. *Materials Today: Proceedings*, *41*, 30–37. https:// doi.org/ 10.1016/j.matpr. 2020.10.998

Wahab A, Hassan A, Qasim MA, Ali HM, Babar H, Sajid MU. 2019. Solar energy systems– Potential of nanofluids. *Journal of Molecular Liquids*, *289*. https://doi.org/ 10.1016/j. molliq.2019.111049