Electronic Supplementary Information

Stably Dispersed High-Temperature Fe_3O_4/Silicone Oil Nanofluids for Direct Solar Thermal Energy Harvest

Yingying Chen[1], Xiaojun Quan[2], Zhongyong Wang[1], Chiahsun Lee[1], Zizhao Wang[1], Peng Tao[1,]*, Chengyi Song[1], Jianbo Wu[1], Wen Shang[1] and Tao Deng[1,]*

[1]State Key Laboratory of Metal Matrix Composites, School of Materials Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Rd, Shanghai, 200240, P. R. China.

[2]MOE Key Laboratory for Power Machinery and Engineering, School of Mechanical Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, P.R. China

*Correspondence: taopeng@sjtu.edu.cn; dengtao@sjtu.edu.cn

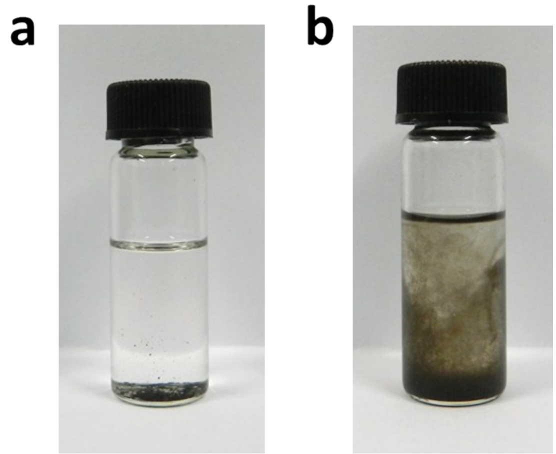

Fig. S1 Photographs of carbon-based nanofluids with poor dispersion stability within silicone oil. (a) Precipitation of reduced graphene oxide (rGO) within silicone oil base fluid. (b) Sedimentation of oleylamine-modified rGO within silicone oil base fluid.

Calculation of van der Waals attraction between NPs within silicone oil

The non-retard Hamaker constant (A_i) for component *i* (benzyl alcohol, Fe_3O_4, silicone) can be calculated using the following equation:

$$A_i = \frac{3}{4}k_B T\left(\frac{\varepsilon_i - \varepsilon_{vac}}{\varepsilon_i + \varepsilon_{vac}}\right)^2 + \frac{3hv_e \left(n_i^2 - n_{vac}^2\right)^2}{16\sqrt{2}\left(n_i^2 + n_{vac}^2\right)^{3/2}}$$

where ε_i and ε_{vac} are the static dielectric constant of component *i* and vacuum, n_i and n_{vac} are the refractive index of component *i* and vacuum, k_B is the Boltzmann constant (1.38×10^{-23} J/K), *T* is the absolute temperature, *h* is the Planck constant ($6.62607004 \times 10^{-34}$ J·s) and v_e is the electronic absorption frequency ($\sim3 \times 10^{15}$ s^{-1}). The specific calculated Hamaker constant values are listed in Table S1.

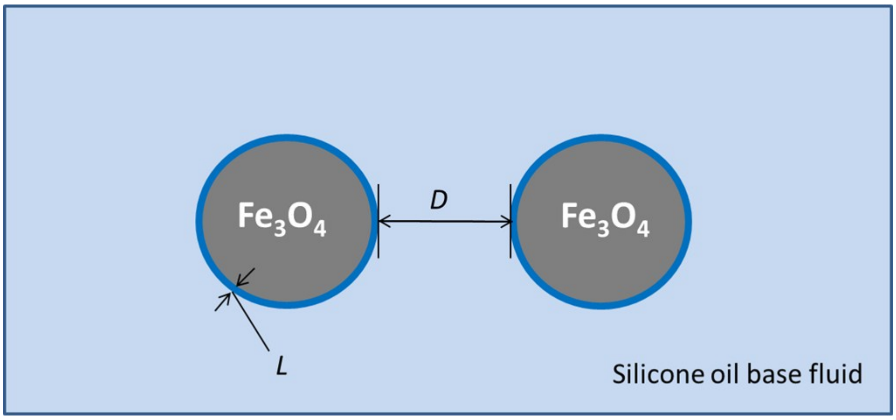

Fig. S2 Schematic of inter-particle attraction within silicone oil base fluid.

The van der Waals attraction between two benzyl-alcohol modified Fe_3O_4 NPs in the silicone oil base fluid can be estimated by:

$$V_{vdW} \cong -\frac{r}{12}\left[\frac{\left(\sqrt{A_{silicone}}-\sqrt{A_{benzyl\ alcohol}}\right)^2}{D}+\frac{\left(\sqrt{A_{benzyl\ alcohol}}-\sqrt{A_{Fe3O4\ NP}}\right)^2}{D+2L}\right.$$

where r is the radius of NPs (4.5 nm), and the separation distance (when they are in van der Waals contact) between two neighboring D is typically taken as 0.165 nm. The capping layer thickness L can be calculated by assuming the benzyl-alcohol modified NPs are core-shell structure. The density of Fe_3O_4 NPs and benzyl alcohol are 5.17 g/cm^3 and 1.044 g/cm^3, respectively. According to 10 wt% TGA weight loss from benzyl alcohol, L is estimated to be 0.708 nm. With these parameters, the van der Waals attraction between two benzyl-alcohol modified Fe_3O_4 NPs in the silicone oil base fluid is estimated to be ~9.45 k_BT.

The non-retard Hamaker constant for the hybrid surface coating layer PDMS-grafted Fe_3O_4 NPs:

$$A_{eff} = \frac{3}{4}k_BT\left(\frac{\varepsilon_{eff}-\varepsilon_{vac}}{\varepsilon_{eff}+\varepsilon_{vac}}\right)^2+\frac{3hv_e\ \left(n_{eff}^2-n_{vac}^2\right)^2}{16\sqrt{2}\left(n_{eff}^2+n_{vac}^2\right)^{3/2}}$$

The effective dielectric constant of the hybrid PDMS-benzyl alcohol layer can be estimated by:

$$log(\varepsilon_{eff})_{=}\varphi_{BA}\times log(\varepsilon_{BA})+\varphi_{PDMS}\times log(\varepsilon_{PDMS})$$

The effective refractive index of the hybrid PDMS-benzyl alcohol layer can be estimated by:

$n_{eff=}\varphi_{BA} \times n_{BA} + \varphi_{PDMS} \times n_{PDMS}$

The corresponding van der Waals attraction between two PDMS-modified Fe_3O_4 NPs in the silicone oil base fluid can be estimated by:

$$V_{vdW} \cong -\frac{r}{12}\left[\frac{\left(\sqrt{A_{silicone}}-\sqrt{A_{hybrid\ layer}}\right)^2}{D}+\frac{\left(\sqrt{A_{hybrid\ layer}}-\sqrt{A_{Fe3O4\ NP}}\right)^2}{D+2L}+\cdots\right.$$

The capping layer thickness L can be calculated by assuming the PDMS-modified NPs are core-shell structure with a hybrid surface coating layer of mixed PDMS and benzyl alcohol. The density of the grafted PDMS is 0.98 g/cm^3. Based on the total 42.3 wt% TGA weight loss from benzyl alcohol (5 wt%) and grafted PDMS (37.3wt%), assuming half of the benzyl alcohol synthetic ligands were replaced by grafted PDMS ligands, L is estimated to be 3.17 nm. With these parameters, the van der Waals attraction between two benzyl-alcohol modified Fe_3O_4 NPs in the silicone oil base fluid is estimated to be ~1.78 k_BT.

Table S1. Calculation of Hamaker constant of each component

Component	***ε***	***n***	***A* (10^{-20} J)**
Fe_3O_4	14.2	2.42	34.85
Benzyl alcohol	13	1.54	8.24
Silicone oil	2.4	1.41	5.03
Hybrid layer	2.89	1.42	5.72

Estimation of sedimentation velocity

The Stokes sedimentation velocity (*V*) of pure Fe_3O_4 NPs within silicone oil base fluid can be estimated by $V = \frac{r^2}{9\mu}(\rho_{NP} - \rho_{Medium})g$, where ρ_{NP} and ρ_{Medium} are densities of the NPs (5.17 g/cm^3) and base fluid (0.959 g/cm^3), respectively and μ is the dynamic viscosity of the nanofluid (47.95 cP).

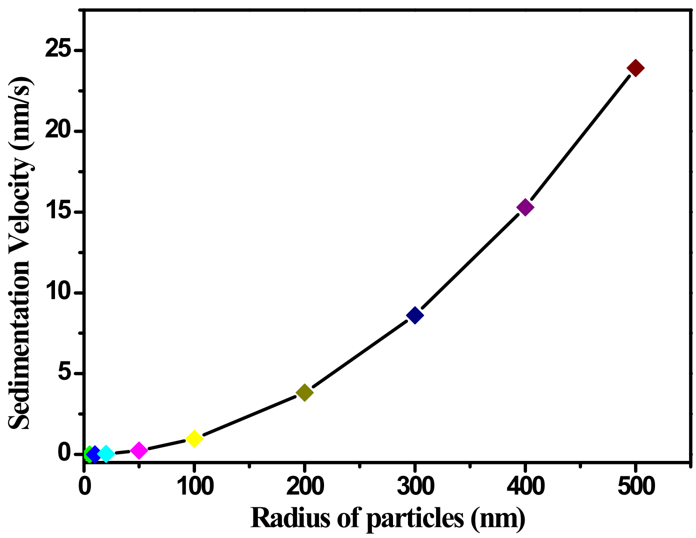

Fig. S3 Sedimentation velocity as a function of particle size in silicone oil.

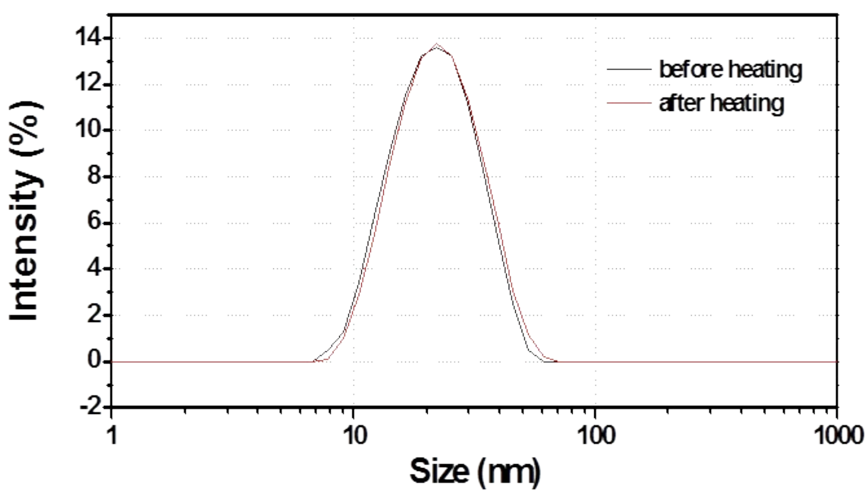

Fig. S4 DLS measurement of PDMS-grafted Fe_3O_4 NPs within silicone oil (0.75 mg/mL) before and after thermal aging at 120 ^{o}C for 12 h.

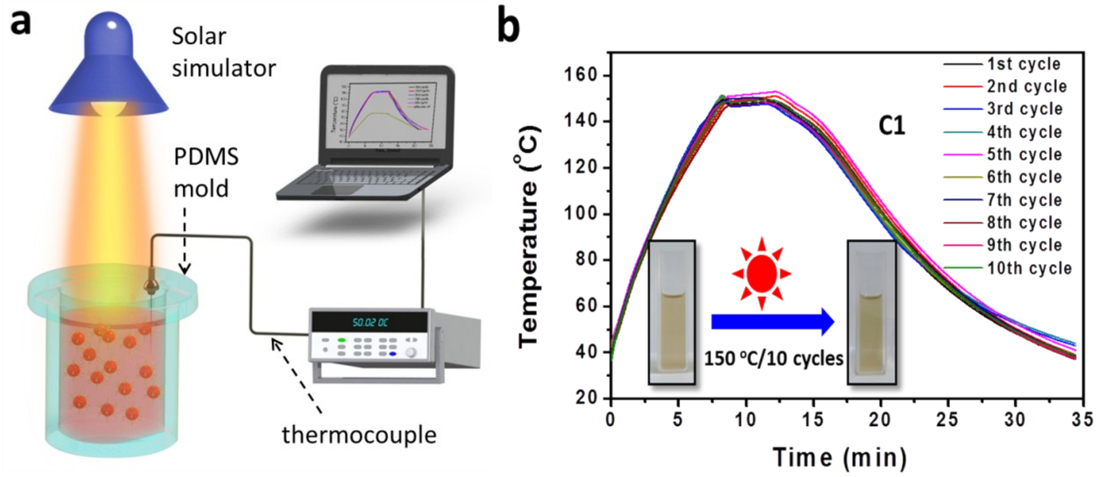

Fig. S5 (a) Schematic of experimental setup for solar-thermal harvest with nanofluids. (b) Solar-thermal harvest with silicone oil nanofluids (C1: 0.75 mg/ml) at an operation temperature of 150 °C.

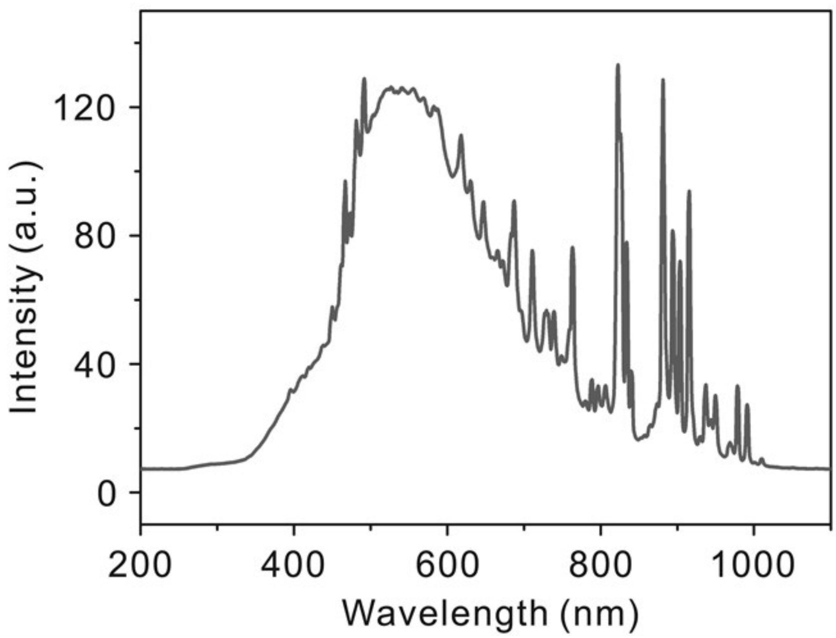

Fig. S6 Emission spectrum of solar simulator.

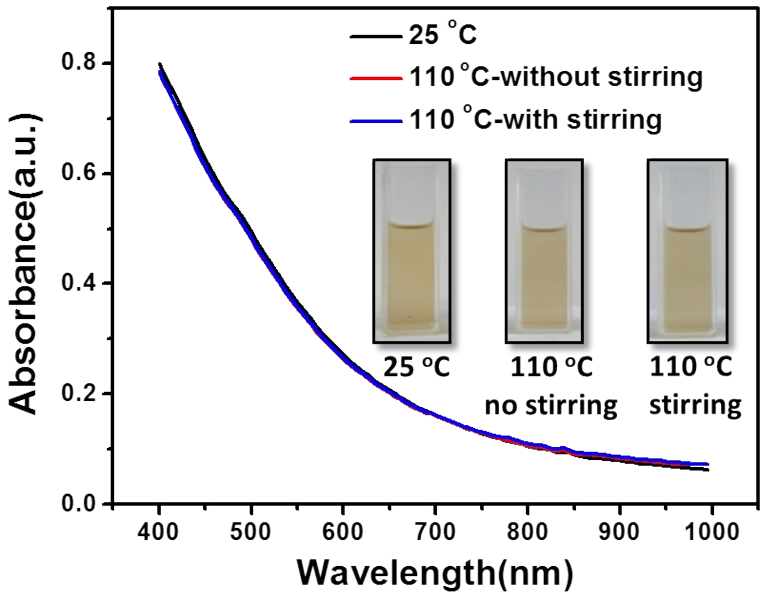

Fig. S7 Absorption spectra of Fe_3O_4/silicone oil nanofluids (C1: 0.75 mg/mL) aging at 110 °C under stirred and non-stirred state. The inset shows the photographs of the nanofluids indicating consistently stable dispersion.