

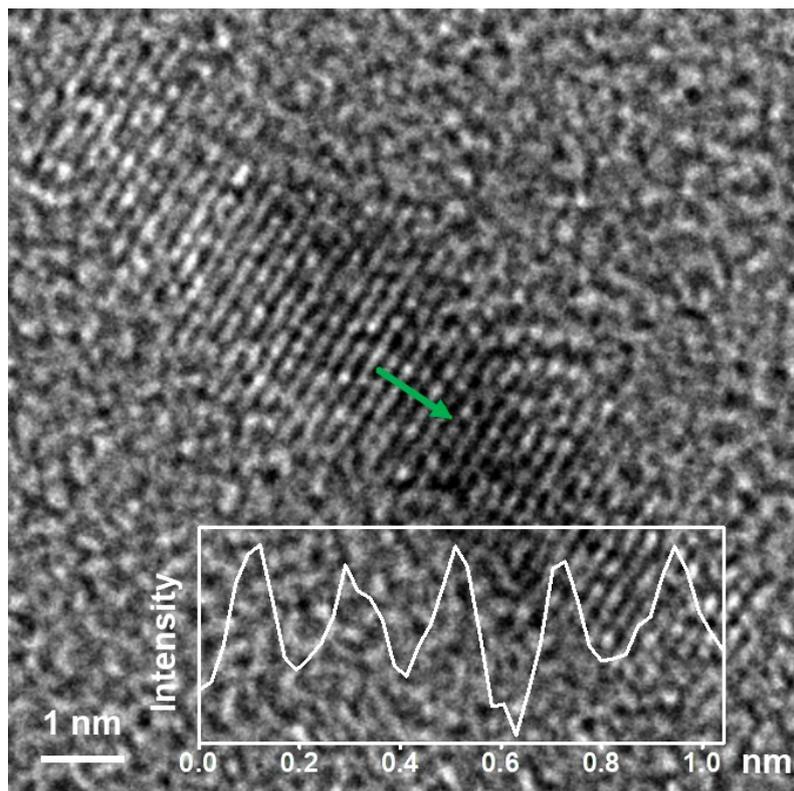
**Supplementary Information**

**Self-dispersible graphene quantum dots in ethylene glycol for direct absorption-based medium-temperature solar-thermal harvesting**

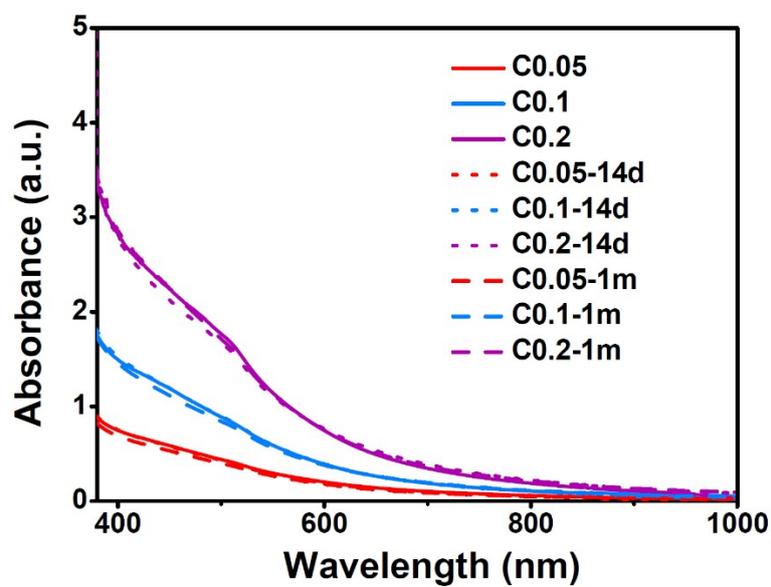
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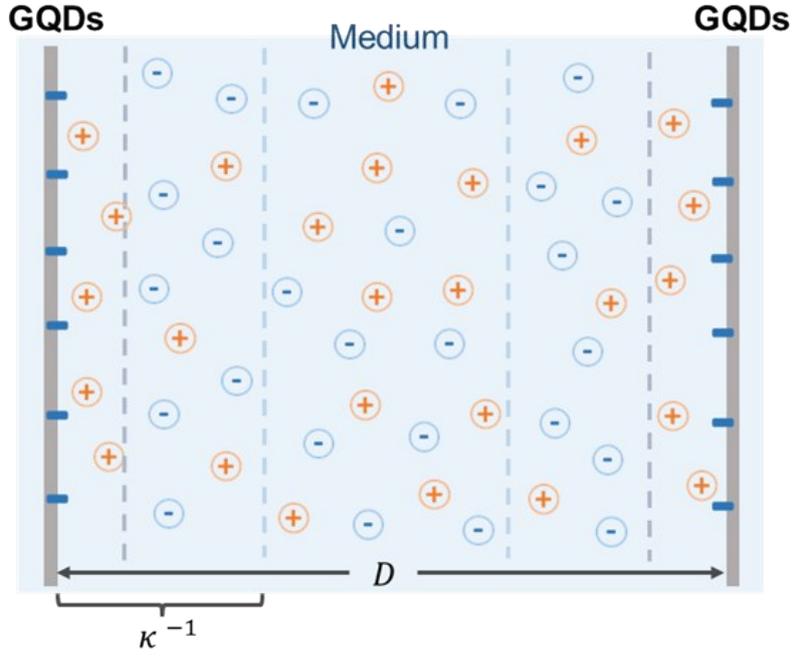
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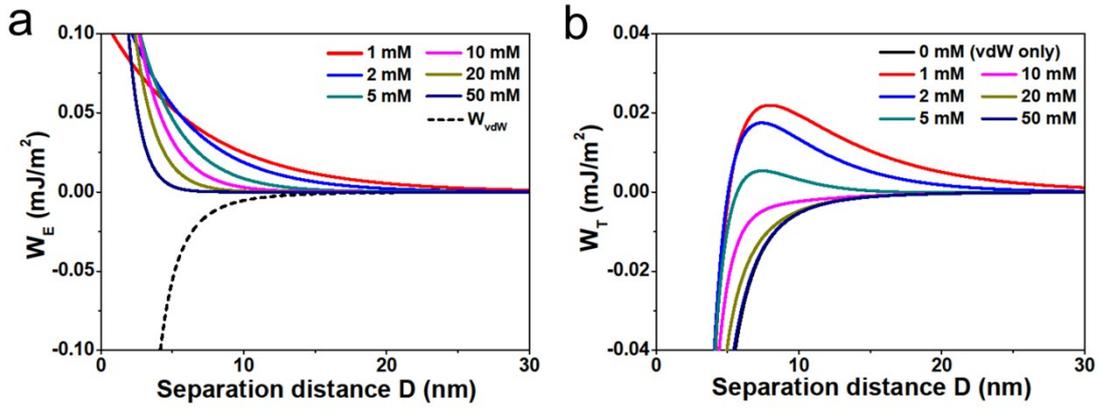
**Fig. S1** Intensity profile along the green line in HRTEM image of OH-GQDs.



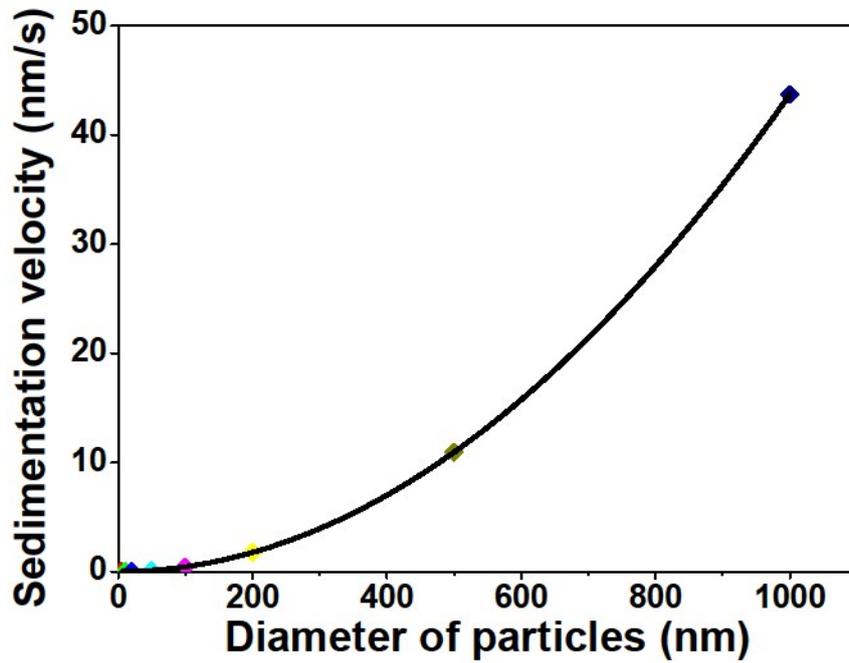
**Fig. S2** Optical absorption spectra of GQD-EG nanofluids before and after being stored at room temperature for 14 days and 1 month.



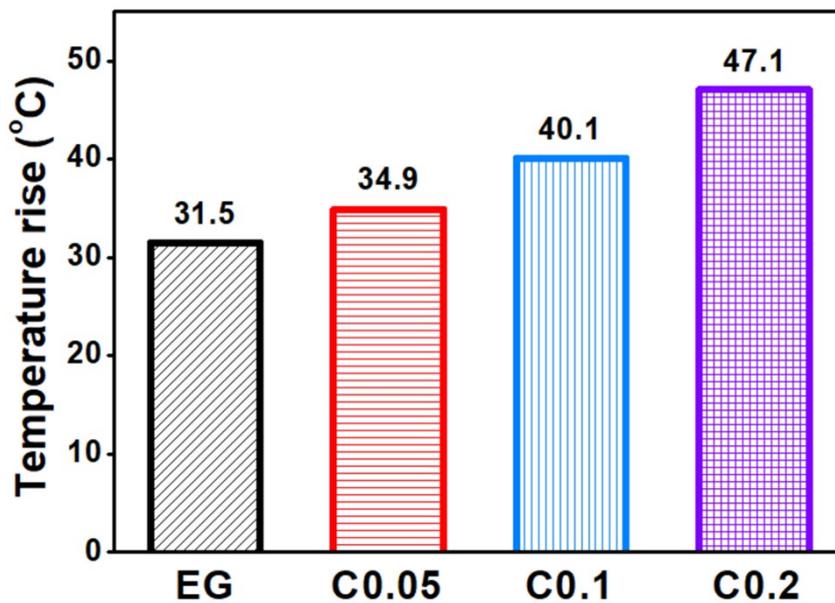
**Fig. S3** Schematic of the electrical double layer model for two parallel GQD plates with a separation distance of  $D$  in the EG base fluid. The separation distance ( $D$ ) is larger than the Debye length ( $\kappa^{-1}$ ).



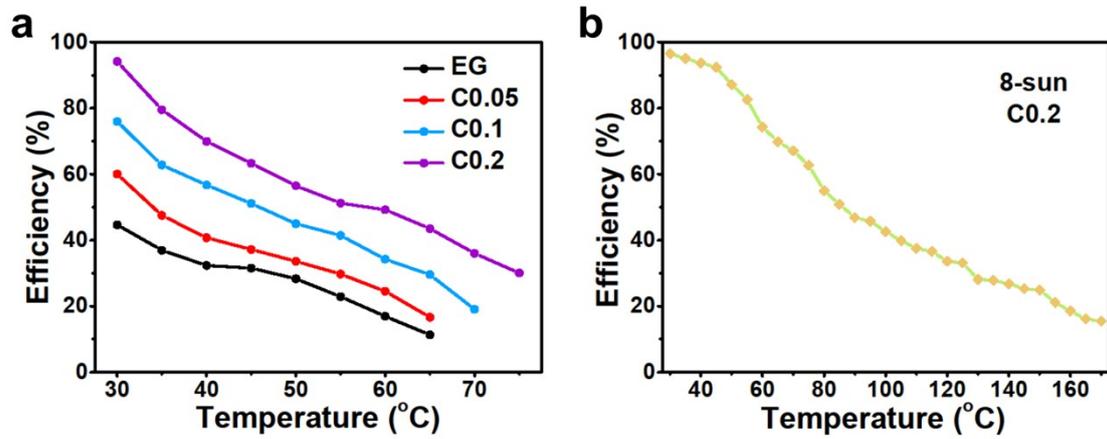
**Fig. S4** (a) The van der Waals attraction energy ( $W_{vdW}$ ) and electrostatic energy ( $W_E$ ) curves as a function of  $D$  with different bulk electrolyte concentration  $c_b$ . (b) Total DLVO interaction energy ( $W_T$ ) curves as a function of  $D$  with different bulk electrolyte concentration  $c_b$ .



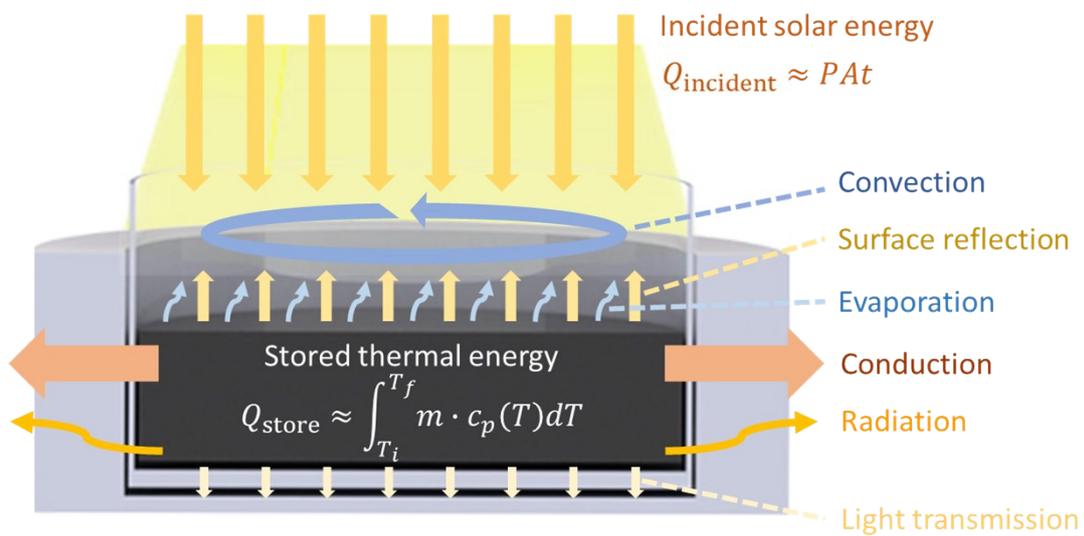
**Fig. S5** Sedimentation velocity of GQDs as a function of particle size in EG at room temperature. The GQDs were treated as spheres to estimate their sedimentation velocity.



**Fig. S6** Temperature rise of the EG and GQD-EG nanofluids under 2-sun solar illumination (2 kW m<sup>-2</sup>) for 30 min.



**Fig. S7** (a) Solar-thermal harvesting efficiency of EG and GQD-EG nanofluids under 2 kW m<sup>-2</sup> solar irradiation; (b) Solar-thermal harvesting efficiency of GQD-EG nanofluids (0.2 mg/mL) under 8 kW m<sup>-2</sup> solar irradiation.



**Fig. S8** Schematic of energy balance for experimental volumetric solar-thermal energy harvesting with GQD-EG nanofluids.

**Table S1. DLS measurement of prepared GQD-EG nanofluids before and after hydrothermal treatment.**

Sample	Particle size (nm)				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	Average	Standard Deviation
Fluids before treatment	2676.6	2778.9	2798.3	2751.3	65.1
Fluids after treatment (180 °C-6 h)	8.54	10.12	9.36	9.34	0.79

**Table S2. Zeta potential of GQD-EG nanofluids before and after heating.**

Sample	Absolute Zeta potential (mV)				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	Average	Standard Deviation
Precursor fluids	31.78	36.82	31.91	33.50	2.87
As-prepared fluids	37.80	36.17	34.40	36.12	1.70
Fluids after heating (180 °C-12 h)	31.58	37.73	37.85	35.72	3.59
Fluids after heating (180 °C-7 d)	37.97	32.79	38.83	36.53	3.27

**Table S3. Calculated factors based on DLVO theory.**

$c_b$ (mmol/L)	$N_b$ (#/m <sup>3</sup> )	$\kappa$ (nm <sup>-1</sup> )	$\kappa^{-1}$ (nm)	Energy barrier $\Delta E_{DLVO}$ (10 <sup>-21</sup> J) ( $k_B T$ )	
0	0	--	--	--	--
1	$6.02 \times 10^2$	0.151	6.60	1.102	0.27
2	$1.20 \times 10^2$	0.214	4.67	0.878	0.21
5	$3.01 \times 10^2$	0.339	2.95	0.269	0.07
10	$6.02 \times 10^2$	0.479	2.09	--	--
20	$1.20 \times 10^2$	0.677	1.48	--	--
50	$3.01 \times 10^2$	1.07	0.934	--	--

**Table S4. Thermal conductivity of EG and GQD-EG nanofluids at 24 °C.**

Sample	Thermal conductivity (mW m <sup>-1</sup> K <sup>-1</sup> )				
	1 <sup>st</sup>	2 <sup>nd</sup>	3 <sup>rd</sup>	Average	Standard Deviation
EG	269.1	268.6	267.0	268.2	0.9
0.05 mg/mL GQD-EG	273.8	270.9	267.5	270.7	2.6
0.1 mg/mL GQD-EG	271.4	272.1	271.7	271.7	0.3
0.2 mg/mL GQD-EG	271.9	278.6	273.1	274.5	2.9

## Note S1

### Calculation of van der Waals attraction, electrostatic repulsion and the total DLVO interaction energy

The energy barrier to aggregation can be estimated by the classical Derjaguin–Landau–Verwey–Overbeek (DLVO) theory. In our analysis, two nearby GQDs in nanofluids are treated as two parallel plates with a separation distance of  $D$ . The dimensions of GQD plates are estimated from experimental characterization (Diameter: 8 nm, thickness: 1.5 nm). The van der Waals interaction energy per unit area between two parallel flat plates of fixed thickness can be estimated by:

$$W_{vdW} = -\frac{A_H}{12\pi} \left[ \frac{1}{D^2} - \frac{2}{(D+L)^2} + \frac{1}{(D+2L)^2} \right]$$

where  $A_H$  is the Hamaker constant and  $L$  is the thickness of the plate. According to Lifshitz theory, the non-retarded Hamaker constant for particles in the medium can be expressed as:

$$A_H = \frac{3}{4} k_B T \left( \frac{\varepsilon_P - \varepsilon_M}{\varepsilon_P + \varepsilon_M} \right)^2 + \frac{3h\nu_e (n_P^2 - n_M^2)^2}{16\sqrt{2}(n_P^2 + n_M^2)^{3/2}}$$

where  $k_B$  is the Boltzmann constant,  $T$  is the absolute temperature,  $h$  is the Planck constant,  $\nu_e$  is the electronic absorption frequency ( $\sim 3 \times 10^{15} \text{ s}^{-1}$ ),  $\varepsilon_P$  and  $\varepsilon_M$  are static dielectric constant of particles (12.0) and the medium (37.0),  $n_P$  and  $n_M$  are the refractive index of particles (2.7) and the medium (1.43).

There is also electrostatic repulsion between two neighboring GQDs due to negatively charged functional groups on the surface and adsorbed counter ions. The electrostatic repulsion can be estimated by Stern's model of electrical double layer, which supposes that there is a layer of ions fixed in space near the electrode followed by a diffuse distribution of ions (Fig. S3). By using the Poisson-Boltzmann equation, we can estimate the electrostatic repulsion energy between two parallel planes per unit area:

$$W_E \approx \frac{64N_b k_B T}{\kappa} \tanh^2 \left( \frac{ez\zeta}{4k_B T} \right) \exp(-\kappa D)$$

where  $N_b$  is the bulk number density of the electrolyte and it is directly related with bulk electrolyte concentration  $c_b$  ( $N_b = N_A c_b$ , where  $N_A$  is the Avogadro constant),  $\kappa$  is the Debye–Hückel parameter,  $e$  is the elementary charge,  $z$  is the valence of electrolyte ( $z = 1$  for 1:1 electrolyte such as NaCl, NaNO<sub>3</sub>, etc.),  $\zeta$  is the zeta potential. It should be noted that this expression only strictly holds for particle surface potential, however we use absolute zeta potential (~35 mV) here because it is experimentally measurable. It should also be noted that this expression is an estimation that is applicable when the separation distance is larger than the Debye length, or  $D > \kappa^{-1}$ .

The Debye–Hückel parameter is defined as

$$\kappa \equiv \left( \frac{2N_b z^2 e^2}{\varepsilon_M \varepsilon_0 k_B T} \right)^{1/2}$$

where  $\varepsilon_0$  is the permittivity of vacuum. In our GQD-EG nanofluids, the pH range is 6~8, which indicates the lack of H<sup>+</sup> and OH<sup>-</sup> electrolytes. However, residual salts on the as-synthesized GQDs (e.g. NaNO<sub>3</sub>) will also contribute to some mobile electrolytes. The electrostatic repulsion effect can be modulated by controlling electrolyte concentration in the base fluids. The total interaction energy per unit area is defined as  $W_T = W_{vdW} + W_E$ . The change of electrostatic repulsion energy  $W_E$  and the total energy  $W_T$  versus the separation distance  $D$  are plotted in Fig. S4a and Fig. S4b, respectively. The DLVO energy barrier is calculated by  $\Delta E_{DLVO} = W_{T,max} A$ , where  $A$  is the surface area of GQD plates (~50.3 nm<sup>2</sup> in the model). The calculated results are presented in Table S3.