Supporting Information

Novel WS₂-based nanofluids for concentrating solar power:

performance characterization and molecular-level insights

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1. Calculation of the ratio of the surface tension components

The liquid phase exfoliation process is favored when the tension at the liquid-solid interface is minimized. This liquid-solid surface tension, γ_{SL} , can be defined as¹⁻²

$$\gamma_{SL} = \gamma_S^p + \gamma_S^d + \gamma_L^p + \gamma_L^d - 2\sqrt{\gamma_S^p \gamma_L^p} - 2\sqrt{\gamma_S^d \gamma_S^d}$$
(S1)

where the subscripts S and L mean solid and liquid, respectively, and the superscripts p and d denote the polar and dispersive components of the surface tension. Alternatively, the equation (S1) can be expressed as

$$\gamma_{SL} = \left(\frac{\gamma_S^p}{\gamma_S^d} + 1\right)\gamma_S^d + \left(\frac{\gamma_L^p}{\gamma_L^d} + 1\right)\gamma_L^d - 2\left(\sqrt{\frac{\gamma_S^p\gamma_L^p}{\gamma_S^d\gamma_L^d} + 1}\right)\sqrt{\gamma_S^d\gamma_L^d}$$
(S2)

Considering both equations, for minimizing γ_{SL} , the values of γ_S^p and γ_L^p and also the values of γ_S^d and γ_L^d must be similar between them. And also, the ratios γ_S^p/γ_S^d and γ_L^p/γ_L^d should be as closer as possible. In our case, the ratio of the polar and dispersive components of the WS₂, γ_S^p/γ_S^d , is 0.52.³ So, it is necessary to know the surface tension and their components of the surface tension can be calculated from⁴⁻⁵

$$\sqrt{\gamma_R^d \gamma_L^d} + \sqrt{\gamma_R^p \gamma_L^p} = \frac{\gamma_L (1 + \cos\theta)}{2}$$
(S3)

where θ is the contact angle, and *R* is a solid which is used a reference. A Teflon support is considered as reference solid, and its surface tension and their components were measured as is described in the literature,³ being the values obtained $\gamma_R^p = 0.07 \text{ mN} \cdot \text{m}^{-1}$, and $\gamma_R^p = 24.6 \text{ mN} \cdot \text{m}^{-1}$. The value of the polar component is close to 0, as is expected, and this allow us to obtain the components of the base fluid using the equation (S3) and from the experimental values of the contact angle and the surface tension. Therefore, the contact angle was measure using a handmade system built in the author's lab in the University of Cádiz, and the surface tension was obtained using stalagmometry.⁶

Then, the first step was to measure the surface tension and their components for the fluid used, that is the eutectic mixture of diphenyl oxide and biphenyl. Table S1 shows the values obtained for the surface tension and their components, and also for the ratio between polar and dispersive components.

Table S1. Values of the surface tension and their components and the ratio between them for the fluid used measured at room temperature.

Liquid	$\gamma_L / \mathrm{mN \ m^{-1}}$	γ_L^p / mN m ⁻¹	γ_L^d / mN m ⁻¹	γ^p_L/γ^d_L
HTF	39.96	16.43	22.81	0.72

Also, cetyltrimethylammonium bromide (CTAB, purity > 99%, Sigma-Aldrich©) was used a surfactant to modify the surface tension and their components for the base fluid in order to fit the ratio between the components with the ratio of the nanomaterial, WS₂. Thus, the most relevant values for the surface tension, their components and the ratio between them for several concentrations of CTAB are shown in the Table 1 in the main article.

2. UV-vis spectra registered for the nanofluids prepared



Figure S1. UV-vis spectra registered when nanofluids were prepared for (a) nanofluid #1; (b) nanofluid #2; (c) nanofluid #3; and (d) nanofluid #4.

The presence of WS_2 nanosheets is confirmed by the observation of the characteristic peak at about 629 nm.⁷

3. Nanofluid performance

A rigorous analysis of the nanofluid performance for Concentrating Solar Power (CSP) applications has been performed based on the Re number and the flow rate. Typically, the analysis of the nanofluid performance of CSP plants is performed from the definition of the useful energy production (Q_u), which is typically defined as⁸

$$Q_u = h A_{ri} \Delta T \tag{S4}$$

where *h* is the heat transfer coefficient, A_{ri} is the inner area of the receiver and ΔT is the difference in temperature between the receiver and the mean fluid. Bellos and Tzivanidis⁹ reported a new formulation for the useful energy production for considering the contribution of the heat transfer coefficient and the amount of the heat transferred. In this formulation, Q_u is defined as

$$Q_u = U_r A_{ri} \Delta T \tag{S5}$$

 U_r is defined in the equation (2) in the main article, and it depends on the heat transfer coefficient, the flow rate, and the term (ρC_P) defined also in the main article.

In this work, the heat transfer coefficient, h, was calculated using the Nusselt number, using the equation¹⁰

$$Nu = 0.023 Re^{0.8} Pr^{0.4} \tag{S7}$$

The relationship between the Nusselt number and the heat transfer coefficient is given by the definition of the Nusselt number, which is

$$Nu = \frac{hD_{ri}}{k} \tag{S8}$$

where D_{ri} is the inner diameter (typically 0.066 m⁹) and *k* the thermal conductivity. Also, for applying the equation S7, the Reynolds (Re) and Prandtl (Pr) numbers should be calculated as

$$Re = \frac{\rho V_{av} D_{ri}}{\mu}$$

$$Pr = \frac{\mu C_P}{k}$$
(S9)

where V_{av} is the mean rate, μ is the dynamic viscosity. In this work, the flow rate analyzed was in the range 100-300 L min⁻¹, with a step of 50 L min⁻¹. So, higher values of U_r lead to lower temperature values in the solar receiver if the useful energy production is assumed to be constant. This means the higher the U_r values, the lower the temperature in the receiver and the lower the thermal losses. If thermal losses are decreased, the thermal efficiency in the solar collector will increase. Therefore, the thermal efficiency will be higher when U_r values are high. The results obtained are shown in Figure 7 in the main article.

4. Base fluid-surfactant-WS₂ interactions

The Transferable Potentials for Phase Equilibria (TraPPE) force field were used for classical Molecular Dynamics calculations. The intra- and intermolecular interactions of the molecules of the base fluid (diphenyl oxide/biphenyl blend), that is, the heat transfer fluid was described by using the transferable potentials for phase equilibria-explicit-hydrogen (TraPPE-EH) force field.¹¹⁻¹² This force field considers aromatic ring and directly linked atoms as rigid entities. The phenyl rings were treated as rigid but they were allowed to rotate with regard to each other around the carbon bond. The Transferable Potentials for Phase Equilibria-United Atom force field (TraPPE-UA) was used for describing both intramolecular and intermolecular interactions of the CTAB.¹³⁻¹⁵ TraPPE-UA force field treats the alkyl groups as a fully flexible model based on single interaction sites (pseudoatoms). A pseudo-atom represents a carbon atom together with all of its bonded hydrogen atoms (CH₂ and CH₃) and treats the nitrogen and the carbon atoms as explicit interaction sites in a rigid unit. A slab of 75 atoms was used for describing the WS₂ from an unit cell with the space group P63/mmc.¹⁶ The non-bonded force field was described from adopting the setting parameters reported elsewhere.¹⁷⁻¹⁸ The TraPPE-EH and TraPPE-UA force fields and the non-bonded force field of the metal nanoparticle use Lennard-Jones (LJ) and Coulomb potentials to represent the non-bonded interactions

$$u(r_{ij}) = 4\varepsilon_{ij} \left[\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right] + \frac{q_i q_j}{4\pi\varepsilon_0 r_{ij}}$$
(S10)

where r_{ij} , ε_{ij} , σ_{ij} , q_i , q_j , and ε_0 are the distances between interaction sites *i* and *j*, the LJ well depth, the LJ diameter, the partial charges on interaction sites *i* and *j*, and the permittivity of vacuum, respectively. The Lorentz-Berthelot combining rules were used to determine LJ parameters for unlike interactions.

The DLPOLY code was used to carry out the molecular dynamics simulation.¹⁹ The canonical ensemble (NVT) was applied in the simulations performed by using periodic boundary conditions and the Nose-Hoover thermostat at 300 K. A cubic box providing the initial configuration was built with the PACKMOL code.²⁰ The length of the box sides was chosen to keep the density of the experimental HTF at 298 K. The Ewald sum methodology was applied to account for electrostatic interactions using a cut-off distance of 9 Å. The simulations run lasted for 1 ns employing a time step of 0.5 fs and the structures were saved every 100 time steps for analyzing the trajectory.

The radial distribution function (RDF) was analyzed for the interactions of WS_2 with the base fluid and the surfactant. For greater clarity, the RDFs at the interaction sites have been recorded with regard to the geometrical center of the WS2 slab with central W atom as reference point. For the description of the interaction between the WS₂ and the CTAB, the N atom of the CTAB was taken for reference to be indicative of the number of molecules of this surfactant around the slab. The RDF of the W-N pair at 300 K shows three clear peaks centered at 5.7, 9.2 and 11 Å that integrate to 1, 1 and 4 N atoms, respectively (Figure S2a). Worth of attention is the intensity of the peaks meaning the position of surfactant molecules should be very fixed to the slab. The RDF of the W-CH₂ pair, being CH₂ the carbon atoms belonging to the chain of CTAB, is shown in Figure S2b. The peaks from 5.0 to 9.2 and 9.2 to 12.0 Å integrate to 12 and 40 C atoms, respectively. Taking into account the geometry of the WS₂ slab, both the width and the high integration number of those peaks indicate a parallel movement of the surfactant chains next to the slab. This result is of interest because the presence of surfactant molecules over the slab may impede molecules of base fluid getting closer this region of the slab defining a preferred interaction site for the base fluid, such as

an edge or near the edge of the slab. The RDF for the W-O pairs (Figure S2c) indicates the number of O atoms around the slab belonging to diphenyl oxide molecules from the fluid, and it shows two peaks centered at 8.2 and 9.5 Å that integrate to one O atom, respectively. Thus, those peaks belong to the O atoms from two diphenyl oxide molecules. Moreover, the intensity of those peaks indicates strong orientation binding of the diphenyl oxide molecules toward the WS₂. The results found for the W-O pair correspond with those of the W-CO pair (Figure S2d). In this case CO refers to the C atoms linked to the O of the diphenyl oxide (CO), that is two CO per diphenyl oxide molecule. The integration of the intense peak centered at 7.8 Å and the wide double peak from 9.2 up to 11.2 Å gives one and three C atoms, respectively. Finally, the RDFs shown in Figure S2e correspond to the interaction between the WS₂ with the C atom of the diphenyl oxide and biphenyl molecules. This RDF shows multiple peaks from 4.2 to 8.8 Å that integrate to 9 C atoms. This multiplicity means the integrated C atoms have fixed positions. This fact corroborates a dramatically orientation of biphenyl or diphenyl oxide molecules near WS₂. The rest of peaks up to 12.0 Å integrate to 28 C atoms and should belong to part of the rings from diphenyl oxide and biphenyl molecules placed far away the WS₂ slab.



Figure S2. RDFs of the (a) W-N, (b) W-CH₂, (c) W-O, (d) W-CO, and (e) W-C pairs in the WS₂ nanofluid.

5. XPS survey spectrum for WS₂ exfoliated extracted from the nanofluid #4.



Figure S3. Survey XPS spectrum of WS2 sample extracted from the nanofluid #4.

Survey spectrum of the WS₂ sample extracted from the nanofluid #4 shows the presence of W(IV) and S⁻². Also, O and C signals are observed. As is described in the main text of the manuscript, the presence of W-C and W-O bonds from the dissociative adsorption of diphenyl oxide molecules on the edge of WS₂ nanostructure is confirmed.

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