Supporting Information

Binding of Lignin Nanoparticles at Oil-Water Interfaces: An Ecofriendly Alternative to Oil Spill recovery

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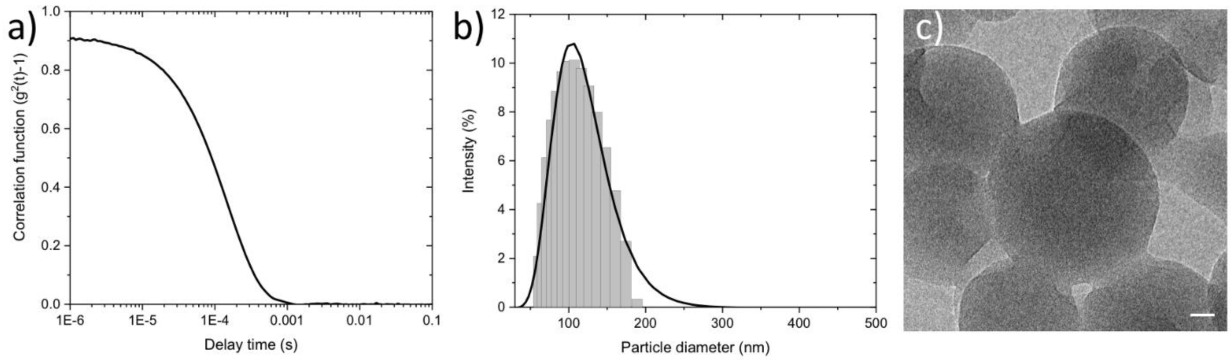

Fig. S1. (a) Time correlation function of lignin nanoparticles in water, as obtained by dynamic light scattering measurements. The smooth and single exponential decay of correlation function indicates low polydispersity in particle dispersion. (b) The intensity distribution of particle sizes obtain by the analysis of the correlation function. The distribution shows that average particle diameter is ~100 nm. (c) Transmission electron microscope image of lignin nanoparticles indicates that the predominant shape of particles is spherical, and the average diameter is ~100 nm which is in agreement with the size obtained from dynamic light scattering measurements. Scale in (c) is 10 nm.

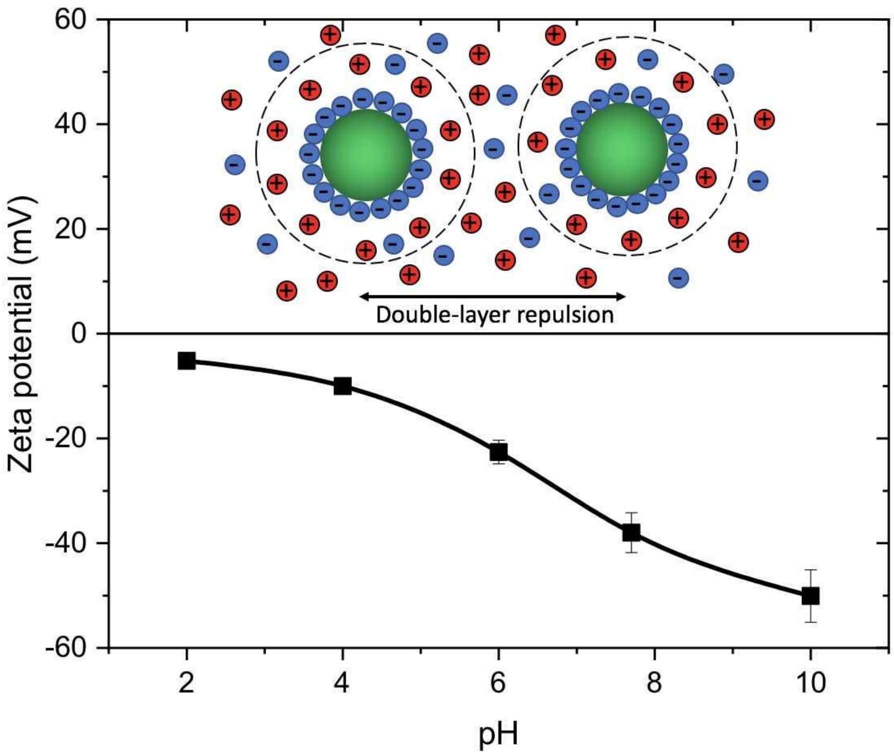

Fig. S2. Zeta potential of lignin NPs as a function of pH. The isoelectric point of the particles is pH < 2, and particle dispersion remains stable at wide range of pH (4-10) due to electrostatic repulsion. The inset schematic shows the principle of double layer repulsions, where the overlap of the diffused counter ion layer induces a repulsive osmotic pressure that stabilizes the particles.

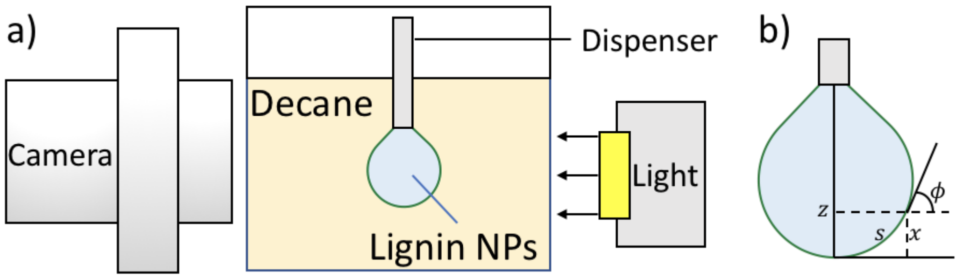

Fig. S3. (a) Schematic of optical tensiometry. The pendant drop of lignin NPs dispersion was introduced in the cuvette with decane, and drop was recorded with the high-speed camera. (b) Schematic of pendant drop to measure decane-lignin NPs dispersion interfacial tension. The interfacial tension (γ) was measured from $\gamma = \Delta\rho g\frac{{R_0}^2}{\beta}$, where $\Delta\rho$ is density difference between fluid, g is gravitational constant, R_0 is radius of drop curvature at apex, and β is a shape factor, calculated from the Young-Laplace equation.[1]

$$\frac{d\phi}{ds} = 2 + \beta z - \frac{sin\phi}{x}$$

$\frac{dx}{ds} = cos\phi$ and $\frac{dz}{ds} = sin\phi$

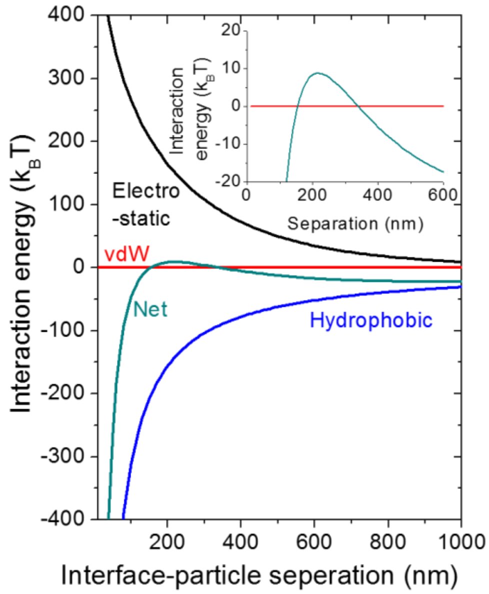

Fig. S4. Pair interaction energy between a lignin NP and a flat oil-water interface as a function of interface-particle distance. The net interaction energy is the sum of electrostatic, van der Waals and hydrophobic interactions between the lignin NPs and decane-water interface.

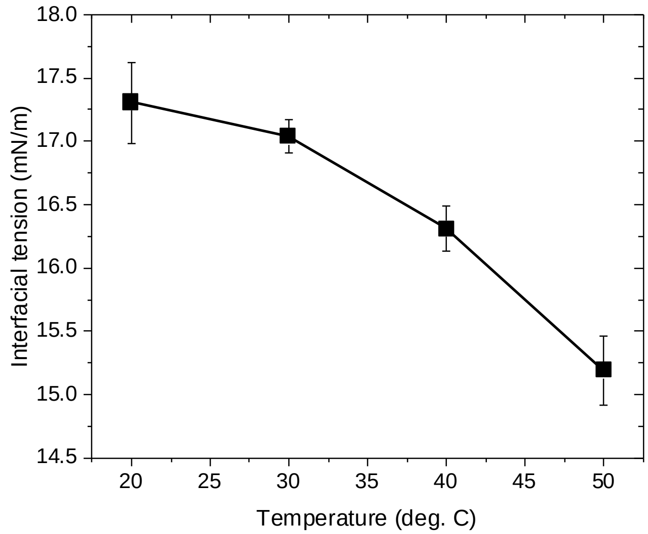

Fig. S5. Interfacial tension between crude oil and 0.1 mg/ml lignin NPs dispersion containing 0.4 M NaCl solution. The interfacial tension decreases with increasing temperature. This is attributed to faster diffusion of NPs toward the oil-water interface at higher temperatures.

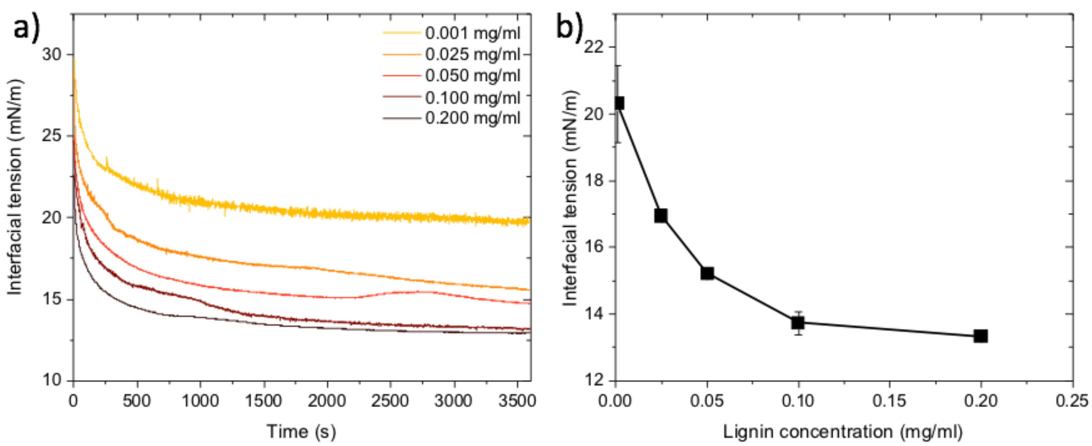

Fig. S6. (a) Decrease in crude oil-water interfacial tension with time at increasing lignin NP concentration. The measurements were performed at 0.4 M NaCl solution which is typical salinity of seawater. The change of interfacial tension of crude oil-water shows a similar behavior as for model decane-water interface (Fig. 2). The equilibrium value of interfacial tension at low concentration of lignin NP (0.001 mg/ml) is achieved at shorter times in the presence of the 1:1 NaCl electrolyte. This faster adsorption is attributed to decrease in electrostatic repulsion between in the negatively charged interface and the particles. (b) The change of equilibrium interfacial tension of crude oil-water interface containing 0.4 M NaCl in aqueous phase as a function of lignin concentration. The critical concentration of lignin NPs is shown at ~ 0.10 mg/ml due to insignificant change of interfacial tension beyond this point.

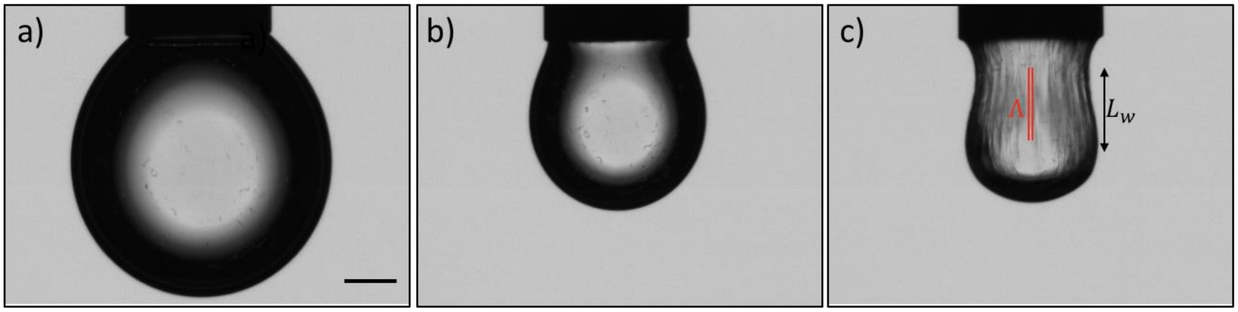

Fig. S7. (a-b) Images of lignin NPs drop in decane. (c) drop after deflation showing wrinkles on the surface. The bending energy was estimated by shape and wrinkle analysis of drop, introduced by Knoche *et al.*[2–4] The bending energy (E_B) is $E_B = \frac{\tau_s \Lambda^4}{16\pi^2 {L_w}^2}$, where τ_s is meridional tension, Λ is a wrinkle wavelength, and L_w is a length of wrinkles. Λ and L_w were measured by image analysis. The estimated values of $\Lambda \sim 0.14 \times 10^{-5}$ m, $L_w \sim 7.6 \times 10^{-4}$ m, and $\tau_s \sim 18.3 \frac{mN}{m}$. Scale bar shown in (a) is 0.5 mm.

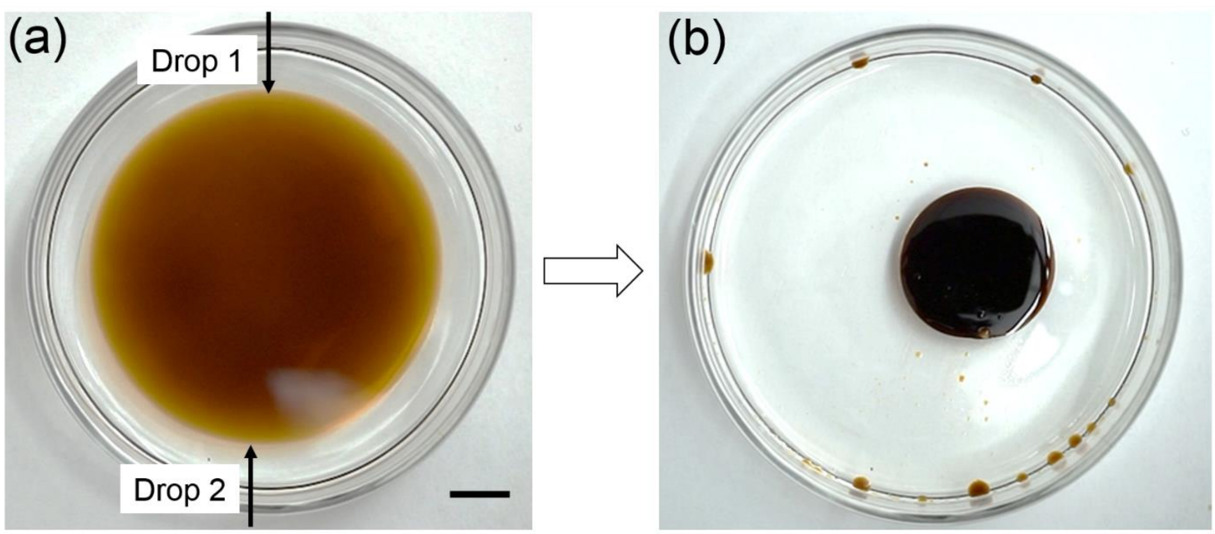

Fig. S8. (a-b) Images showing herding process by adding two droplets of lignin NPs-pentanol mixture from direction indicated by the arrows in (a). The herded oil slick is at the center of petri dish due to the Marangoni flow and interfacial mass transfer generated by two droplets. Scale bar shown in (a) is 1 cm.

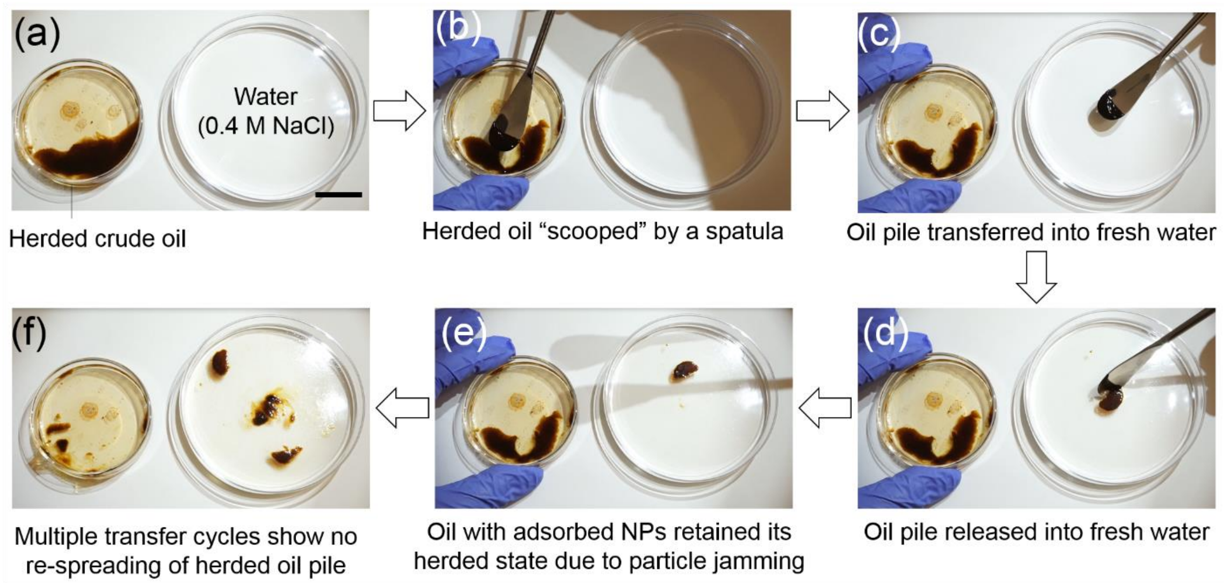

Fig. S9. (a-f) Sequence of images showing the transfer of herded oil slick into fresh water surface contained in a Petri dish. The crude oil herded with lignin NPs-pentanol mixture retained its herded state on the fresh water surface. This ability to retain droplet shape highlights that the lignin NPs are irreversibly adsorbed on to the interface, which further restrict re-spreading of the oil onto water surface. Scale bar shown in (a) is 2 cm.

Spreading coefficient calculations

Spreading coefficient is defined as

$$S = \gamma_{A/W} - (\gamma_{O/W} + \gamma_{A/O})$$

Here $\gamma_{A/W}$ is air-water surface tension
$\gamma_{O/W}$ is oil-water interfacial tension
$\gamma_{O/A}$ is air-oil surface tension

A. Before adding the herder

$\gamma_{A/W}$ = 72 mN/m
$\gamma_{O/W}$ = 32 mN/m
$\gamma_{O/A}$ = 22 mN/m
***S* = +18 mN/m**

B. **Immediately after spraying mixture of lignin NPs and pentanol**

$\gamma_{A/W}$ = 26 mN/m (after formation of pentanol layer on water)
$\gamma_{O/W}$ = 32 mN/m
$\gamma_{O/A}$ = 22 mN/m
***S* = -28 mN/m**

$\gamma_{A/W\ or\ A/pentanol}$ is reduced significantly because of lower surface tension of 1-pentanol which spreads over the air water interface, which results the negative spreading coefficient.

C. **After solubilization of pentanol**

$\gamma_{A/W}$ = 56 mN/m (reduced due to adsorption of lignin NPs and pentanol at air-water interface)
$\gamma_{O/W}$ = 13 mN/m (reduced due to adsorption of lignin NPs on oil-water interface)
$\gamma_{O/A}$ = 22 mN/m
***S* = +21 mN/m**

Despite the positive spreading coefficient, the herded crude oil remains as a thick slick due to adsorbed lignin NPs at oil-water interface which prevents re-spreading into a thin film.

References

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