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Supplementary Information

Analysis of the effect of organic solvent-sheets interfacial interaction on the exfoliation of sulfur-doped reduced graphene oxide sheets in a solvent system using molecular dynamics simulations

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Potential energy function

In this study, the potential energy was calculated using the COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies) II force field. The potential function is expressed as

$$
\begin{aligned}
E = & \sum_{bond}\left[K_{b2}(b-b_0)^2 + K_{b3}(b-b_0)^3 + K_{b4}(b-b_0)^4\right] \\
& + \sum_{angle}\left[K_{a2}(\theta-\theta_0)^2 + K_{a3}(\theta-\theta_0)^3 + K_{a4}(\theta-\theta_0)^4\right] \\
& + \sum_{dihedral}\left[K_{d1}(1-cos\phi) + K_{d2}(1-cos2\phi) + K_{d3}(1-cos3\phi)\right] \\
& + \sum_{Improper} K_{\chi}(\chi-\chi_0)^2 \\
& + \sum_{b,b} K_{bb}(b-b_0)\left(b'-b'_0\right) + \sum_{b,a} K_{ba}(b-b_0)(\theta-\theta_0) \\
& + \sum_{a,a} K_{aa}(\theta-\theta_0)\left(\theta'-\theta'_0\right) + \sum_{b,d}(b-b_0)[K_{bd1}cos\phi + K_{bd2}cos2\phi + K_{bd3}cos3\phi] \\
& + \sum_{a,d}(\theta-\theta_0)[K_{ad1}cos\phi + K_{ad2}cos2\phi + K_{ad3}cos3\phi] \\
& + \sum_{a,d,a} K(\theta-\theta_0)(\phi-\phi_0)\left(\theta'-\theta'_0\right) \\
& + \sum_{non-bond}\{\varepsilon_{ij}[2(r^0{}_{ij}/r_{ij})^9 - 3(r^0{}_{ij}/r_{ij})^6] + (q_i q_j/4\pi\varepsilon_0 r_{ij})\}
\end{aligned}
\tag{1}
$$

where the potential energy terms are divided into the bonded energy term, coupling energy term, and non-bonded energy term. In bonded energy term, b is the bond length, θ is the angle formed by three atoms, ϕ is the dihedral angle of four atoms, and χ is the out-of-plane angle. K is the force constant at each of energy terms. The cross interaction energy is calculated by the coupling terms such as bond-bond, bond-angle, angle-angle, bond-dihedral, angle-dihedral, and angle-dihedral-angle. In non-bonded energy term, r is the distance between two atoms, ε is the energy constant between non-bonded atoms, and q is the atomic charge. The electrostatic energy was calculated using the atomic charge assigned by the COMPASS II force field.

Materials

Graphite powder (natural microcrystal grade, 99.9995 %) was obtained from Alfar Aesar. Sulfolane (SF, 99.0 %), toluene (> 99.8 %), *N*-methyl-2-pyrrolidone (NMP, > 99.0 %), tetrahydrofuran (THF, inhibitor-free, 99.9 %), nitric acid (HNO_3, fuming, > 90.0 %), sodium chlorate ($NaClO_3$, > 99.0 %), and element sulfur (reagent grade, powder) were obtained from Sigma Aldrich. All reagents and organic solvents were used as received.

Methods

Synthesis of sulfur-doped reduced graphene oxide (SrGO)

The graphene oxide (GO) was prepared from graphite powder using the Brodie method.[1] SrGO was prepared using elemental sulfur as reducing agent and solvent. The GO 2 g and element sulfur 8 g were uniformly mixed, and slowly heated to 170 °C. The reaction temperature was maintained for 4 h. The crude solid was sonicated in toluene to remove unreacted sulfur. Suspension was filtered to collected solids and washed with toluene and ethanol. The solids were vacuum dried at

170 °C.

Dispersion stability test of SrGO in organic solvents using Turbiscan

The dispersion stability was investigated using a Turbiscan Lab Expert.[2] Samples were prepared using toluene, THF, SF, and NMP, respectively, at a concentration of 0.2 mg/mL. All turbiscan samples were prepared sonicated for 1 h and mechanical stirring for 12 h.

Results

The spectra were measured by tracing the change in transmittance through 20 mL vial full height at 1 hour intervals for 24 h (Fig. S1). Among the four suspension, SF suspension showed the best dispersion stability and the change in transmittance after one day was less than 4.84 %(Fig. S1(a)). These results indicate that SrGO sheets formed a homogeneous and stable suspension in SF. The suspension of NMP and THF also showed changes in transmittance of about 17.11 and 37.49 % after 24 h. Toluene spectra showed the most unstable dispersion stability and the most sedimentation behavior. In Fig. S1(d), which is an unstable dispersion state, the change in transmittance value (about 56.37 %) is large. Because of irregularly floating particles, transmittance value change via height is rough. In addition, clear differences in dispersion were observed in digital images of SF and toluene suspensions. Toluene image showed sediment on the bottom, but no sediment was found in SF.

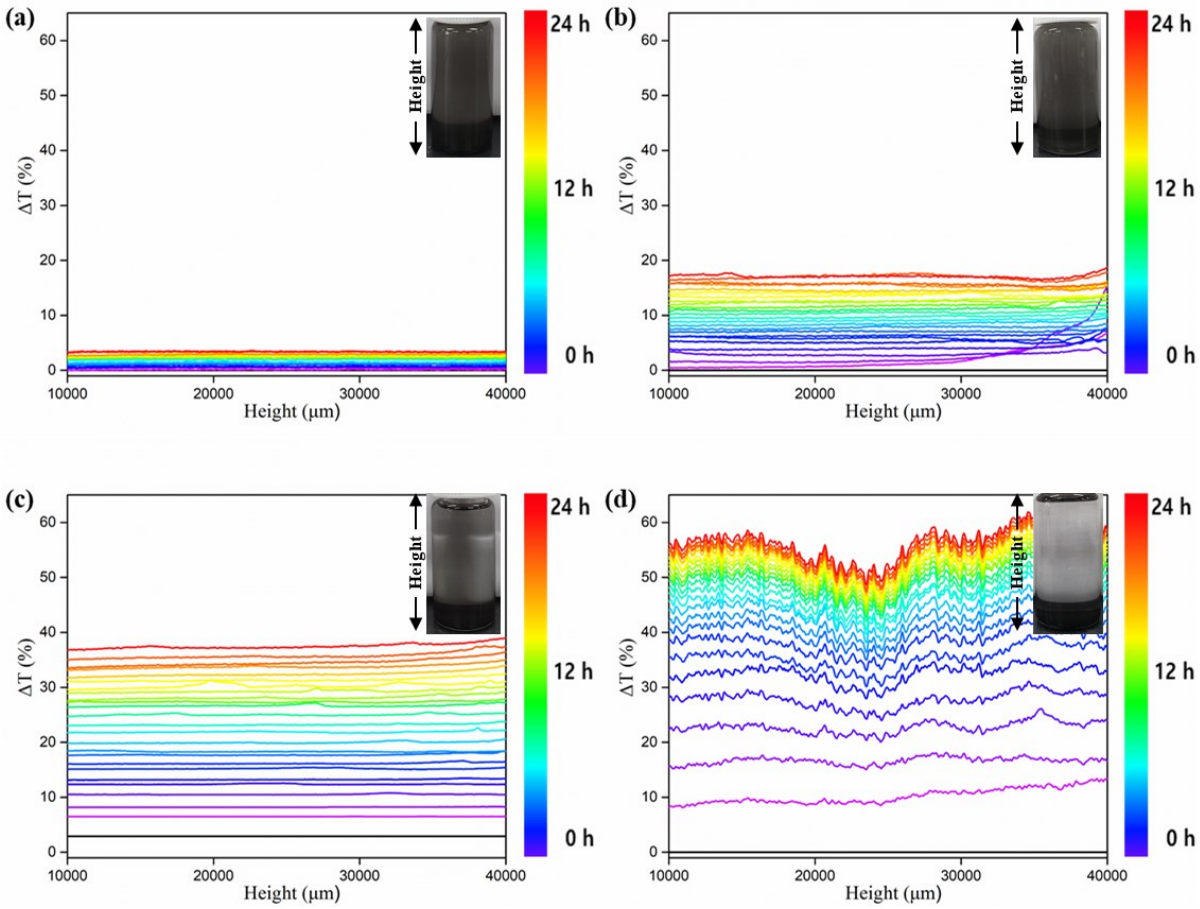

Fig. S1. Turbiscan data of SrGO dispersion (0.2 mg/mL) for 24 h. (a) SF, (b) NMP, (c) THF, and (d) toluene suspensions.

References

1 B. C. Brodie, *Trans. R. Soc. Lond.*, 1859, **14**, 249-259.
2 H. Lim, B. L. Suh, M. J. Kim, H. Yun, J. Kim, B. J. Kim, S. G. Jang, *J. Membr. Sci.,* 2018, **551**, 172-179.