Supporting Information for

Molecular Dynamics Study on the Mechanism of Graphene Oxide to Destabilize Oil/Water Emulsion

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Section S1. Configurations in the VD system

In the VD system, 24 VO-79 molecules were added randomly in the toluene phase at the initial time (Figure S1a). After the simulation of 60 ns shown in Figure S1b, all VO-79 moved to the toluene/water interface. The final configuration of VO-79 on the interface (Figure S1b) was adopted as the initial configuration of VO-79 in the simulations of VL-GinW and VL-GinT systems.

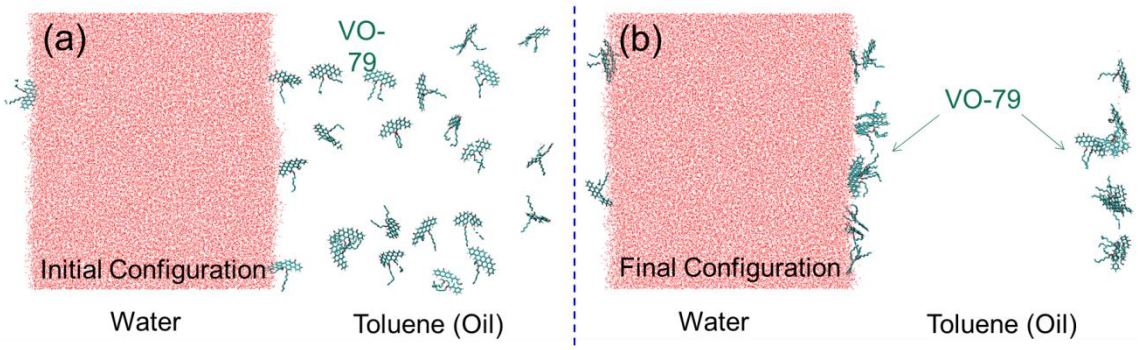

Figure S1. (a) Initial and (b) final configurations in the VD system. VO-79 and water molecules are shown in olive and red, respectively. Toluene molecules are not shown for clarity.

Section S2. Peaks in mass density profiles

The *z* position of the toluene/water interface is defined using the intersect of the density profiles for water and toluene in Figure 4. The *z* positions of the peaks in the mass density profiles of GO and VO-79 near the interface are determined and the distances from these peaks to the toluene/water interface are calculated. The results are shown in Table S1, along with the magnitude of the corresponding peaks. Negative distance indicates location of the peak to the left of the interface, and positive distance indicates location to the right of the interface.

Table S1. *z*-coordinates (*z*, nm) of the toluene/water interface and peaks in the density profiles of GO and VO-79. Also shown are the mass density (ρ, kg/m^3) at the peaks, and the distance (*d*, nm) between the peaks and the interface.

system	Interface	GO			VO-79		
	z	*z*	ρ	*d*	*z*	ρ	*d*
VD	11.91				12.57	67.58	0.66
VL-GinW	11.95	12.23	175.05	0.28	12.32	97.96	0.37
VD-GinW	11.91	11.58	235.39	-0.33	12.56	65.24	0.65
VL-GinT	11.90	12.09	232.70	0.19	12.23	89.34	0.33
VD-GinT	11.97	12.03	189.39	0.06	12.52	71.49	0.55

Section S3. Change of interaction energy (ΔE)

Table S2 shows the change of interaction energy between individual components in each simulated system. Each ΔE was calculated by the difference between the average interaction energies in the first 0.1 ns and in the last 5 ns. ΔE that makes major positive contribution (large negative number) to interfacial film formation is highlighted in blue, while that making major negative contribution (large positive number) is highlighted in red.

Table S2. Change of interaction energy (ΔE, kJ/mol) between individual components.

system	ΔE	GO-VO79	GO-GO	VO79-VO79	GO-Wat.	VO79-Wat.	GO-Tol.	VO79-Tol.	Wat.-Tol.	Wat.-Wat.	Tol.-Tol.
VL-GinW	ΔE_{elec}	-186.9	-1773.3	29.0	6441.9	453.1	-171.6	4.3	140.6	-10359.0	-46.1
	ΔE_{vdW}	-2367.4	-4405.7	427.2	5720.9	289.8	-3466.6	408.3	802.8	-858.0	-89.0
VD-GinW	ΔE_{elec}	-165.7	-1476.9	-9.7	4816.4	-446.0	-115.2	93.8	38.7	-6178.6	-8.6
	ΔE_{vdW}	-1436.8	-5244.7	-1016.6	4649.2	-146.9	-1523.3	2494.5	427.8	-457.6	-1772.3
VL-GinT	ΔE_{elec}	-277.0	-134.1	13.3	-6325.8	440.5	736.6	2.9	218.7	-1385.2	-53.5
	ΔE_{vdW}	-2480.2	-3758.5	474.2	-2433.3	167.6	11564.5	114.4	1288.1	-334.0	-3944.3
VD-GinT	ΔE_{elec}	-402.2	-56.4	-19.2	-5603.8	-344.7	710.6	102.5	290.7	-1463.4	-24.6
	ΔE_{vdW}	-3175.8	-2928.2	-470.0	-2134.3	-316.7	10539.4	3048.5	1591.7	-320.3	-4810.8

Section S4. Details of calculation for the adsorbed VO-79/GO molecules on the interface

To calculate the number of VO-79 molecules adsorbed on the interface, we defined the water phase along with the adsorbed VO-79 as a cluster. The number of molecules in this cluster (n_1), including water and VO-79, was determined by using single linkage algorithm with a cutoff value of 0.5 nm. The number of water molecules (n_2) involved in this cluster was also calculated. The number of VO-79 molecules adsorbed on the interface is given by $n = n_1 - n_2$. The number of GO molecules adsorbed on the interface was calculated in the same way.

Section S5. Details of calculation for the effective thickness of the binary film and the distribution of VO-79 and GO in the two solvents

As shown in Figure 4, the toluene/water interface is located at about z = 12 nm (accurate location of the interface is defined in Section S2 and given in Table S1). The density profile of VO-79 and GO each shows a peak near the interface but becomes zero at a certain distance away from the interface. For instance, in Figure 4b, the VO-79 density is non-zero from z = 10.73 to z = 15.23 nm, while the GO density is non-zero from z = 10.73 to z = 14.22 nm. The effective thickness for the binary film is defined by the difference between the minimum and maximum of these 4 locations, in this case 15.23 – 10.73 = 4.50 nm. The results are collected in Table 2 of the main text.

To determine whether a VO-79 or a GO molecule is primarily located in water or in toluene, we first calculate z-location of the center of mass (COM) of each VO-79 and GO molecule, averaged over the last 5 ns. The location is then compared with the z-location of the interface. If it is to the left of the interface, the molecule will be considered to be in the water phase. Otherwise, it will be considered to be in the toluene phase. Such calculation is done for all VO-79 and GO molecules, and the numbers are counted and presented in Table 2 of the main text.

References

(1) Liu, J.; Li, X.; Jia, W.; Li, Z.; Zhao, Y.; Ren, S. Demulsification of crude oil-in-water emulsions driven by graphene oxide nanosheets. *Energy Fuels* **2015,** *29*, 4644-4653.

(2) Wang, H.; Liu, J.; Xu, H.; Ma, Z.; Jia, W.; Ren, S. Demulsification of heavy oil-in-water emulsions by reduced graphene oxide nanosheets. *RSC Adv.* **2016,** *6*, 106297-106307.

(3) Liu, J.; Wang, H.; Li, X.; Jia, W.; Zhao, Y.; Ren, S. Recyclable magnetic graphene oxide for rapid and efficient demulsification of crude oil-in-water emulsion. *Fuel* **2017,** *189*, 79-87.

(4) Fang, S.; Chen, T.; Wang, R.; Xiong, Y.; Chen, B.; Duan, M. Assembly of graphene oxide at the crude oil/water interface: A new approach to efficient demulsification. *Energy Fuels* **2016,** *30*, 3355-3364.