Supporting Information

Surface Tension Mediated Conversion of Light to Work

David Okawa, Stefan J. Pastine, Alex Zettl, and Jean M. J. Fréchet

College of Chemistry and Department of Physics, University of California, Berkeley, California 94720-1460, and Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Materials and Methods

Carbon Nanotube Growth:
Vertically aligned carbon nanotubes (VANTs) were grown by chemical vapor deposition (1) on Silicon substrates with ~1.5 nm Fe on 10 nm Al₂O₃ as a catalyst system. The substrates were loaded into a 1” Linderberg/Blue M Mini-Mite Tube Furnace, heated to 450 °C under 200 standard cubic centimeters per minute (sccm) nitrogen, soaked in a reducing atmosphere (hydrogen 40 sccm: nitrogen 200 sccm) for 5 minutes, and then heated to 750 °C. Ethylene (40 sccm) was introduced for 30 minutes along with 2 sccm of water saturated nitrogen. VANTs were characterized with scanning electron microscopy (SEM) conducted with a FEI Sirion XL30 SEM. The VANTs were hundreds of microns tall with average diameters of ~10 nm.

Composite Production:
To maintain the roughness necessary for the high absorptivity and superhydrophobicity, composites were prepared by contact curing PDMS (Slygard 184 Silicone Elastomer Kit) on VANT substrates preheated to 200 °C. This prevented the PDMS from fully impregnating the VANT substrate and left the bottom ends of the nanotubes exposed. The embedded forests emerge from the PDMS by ~100 µm (SI Fig. 2) and are stable to solvents and mild mechanical pressure. Surface contact angles were measured on a Krüss Model G10 goniometer at room temperature and ambient relative humidity using 18MΩ water according to the sessile drop method. Composites can be cut to any desired shape.

Alternative light absorbing materials such as homogenous carbon black-PDMS and MWNT-PDMS composites were made by thoroughly mixing the absorbing material (1-5 wt. %) with PDMS and curing at 100 °C in a box furnace for 2 hours.

Composite Testing:
Laser induced heating of composites was tested by embedding a thermocouple in the PDMS support, close to the back of the VANT. Collimated laser irradiation was used to observe the temperature change. This gave an estimate of the temperature change in air at 150 °C. This is likely a lower limit as the thermocouple was not placed directly at the interface to avoid direct heating of the probe. A temperature change as a result of the direct irradiation of the thermocouple was eliminated as no change in temperature was found when the thermocouple was placed behind, but not touching, the composite under illumination.

The composites were floated on various liquids including deionized water, brine, fluorinert® FC-75, DMF, glycerol and irradiated with either focused sunlight using a Fresnel lens (Fresnel Tech, Inc), glass lens or a near-IR diode laser (450mW B&W Tek, Inc 785-
Illumination conditions varied, though motion was typically tested with the object near the focal point and roughly 5-20 cm away. Speed tests were performed in an aluminum trough filled with the appropriate liquid. Both continuous illumination and single pulse illumination experiments were undertaken. Objects tested ranged from 20 mg to 25 g and <1 mm to multiple centimeters and showed light responses. Resulting motion was recorded using a Casio Exlim Pro EX-F1 at 30-1200 frames per second (fps). Motion typically began within 0.1 s of illumination. For heavy composites a qualitatively longer lag was observed but not quantified.

Force values were determined by evaluating the recorded motion of the composites using ImageJ software with Manual Tracking to determine the location of the object at each time point. With this location and time information Igor Pro 6.04 was used to perform the fit. To determine the force associated with constant illumination we began with the net force equation:

\[
F_{\text{net}} = F_L - Rv^2 = ma
\]

\[
R = \frac{1}{2} \rho AC_D
\]

where \(F_{\text{net}}\) is the net force, \(F_L\) is the force due to the light based modulation of the surface tension, \(m\) is the mass of the composite, \(R\) is defined from the drag equation as in (2): \(v\) is the velocity, \(a\) is the acceleration, \(\rho\) is the density of the solution, \(A\) is the displaced area, and \(C_D\) is the drag coefficient. Integrating equation 1 twice gives the location as a function of time (equation 3):

\[
X = \frac{m}{R} \log \left[ \cosh \left( \sqrt{\frac{F_L \cdot R}{m}} (t - t_0) \right) \right] + D
\]

where \(X\) is the location, and \(t_0\) and \(D\) are integration constants. A typical location vs. time plot with fit is shown in Fig. S4.

Temperature changes were calculated from the force measurements using the temperature dependence of the surface tension. For instance, the temperature dependence of the surface tension for water is \(\sim 1.8 \mu N/cm K\). If the absorber has an absorbing face of 0.2 cm and the derived force is 10 \(\mu N\), one obtains a change in temperature of \(\sim 28 K\) as shown in equation 4:

\[
\frac{10 \mu N}{1.8 \mu N/cm K \times 0.2 cm} = 28 K
\]

Control experiments:
A) Illumination of pristine (transparent) PDMS, MWNT-PDMS, and carbon black-PDMS

Pristine PDMS was found to have no response to laser illumination. MWNT (0.1, 1, and 5 wt. %)-PDMS composites were compared with a VANT-PDMS composite. All composites had masses of \(\sim 250 mg\). To control for the fact that the dispersed composites can absorb throughout the entire object, larger composites were used so the collimated laser beam would only heat the back face of the object. Forces of 1.0±0.1 \(\mu N\), 1.9±0.3 \(\mu N\), 2.2±0.3 \(\mu N\), 2.9±0.9 \(\mu N\) were obtained for 0.1, 1, 5 wt. % and VANT-PDMS composites respectively under constant, collimated illumination. It should be noted that latent heat of the objects, after testing, causes them to continue to be propelled forward. This is more obvious with the dispersed composites,
which absorb throughout the material, then with the VANT-PDMS composites. This suggests that the VANT-PDMS composites transfer heat more effectively to their surroundings than the dispersed composite.

The ability to select the face that is illuminated in order to enact control is an advantage of the dispersed composites (as described in Fig S1 and in Movie_S3). It is notable that since the absorbing material is only on one face of the VANT-PDMS composites (i.e. the back of the boat), absorption and forward propulsion can still be achieved with frontal laser irradiation, as the laser beam can pass through the transparent PDMS. This result suggests that radiation pressure from the incident light is not the dominant force.

B) Surfactant effect

To test surfactant effects on the light controlled motion of objects, VANT-PDMS composites (3 mm x 10 mm x 1 mm) were floated on water in an aluminum trough (64 cm x 3.3 cm x 1.5 cm) and irradiated with nIR laser light to verify light induced motion. Sodium dodecyl sulfate (~70 mg) was dropped onto the surface of the solution and allowed to dissolve (~0.5 min). The composite was then irradiated with nIR light. No motion was observed even under the highest focus, as shown in Figure S5. When laser light was highly focused, bubbles formed as the water locally boiled, a phenomenon not observed when in pure water. If an intermediate amount of surfactant was used (~30 mg), light induced motion was retarded but not completely eliminated for highly focused irradiation.

Solvent Comparison:

To test the effect of the liquid on the light controlled motion of objects, VANT-PDMS composites (3 mm x 10 mm x 1 mm, 36.2 mg) were floated on water, isopropyl alcohol, or DMF and the response was quantified. Small composites were used so as not to break the surface tension (particularly for the IPA) holding the object above the surface. The objects were then irradiated with nIR laser light at an angle of 45º and the motion recorded. In order to control illumination intensity, constant, collimated laser conditions with a spot size of ~4.5 mm were used. Forces were determined as described above. In water, forces of 1.19 ±0.36 µN were observed over seven measurements, error is reported as plus or minus one standard deviation. In isopropyl alcohol, forces of 0.23±0.12 µN were observed over five measurements. In DMF, forces of 0.13±0.03 µN were observed. The forces correlate to temperature changes of 2.9 ºC for the water system and 0.96 ºC for the isopropyl alcohol system. Motion was also observed on fluorinert® FC-75, brine, glycerol, or at the boundary between water and fluorinert®, but the forces were not quantified.
Supplementary Figures and Legends 1-3:

**Figure S1.** Basic scheme for the application of opto-thermal surface tension gradients to the motion of objects on liquids. Controlled linear motion can be obtained from VANT-PDMS composites or dispersed carbon black or carbon nanotube PDMS composites (center). Surface tension forces are depicted as either black arrows (unheated) or red arrows (heated and thus of diminished magnitude). Left panel, top view optical images of a dispersed MWNT-PDMS composite. Selective placement of focused light heats one region of the object, resulting in a local decrease in the surface tension. This causes the object to be pulled away from the heat. Motion can be controlled by selecting the face of the object that is heated (left top and middle), or by selecting the region of a specific face (left bottom). Further evidence is shown in supplemental videos (Movie_S2_Controlled_Linear_VNTPDMS.mov and Movie_S3_MWNTPDMS_Sunlight.mov). This principle can be extended to device design (upper right). Rotors can be made with light absorbing VANTs selectively placed on the clockwise face of each fin. When optical heating occurs, the surface tension gradients are focused near the light-absorbing material resulting in asymmetric forces and rotation, as shown here schematically and in video form in the SI (Movie_S4_Sun_Rotor.mov). The videos show both Sunlight and Laser powered motion.
Figure S2. Characteristic contact angle images for VANT-PDMS composites. Droplets quickly roll off the substrate if not attached to the needle. Contact angles are consistently >155º. Droplets bounce off the surface when dropped from a distance. Pinning only occurs at defect sites.

Figure S3. Depicts the motion induced by the continuous irradiation of a VANT-PDMS composite with 450 mW of 785 nm laser light. The location data and fit with fit parameters are shown. For the fit, m is in grams, R is in grams/cm, t₀ is in seconds, Fl is in 10 µN, and C is in cm. In this case, the force on the object was roughly 16.5 µN.
Supplemental Movies:

**Movie_S1_Linear_Motion.mov**: Linear motion of a VANT-PDMS object floating on water under laser irradiation. Motion begins slowly and speeds up as the composite approaches the focal point of the laser. After passing through the focal point illumination is terminated.

**Movie_S2_Controlled_Linear_VNTPDMS.mov**: Controlled linear motion of a VANT-PDMS object floating on water under constant laser irradiation. Object is controllably moved to the right, turned around in a circle, and then moved to the left.

**Movie_S3_MWNTPDMS_Sunlight.mov**: Sunlight controlled motion of a dispersed MWNT-PDMS composite floating on water. Object is moved from left to right and then back again using a simple glass lens.

**Movie_S4_Sun_Rotor.mov**: Sunlight powered VANT-PDMS rotor. Rotor starts at rest and when illuminated with focused sunlight speeds up to ~70 rpm.