Electronic Supplementary Material (ESI) for Soft Matter.

Supplementary Information

Magnetic Propulsion of Colloidal Microrollers controlled by Electrically Modulated Friction

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Content:

Supplementary Text

Programmable motion and cargo transport mechanism

Sedimented, magnetically-responsive Janus colloids were made to roll, and thereby translate, through the application of a rotating magnetic field (see sketch in Figure S1a). Various forces act on a rolling colloid with radius R that moves at speed V and angular velocity ω (the surface velocity is V_ω): the load L, the normal force N, the hydrodynamic drag F_d and the translational friction force F_f (Figure S1b). The direction of the moving colloidal particle can be controlled by changing the axis of the rotating magnetic field, which allows us to program the path that the particle undertakes on top of the substrate (Figure S1c). Such programmability is illustrated by overlaying time lapse images of a particle that was magnetically manipulated to first roll in one specific direction and then make a 90° turn, forming a pre-defined L-shaped path.

Translational motion of the Janus colloid powered by a rotating magnetic field can be employed to trap, transport and release other cargo colloids from one place to another if dipolar attractive interactions are created between the Janus microroller and the dielectric cargo particles[23]. To induce such dipolar interactions, the Janus and cargo colloids are placed between transparent ITO electrodes and are subjected to an external alternating electric field (Figure S1d). Under an alternating electric field at 1 MHz, a positive dipole is induced at the metallic side of the Janus particle, while the polystyrene cargo develops a negative electric dipole[53]. This favors an attractive arrangement between the induced dipoles. The possibility to electrically manipulate the attractive dipolar interactions between the metallic side of the Janus colloid and the cargo colloid allows for the reversible trapping and release of cargo on-demand (Figure S1e). The attractive dipolar interactions induced by the applied electric field enables loading of the model cargo particles predominantly at the metallic half of the Janus colloid (Figure S1f). Provided that the field is on, such attractive interactions are sufficiently strong to hold the cargo on the Janus microroller as it moves across the substrate under the propelling action of the rotating magnetic field (Figure S1g and Movie S1).

Interactions between Janus colloid and substrate

The Janus colloid and the substrate may interact through gravitational, van der Waals, hydrophobic and electrostatic forces. Our colloid-substrate system was experimentally tuned to ensure that the particles are not fully stuck to the substrate, allowing them to still roll and thereby translate. Presumably, this is caused by repulsive electrostatic interactions that compensate for the attractive van der Waals and gravitational forces. Electrostatic interactions in water depend on the isoelectric point (IEP) of the material, which corresponds to the pH at which the surface exhibits zero net electric charge. At pHs lower (higher) than the IEP the surface charge becomes predominantly positive (negative). Assuming IEP values of 2, 6 and 12 for silica, ITO and MgO, respectively, one should expect repulsive electrostatic interactions between the ITO substrate and the MgO hemisphere of the

Janus particle at the pH of 5 of the aqueous medium. Conversely, attractive forces should dominate the interactions between the oppositely charged ITO substrate and the silica hemisphere of the Janus colloid at this pH. We experimentally observed that if the Janus particle is not covered by the MgO hemisphere layer, it sticks strongly to the ITO substrate. By contrast, covering one hemisphere of the particle with the MgO layer leads to repulsive electrostatic forces, which lifts the particle away from the surface and enables motion. To minimize hydrophobic interactions we intentionally added a polysorbate-type non-ionic surfactant (Tween 20) to the aqueous solution.

Goldman derivation and height estimation

In the hydrodynamic coupling regime described by Goldman *et al.*[24], Eq. (1) from the main text can be derived by utilizing expressions 2.65a,b and 3.13a,b from the cited work and subsequently solving for 4.1a,b using these expressions. This is shown in the Mathematica notebook that accompanies this publication. The above expression may also be inverted to estimate the height of the colloid above the substrate, also displayed in the accompanying Mathematica notebook. This was used to estimate the height of the particle in Figure 2f.

Estimation of dipolar interactions

The repulsive force between the colloid and the substrate in experiments performed in the flipped electrode configuration (Figure 2d) can be estimated from electrically induced dipolar interactions. The dipolar force F_{dipole} between two dipoles A and B under an electric field E is given by[54]:

$$F_{dipole} = \frac{4Re\left(\alpha_A^* \alpha_B\right)E^2}{3\epsilon_0 \epsilon_s d^4} \quad \text{(Eq. S1)}$$

where Re is the real component, the star indicates the complex conjugate, d is the separation between the dipoles, ϵ_s the polarizability of the medium. The polarizability can be calculated from the relation: $\alpha = 4\pi\epsilon_0\epsilon_s K R^3$, where K is the complex dipole coefficient (not to be confused with our parameter K for the friction) and R is the particle radius. Taking $d = 2R$, $R = 2.3 \times 10^{-6}$ m, $E = 0.015$ V/μm, and assuming $K = 1$ for metals and $K = 0.5$ for silica, we estimate the electrically induced repulsive force to be 11 pN. This force increases to 79 pN for $E = 0.04$ V/μm, which is the maximum electric field applied in this experiment.

Estimation of osmotic pressure

The osmotic pressure (P) generated by colloidal shuttling dye-laden cargo particles between two sides of a fluidic chip was estimated using Van't Hoff's equation:

$$P = nRT, \quad \text{(Eq. S2)}$$

where n is the molar concentration of excess solute, R is the universal gas constant (8.314 J/mol.K) and T is the absolute temperature. The molar concentration of dye molecules at one end of the chip after 7 sequential shuttling events was calculated using the following relation:

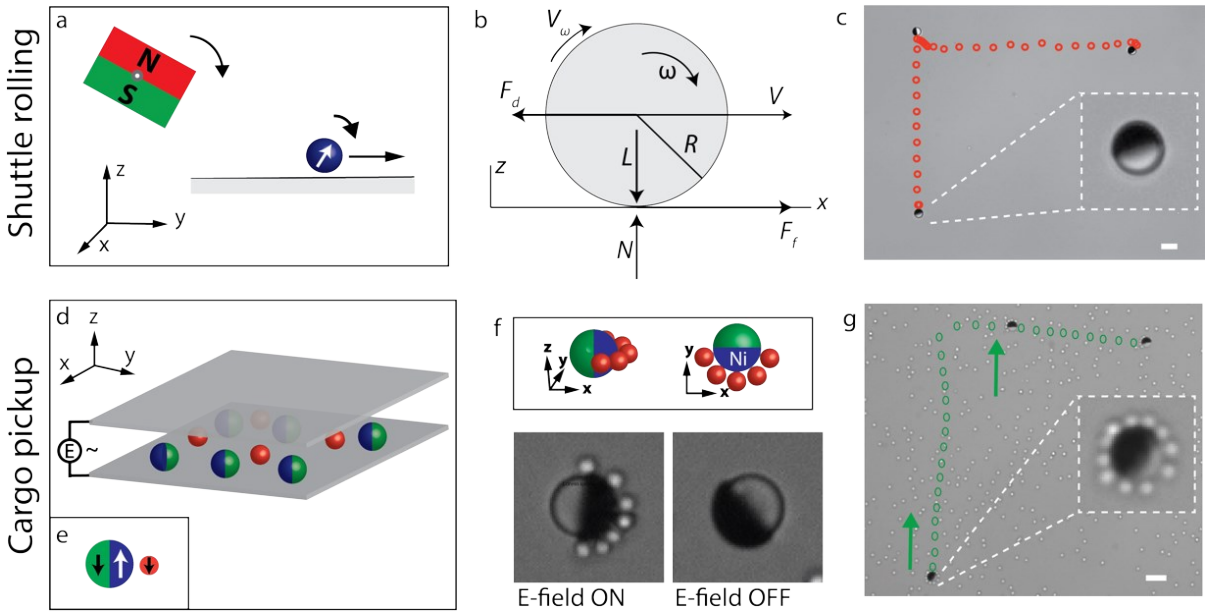
$$n = \frac{4\pi N \rho_{cargo} r_{cargo}^{3} \chi \Delta}{3 M_{dye}}, \qquad \text{(Eq. S3)}$$

where N is the difference in number of particles between the two sides of the chip, ρ_{cargo} is the specific gravity of the cargo particle, r_{cargo} is the radius of the cargo particle, χ is the dye loading in terms of mass of dye relative to the mass of cargo particles, Δ is the volume of half of the chip compartment and M_{dye} is the molar mass of the dye molecule. Assuming $N = 60$, $\rho_{cargo} = 1.1\ g/cm^3$, $r_{cargo} = 1\ \mu m$, $\chi = 0.1$, $\Delta = 10^{-9} L$ and $M_{dye} = 479\ g/mol$, we estimate the osmotic pressure to be approximately 0.144 J/L or 144 Pa at room temperature (T = 300 K). If this osmotic pressure were used to raise a column of water, the level of water vertically displaced would be approximately 1.5 mm. For this calculation, the water displacement (d) was estimated using the following relation for the hydrostatic pressure (P_h):

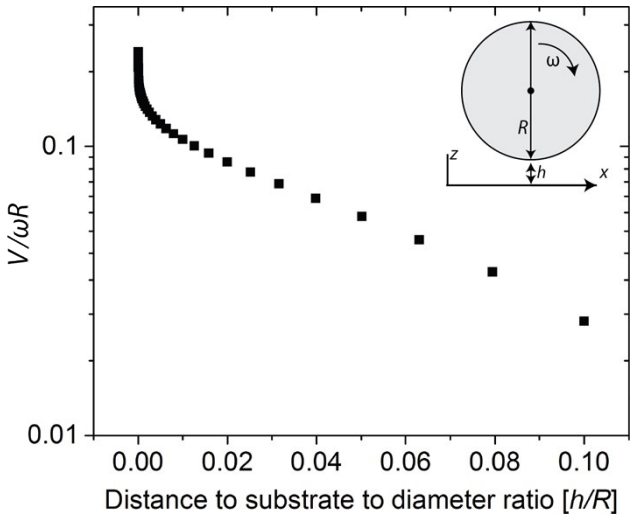
$$P_h = \rho_w g d, \qquad \text{(Eq. S4)}$$

where ρ_w is the specific gravity of water and g is the gravitational acceleration constant (9.81 m/s^2). This calculation assumes an effective release of the molecular dye from the mesoporous silica into the suspending medium. This hypothetical scenario is meant to show the potential of such a cargo-transport mechanism to generate work.

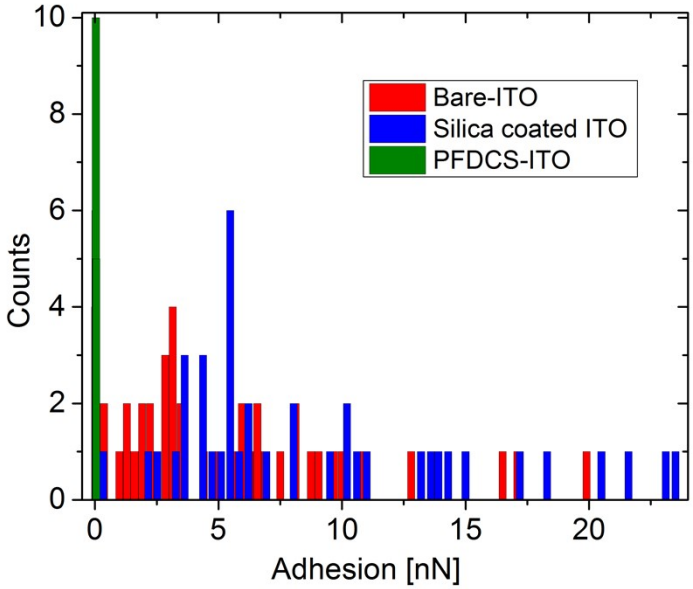
Supplementary Figures



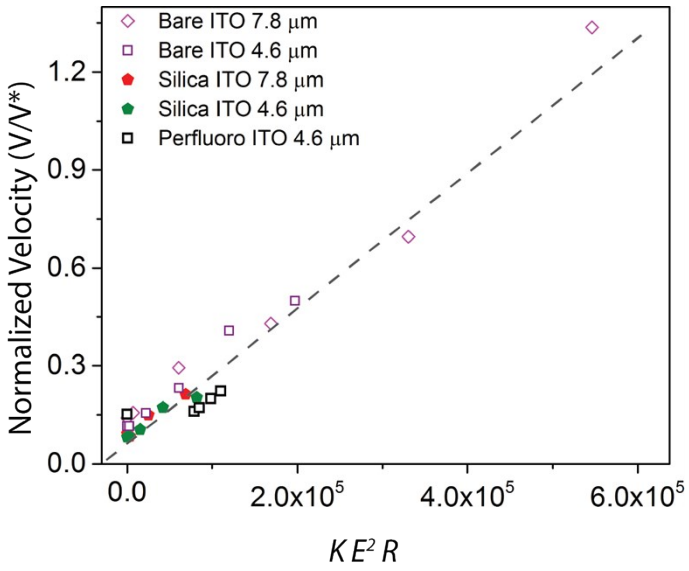
Supplementary Figure S1: Manipulation of a colloidal microroller under orthogonal magnetic and electric fields. (a) Setup used for rolling the magnetically responsive Janus colloid under a rotating magnetic field. (b) Schematics of the forces acting on the Janus colloid during rolling. The nomenclature utilized in this diagram is described in the main text. (c) Programmed motion of a Janus colloid along a pre-defined L-shaped track. Motion of the Janus particle is controlled by turning the axis of the rotating magnet. (d) Setup used to apply an electric field to the liquid phase containing sedimented Janus and cargo colloids. (e) Sketch of the expected electric polarization of the Janus particle under an external electric field, indicating the dipoles formed in the metallodielectric Janus colloid and in the polystyrene colloid used as cargo. The anti-parallel orientation of electrically induced dipoles in the cargo and in the metallic (blue) side of the Janus particle results in attractive forces that hold the cargo (red) around the Janus particle. (f) Sketch illustrating the formation of assemblies of Janus and cargo colloids arising from electrically induced dipolar interactions. These interactions are fully reversible and can be used to trap and transport the cargo colloids when the electric field is applied and to release them when the field is turned off. (g) When a Janus particle is rolled along a pre-defined track in the presence of cargo colloids and an electric field, it carries the cargo particles along and delivers them as soon as the field is turned off. All scale bars are 5 μm.



Supplementary Figure S2. Micro-roller in the wet friction lubrication regime. Theoretical prediction of the translational velocity of a rolling particle, V, as a function of its distance to a solid substrate, h, in the lubrication regime[24]. The symbols ω and R represent the rotational velocity and the radius of the particle, respectively.



Supplementary Figure S3. Adhesion forces of metal-coated silica particle on bare ITO, silica-coated and perfluorinated (PFDCS) ITO surfaces measured by colloidal probe AFM. The graph displays the distribution of adhesion forces obtained from multiple measurements in air.



Supplementary Figure S4. Generalized description of the rolling Janus particles under an electric field. Master plot illustrating the linear scaling of the normalized velocity data with a physically relevant term KE^2R including the data obtained for the perfluoro-coated ITO sample (black squares).

Table S1. Gravitational length and buoyant-mass calculations for the investigated Janus colloids.

Size of colloid [μm]	2.4	4.6	6.1	6.7	7.8
Gravitational length [nm]	8	2	1	0.8	0.6
Buoyant mass [kg]	5×10^{-14}	2×10^{-13}	4×10^{-13}	5×10^{-13}	7×10^{-13}

The buoyant mass of the colloid was estimated with the following formula; $M_B = g\Delta\rho V_p$, where *g* is the standard gravity, $\Delta\rho$ is the buoyant density and V_p is the particle volume. The buoyant density is given by: $\Delta\rho = \rho_p - \rho_w$, where ρ_p and ρ_w are the densities of the particle and of the dispersing medium (water in our case), respectively. The gravitational length is estimated using the following formula: $l_g = \frac{k_B T}{g\Delta\rho V_p}$, where k_B is the Boltzmann constant and T is the temperature.

Supplementary Movies

Movie S1 demonstrates the programmed colloidal cargo transport via electrically induced dipolar interactions between the cargo and the Janus microrobot. The Janus particle moves together with its cargo in an L-shaped path and delivers the cargo upon turn-off of the electric field.

Movie S2 demonstrates the motion of the Janus particle in the absence of an applied electric field.

Movie S3 displays the motion of the Janus particle in the presence of an applied electric field.

Movie S4 shows the pick-and-place cycle used to transport cargo colloids between two sides of the chip, thus creating a gradient in the local concentration of chemical species.