Supporting information

Synthesis of conducting asymmetric hydrogel particles showing autonomous motion

Anandi Srinivasan, Jérome Roche, Valérie Ravaine, Alexander Kuhn*

Université de Bordeaux, ISM, UMR 5255, ENSCBP, 16 Pey Berland, 33607 Pessac, France.

Experimental Section

a) Materials

Aniline monomer (ACS reagent ≥ 99.5 %), ammonium persulfate (ACS reagent ≥ 98%), hydrochloric acid (37 w %), low molecular weight sodium alginate, calcium chloride and ethanol solvent were purchased from Sigma-Aldrich and were of analytical grade. All aqueous solutions were prepared using Milli-Q water (Millipore, resistivity 18.2 M Ω·cm at 25°C).

b) Bipolar modification on electroconductive PANi-alg beads

Asymmetric modifications were performed at room temperature, in a polypropylene electrochemical cell with a distance of 1.5 cm between the feeder electrodes and the electroconductive PANi-alg beads positioned in between. The feeder electrodes were platinum and gold plates for anode and cathode respectively. The cell was filled with 1 mM NH_4Cl ethanol solution and the electric field was applied using a DC power supply. The choice of medium for the bipolar electrochemistry is due to the fact that we want to prevent solvent exchange during the exposure to the electric field. As the final beads need to be loaded with ethanol for the motion it is convenient to use ethanol also during this step. NH_4Cl is used as an electrolyte soluble in ethanol in order to allow current to flow. A potential of 100V has been applied between the two feeder electrodes, corresponding to an electric field

of 66V/cm when taking into account the distance between them. Application of the electric field was between 5min and 30min, depending on the needed progress of oxidation.

c) Measurement of ethanol release from modified a PANi-alg gel

Concentration of ethanol release from the oxidized and reduced side of modified conductive hydrogels was measured using UV-Vis spectrophotometer. A special configuration was designed for this purpose. Polyaniline–alginate conductive hydrogel was formed inside a 2 cm long glass capillary, loaded with a solution of ethanol /food dye (E-124) for one hour, and modified by the bipolar electrochemical route as described in the manuscript. The dye loaded capillary was then placed inside the cell containing two compartments filled with equal volumes of water as shown in Figure S1(a). The dye release is initiated instantaneously when both ends of the capillary come in contact with the water. Samples were collected from both compartments after one minute and UV absorption spectra were obtained with a Varian CARY 100, double beam UV–visible spectrophotometer. All measurements were carried out using 1 cm glass cuvettes.
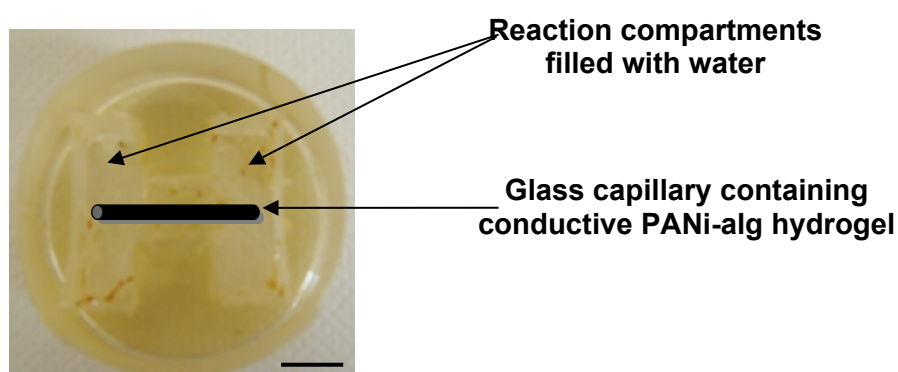

Figure S1: Control experiment where food dye is mixed with ethanol to quantify its release from both ends of the modified conductive hydrogel contained inside the capillary. Schematic top-view of the experimental setup. Scale bar = 1 cm.
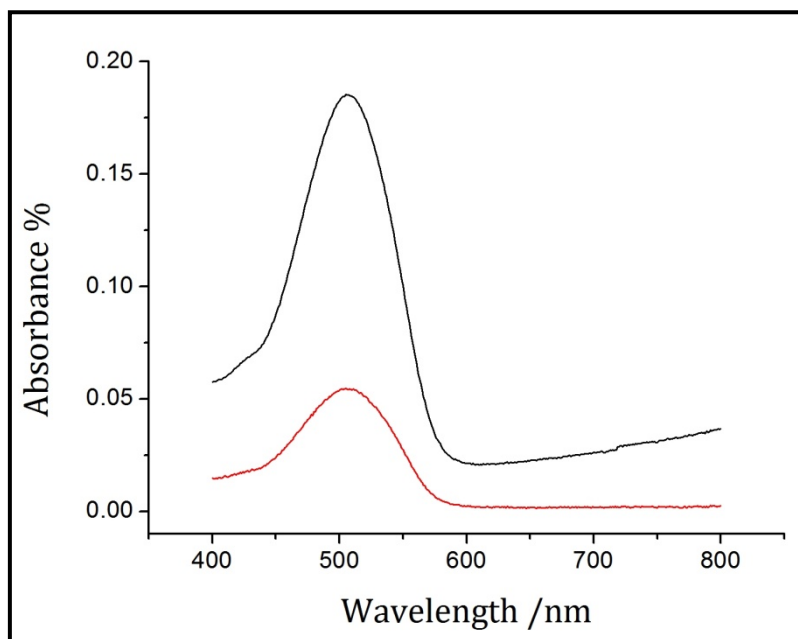
Figure S2: The concentration of released dye from the oxidised and reduced side of the capillary filled with conductive hydrogel was measured using UV-Vis spectrophotometer. The black line indicates dye release from the oxidized side whereas the red curve has been measured in the solution collected from the reduced end. The absorbance curves show a 3.5 times higher concentration of released dye from the oxidized end.

d) Recording of pulsating bead motion

In order to evaluate the effect of oxidation on the self-propelling behavior, we characterized in the case of the pulsating motion the relationship between the waiting time (time between the two consecutive jumps) and the distance travelled by these beads in each jump as a function of time. The study was performed with beads having the same amount of ethanol loading, but different oxidation times (b5 and b15 denotes beads oxidized for 5 and 15 min respectively). The following conclusions were drawn from the aforementioned study. The b15 type beads initially travel a longer distances (~2cm) during every jump, which decreases gradually with time; also the waiting period of the b15 type beads, which was initially quite short, increased considerably later on due to the depletion of ethanol inside the beads. A similar trend was also observed for b5 beads, but the absolute values are significantly different as summarized in Figure S3.
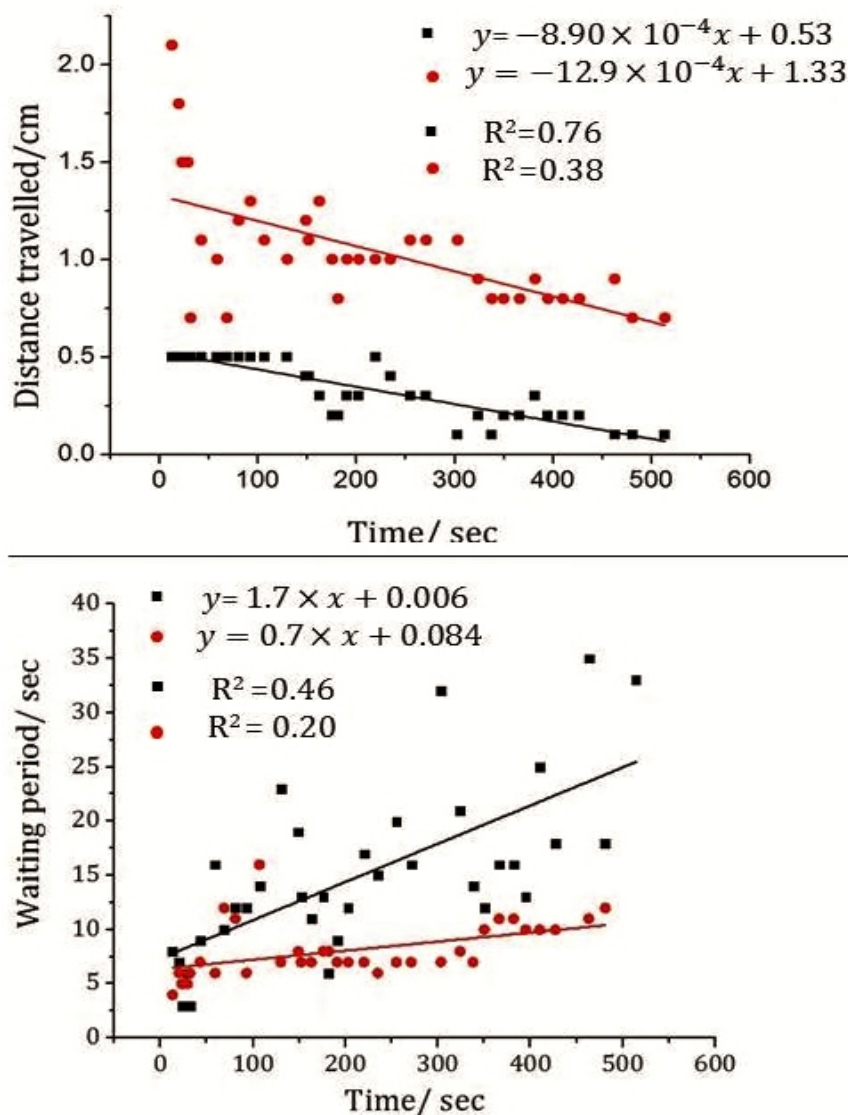
Figure S3: Experimental data of the variation as a function of time of the (a) distance travelled during each pulse and (b) the waiting period. The measurement was performed with beads having the same amount of ethanol loading but different oxidation times. (Black maker represents a bead oxidized for 5 min while the red maker stands for 15 min oxidation).

Motion of the modified beads was recorded with a Sony DSC-F828 digital camera. The paper marked with 0.5 cm X 0.5 cm square patterns was placed underneath the Petri dish to allow a better reading of the location of the beads.

e) Theoretical estimation of characteristic time of motion

Velev *et al.* [5] developed a model in order to calculate the release rate of ethanol from their Marangoni effect based self-propelled hydrogel object at the water/air interface. More specifically, the quantities of ethanol released between each motion pulse as well as the pulse intervals were calculated. Taking into account an average value of those parameters and the surface of the particle involved in this mass transfer, one can calculate an average ethanol

flow density released from the particles. The following equation describes the value of this average flow density using the formalism by Velev *et al.*:

$$J^* = \frac{\Delta Q^*}{\Delta t^* S}$$

J* is the average exchange flow density (g.cm^{-2}.s^{-1}), ΔQ^* is the average quantity of ethanol released between two pulses (6.10^{-7} g), Δt^* is the average pulse interval (3 s) and S is the ethanol exchange surface (7.85.10^{-3} cm^{-2}). The * exponent describes an average value instead of a discrete one.

In order to apply this formalism to the average ethanol exchange flow density of the present system, the following assumptions had to be made due to the high complexity of the system:

-ethanol is released homogeneously through half of the sphere surface, corresponding to the oxidized part of the bead.

-the present hydrogel releases ethanol with a rate of comparable order of magnitude with respect to the one reported in the literature

-initially, the ethanol content of the bead is considered to be 100%.

Under those conditions, one can calculate a rough estimation for the time necessary for the ethanol to entirely diffuse out of the bead in a zero concentration bath with the same average exchange flow density. This estimated value is 3100 s and is in good agreement with the experimentally observed time scale of motion.

f) Measurements of contact angle

Contact angle measurements were carried out using a KSV CAM 200 goniometer (KSV Instruments). The Janus particle was deposited on a planar substrate, either glass or plastic. The equatorial plane separating the two hemispheres was oriented perpendicular to the substrate, facing the camera. Each side of the particle thus corresponded to each hemisphere. A drop of water having various volumes below 100 µL, was deposited carefully at the foot of the particle to create different heights of immersion. The particle and the drop were imaged using a planar CCD camera combined with LED based background lightning. No significant differences in contact angle could be observed between the right and left side of the particle. Slight apparent deviations from a complete symmetric wetting behavior are due to irregularities in the shape of the particle.
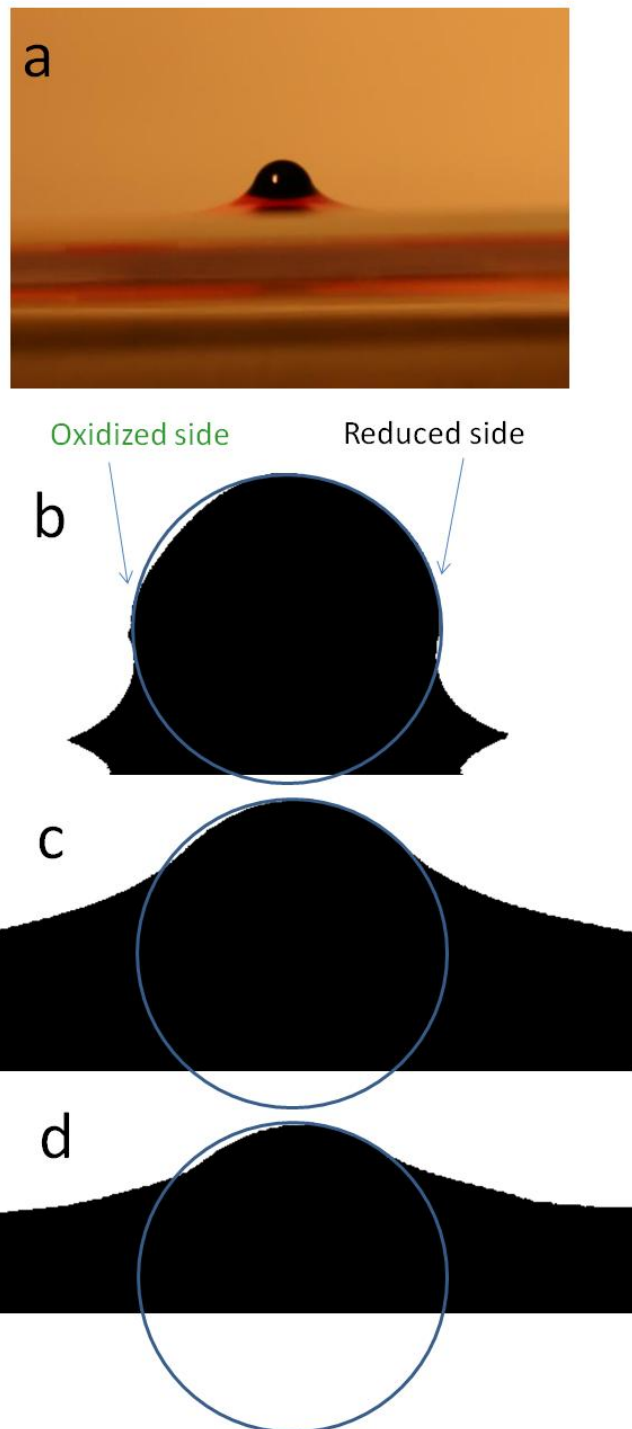
Figure S4: Images obtained during the contact angle measurements. a) Front light illumination b)-d) background illumination for a bead sitting in a water film with increasing thickness.

Video 1: Continuous motion of PANi-alg beads

Video 1 displays the continuous motion of an electroconductive PANi-alg bead loaded with ethanol for 30 min and oxidized for 10 min.

Video 2: Pulsating motion

Video 2 illustrates the pulsating motion of a bead with 10 min of ethanol loading and 10 min oxidation.

Video 3:   Control experiment to trace the asymmetric release of ethanol.

The movie illustrates the selective asymmetric release of ethanol at the oxidized end of the modified PANi-alg bead. Fluorescein dye is mixed with ethanol during the modification step. The movie is recorded with an epifluorescence microscope with 2X magnification and gain =1. The movie is accelerated four times.

Video 4: Whirling motion

Video 4 represents the case of an unmodified bead loaded with ethanol for 30 min. Such beads exhibit whirling motion for very short duration (2 min). The movie is speed up by a factor 2.