

Asymmetry controlled dynamic behavior of autonomous chemiluminescent Janus microswimmers

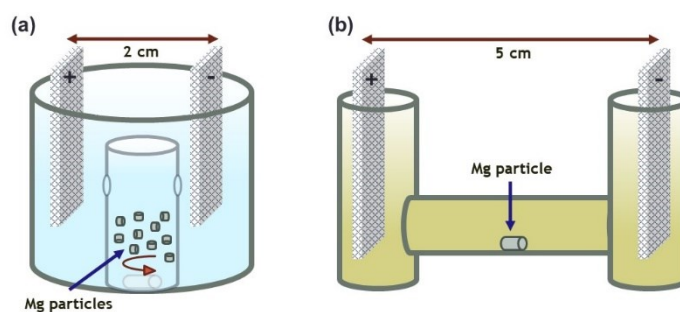
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Experimental details

H_2SO_4 (J. T. Baker, 95-97%), absolute ethanol (Aldrich, $\geq 99.8\%$), Resydrol AY498w/35WA electrophoretic paint (EP) (Cytech Austria GmbH), $\text{K}_2\text{S}_2\text{O}_8$ (Fluka, $> 98\%$), Tris(2,2'-bipyridine) ruthenium (II) hexafluorophosphate (Aldrich, 97%), magnesium wire ($d = 0.5\text{ mm}$) and anhydrous acetonitrile (ACN, Aldrich, 99.9%) were used. All solutions were prepared with deionized water (MilliQ Direct-Q[®], resistivity $18.2\text{ M}\Omega\cdot\text{cm}$ at 25°C). The bipolar electrochemistry (BP) experiments were performed with an elc[®] power supply (30 V, 2 A) by using two platinum meshes as feeder electrodes. Homemade BP cells were used for the bipolar electromilling and the asymmetric modification (Scheme S1). The EP was diluted ten times with deionized water prior to use. The Mg wire was cut using a surgical scalpel. The precise length of the Mg particles was measured by using a microscope (LEICA Z16 APO) and the average length is presented. The swimmers were placed at the solution/air interface at the center of a glass crystallizer of 7 cm in diameter. Trajectories were monitored by using a CCD camera (CANON EOS 70D, Objective Canon Macro Lens 100 mm 1:2.8). Images and videos (AVI encoding) were processed with Image J software and finally converted to MP4 format. Each video can be summarized as an accumulation of frames, resulting in a stack projection. The time projection of the maximum light intensity of each video is presented in order to correlate motion with light intensity emitted by the Janus swimmer. A lookup table (Fire LUT) was used to improve the changes of light intensity.



Scheme S1. Schematic illustration of the BP cells used; (a) bipolar electromilling of 20 Mg particles in 5 mM H_2SO_4 /ethanol solution, positioned inside a cylindrical membrane in order to avoid direct contact of the particles with the feeder electrodes during stirring and (b) asymmetric modification of an individual Mg particle in an electrophoretic paint/water solution (1:10).

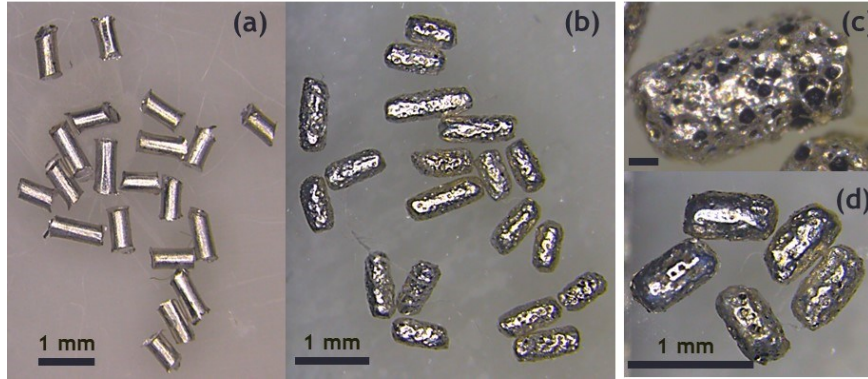


Figure S1. Optical pictures of Mg wires with an initial length of 1.2 ± 0.1 mm (a) before and (b) after 40 hrs of electrolysis in 5 mM H_2SO_4 /ethanol solution at constant $\mathcal{E} = 15 \text{ V cm}^{-1}$. (c) Close-up of Mg particles after 40 hrs of electrolysis; scale bar 0.1 mm. (d) Optical picture of selected Mg particles with a final average length of 0.65 ± 0.04 mm.

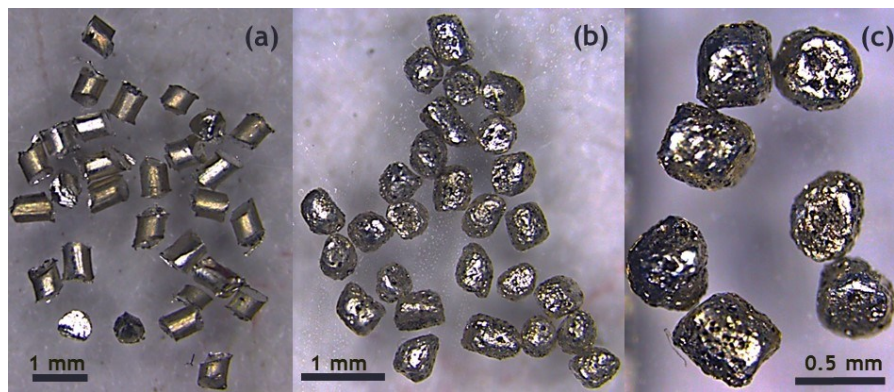


Figure S2. Optical pictures of Mg particles with an initial length of 0.6 ± 0.1 mm (a) before milling with an anisotropic shape (b) after 40 hrs of bipolar electrolysis a 5 mM H_2SO_4 /ethanol solution at constant $\mathcal{E} = 15 \text{ V cm}^{-1}$. (c) Optical picture of selected isotropic Mg particles with a final average diameter of 0.48 ± 0.04 mm.

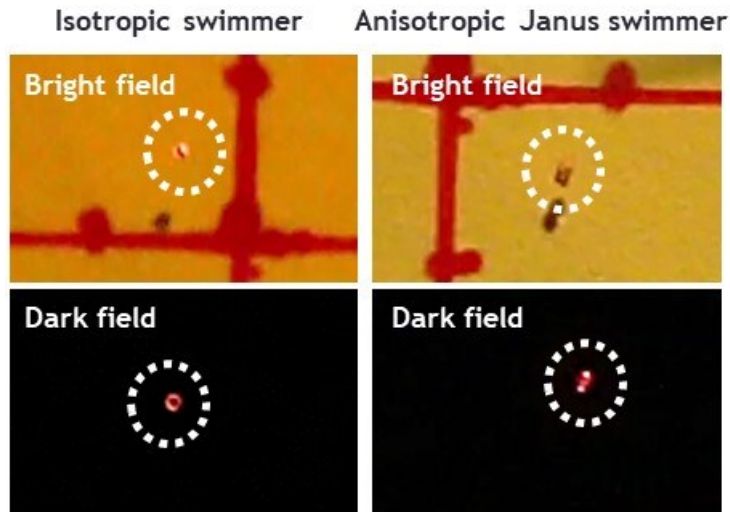


Figure S3. Frame in the bright (top) and dark field (bottom) of an isotropic swimmer and an anisotropic Mg/EP Janus swimmer at the surface of a 1 mM $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$, 20 mM $\text{K}_2\text{S}_2\text{O}_8$, 20 mM H_2SO_4 in $\text{H}_2\text{O}/\text{ACN}$ (1/1) solution. In the bright light view one can clearly distinguish the different shapes (spherical vs. rod like). The shadow (brown spot slightly below-left of the swimmers) also illustrates this difference in shape. After switching off the light, the difference in symmetry can still be observed via the CL emission and they start an erratic motion for the left one (see video S3) and a linear motion for the right one (see video S1).

Video S1. Anisotropic Mg/EP Janus swimmer moving at the surface of a 1 mM $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$, 20 mM $\text{K}_2\text{S}_2\text{O}_8$, 20 mM H_2SO_4 in $\text{H}_2\text{O}/\text{ACN}$ (1:1) solution.

Video S2. Isotropic Mg/EP Janus swimmer moving at the surface of a 1 mM $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$, 20 mM $\text{K}_2\text{S}_2\text{O}_8$, 20 mM H_2SO_4 in $\text{H}_2\text{O}/\text{ACN}$ (1:1) solution.

Video S3. Fully isotropic Mg particle moving at the surface of a 1 mM $\text{Ru}(\text{bpy})_3(\text{PF}_6)_2$, 20 mM $\text{K}_2\text{S}_2\text{O}_8$, 20 mM H_2SO_4 in $\text{H}_2\text{O}/\text{ACN}$ (1:1) solution.