

Supporting Information for

Bio-templated Hybrid Microrobots for Enhanced Photocatalytic Water Remediation under Continuous Magnetic Propulsion

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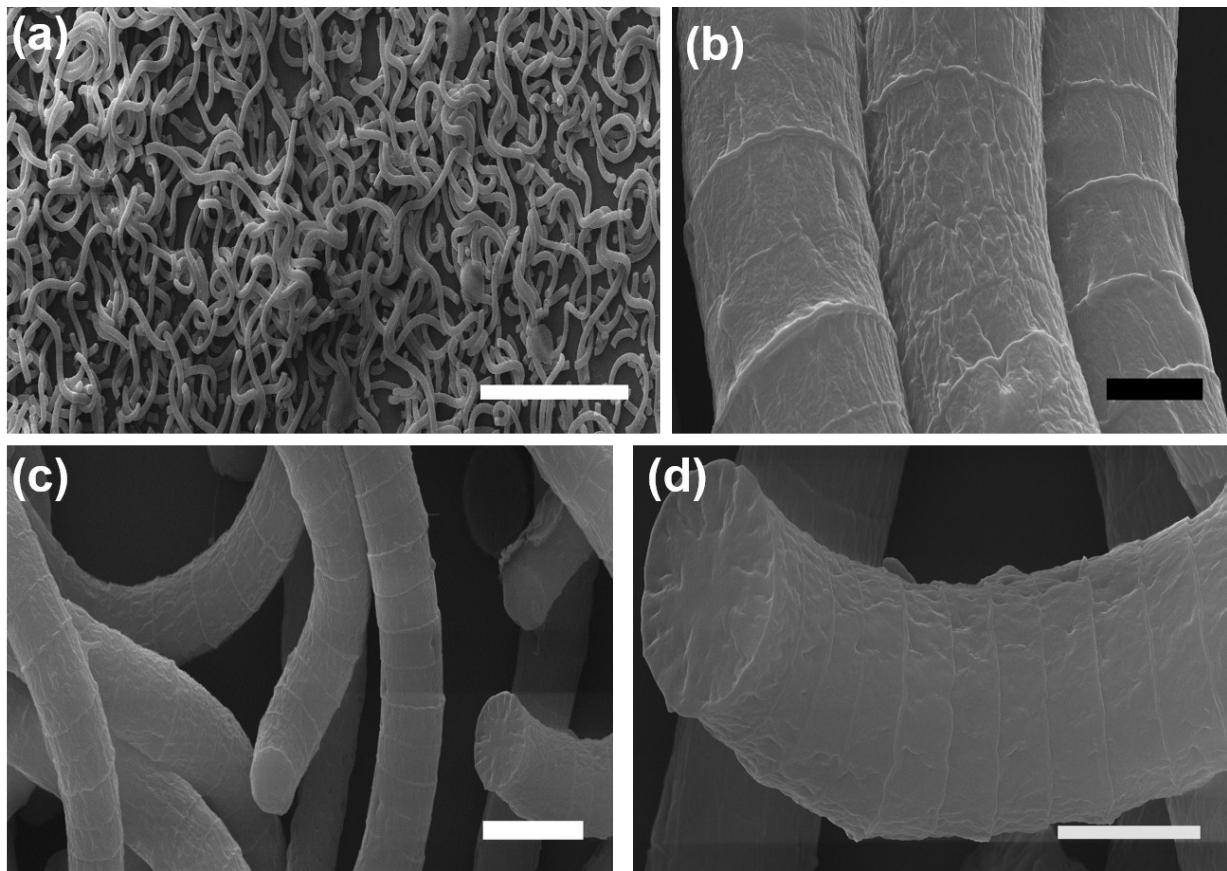


Figure S1: SEM images of helical *Spirulina platensis* bio-template. (a) SEM image showing many overlapping, helical bio-templates. (b-d) SEM images showing a magnified view of the bio-template, clearly depicting the presence of many circular ridges and a rough morphology. Scale bars: (a) 150 μm , (b) 3 μm , (c) 10 μm and (d) 5 μm .

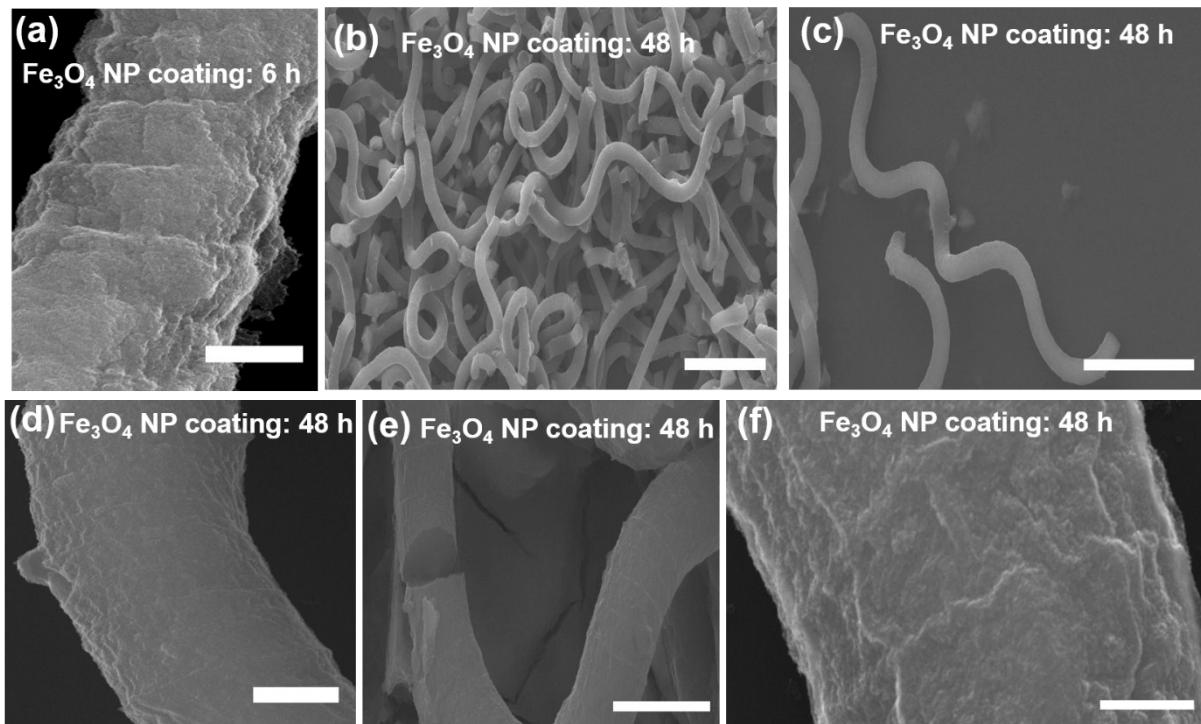


Figure S2: SEM images of Fe₃O₄ NP coated helical bio-templates (a) after 6 hours of coating showing a rough morphology as seen in the bare bio-template. (b-f) SEM images of bio-templates coated for 48 h showing a smooth morphology and even coating of NPs on the helical bio-template. Scale bars: (a) 3 μm , (b)-(c) 40 μm , (d) 4 μm , (e) 10 μm and (f) 1 μm .

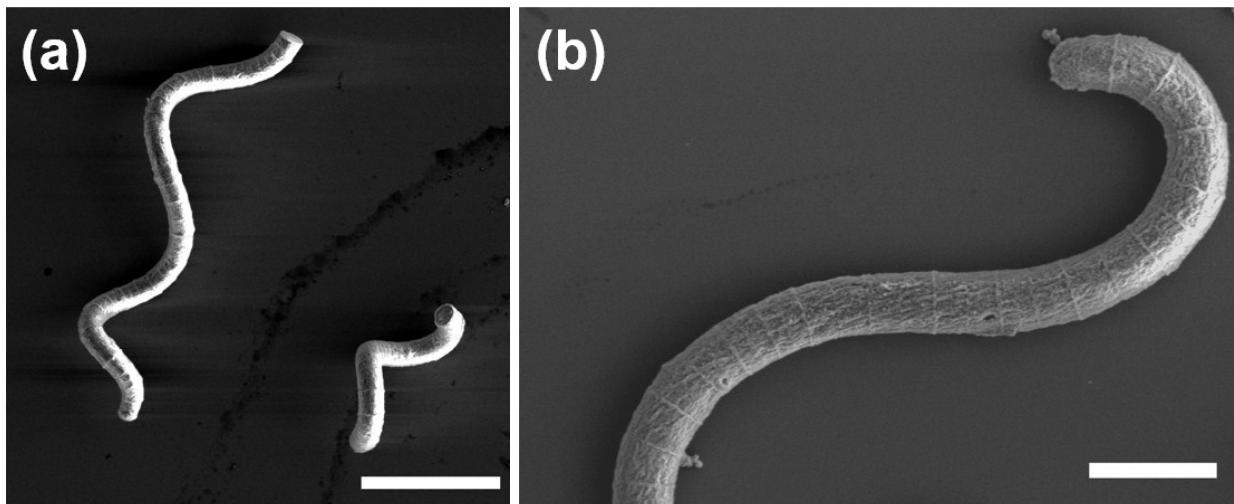


Figure S3: (a,b) SEM images of Fe₃O₄@TiO_x helical bio-templates before annealing showing a uniform coating of the templates with TiO₂. Scale bars: (a) 30 μm and (b) 10 μm .

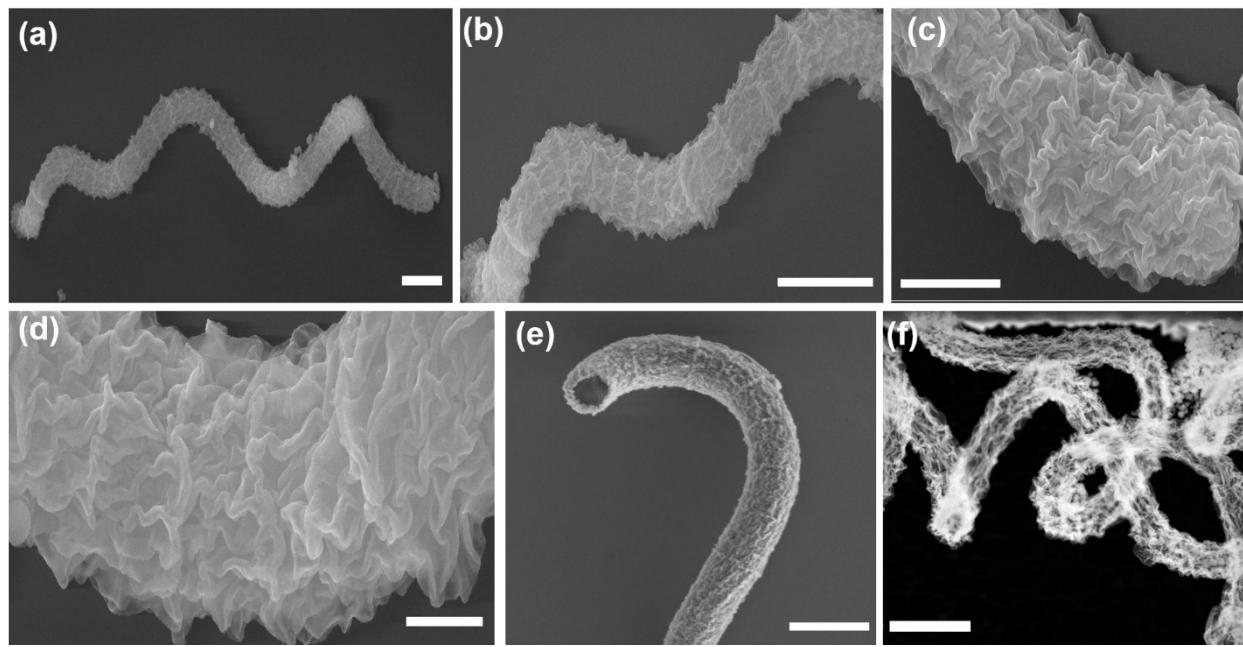


Figure S4: SEM images of annealed hybrid $\text{Fe}_3\text{O}_4@\text{TiO}_2$ helical bio-templates showing (a, b) that they still retained their helical shape, even after removal of the bio-template. (c, d) SEM images showing a dramatic change in their smooth morphology post-annealing, which is replaced by a very rough surface and (e, f) SEM and TEM images showing development of hollow micro-structures post-annealing. Scale bars: (a) 5 μm , (b) 5 μm , (c) 2 μm , (d) 1 μm , (e) and (f) 5 μm .

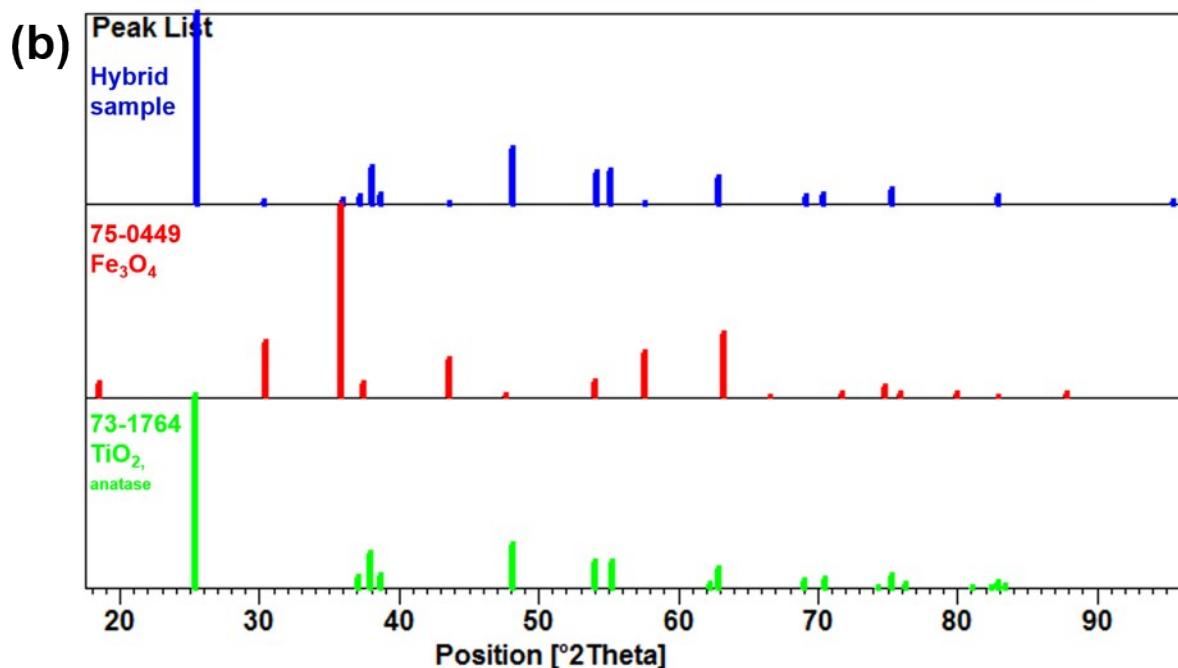
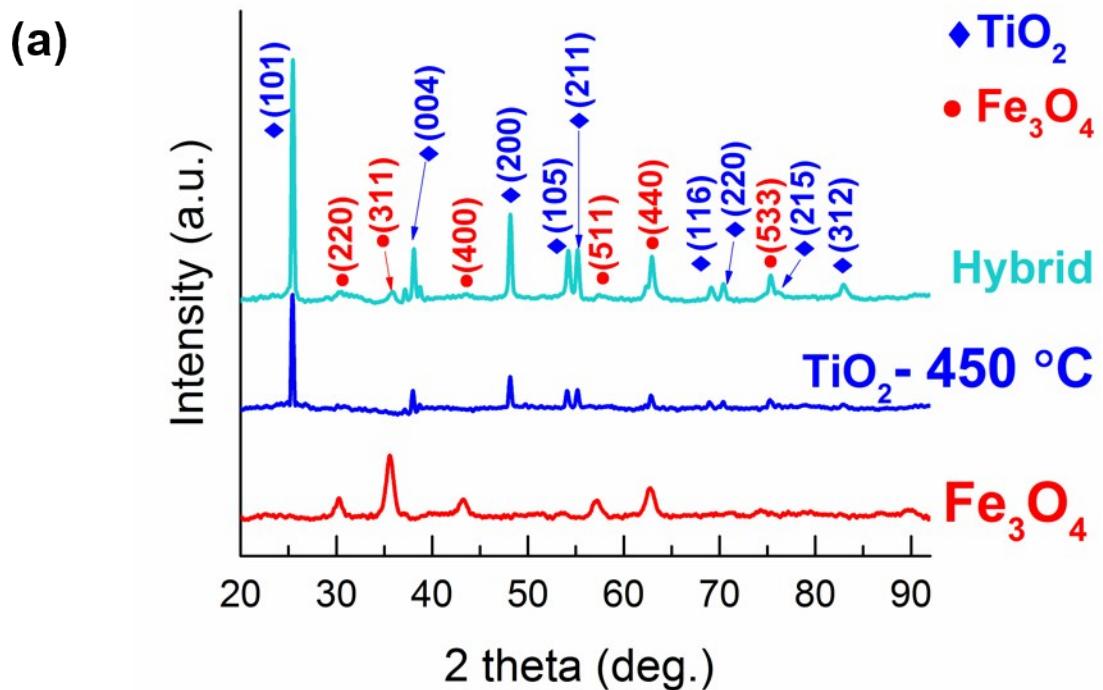


Figure S5: (a) XRD analysis of bio-templates coated with Fe_3O_4 NPs, with TiO_2 and annealed and the hybrid micro-structures after annealing. (b) XRD patterns of hybrid sample and its comparison with the JCPDS patterns of Fe_3O_4 (75-0449) and anatase TiO_2 (73-1764).

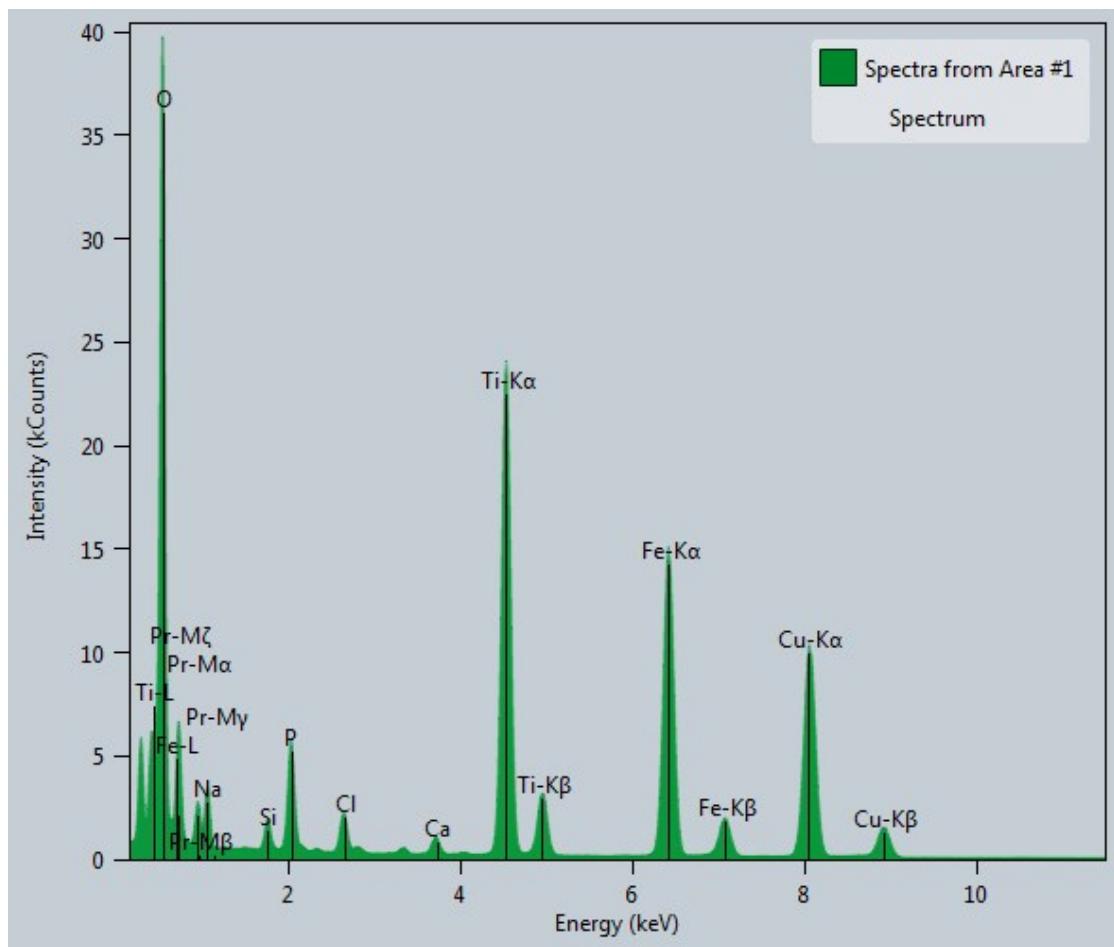


Figure S6: EDX spectrum obtained from hybrid micro-structures after annealing clearly show the presence of peaks arising from Ti, O and Fe.

Architecture/ Composition	Light source	[Pollutant]/ [photocatalyst] (g / g)	k-value (min⁻¹)	Ref
TiO ₂ -Fe ₃ O ₄ microhelices	450 W 300 nm < λ < 600	0.01 Rhodamine B	0.047	This work
Ni/PtPd/TiO ₂ coaxial nanotubes	450 W, λ > 420 nm,	0.006 Rhodamine B, Methyl Orange Methylene blue	0.0074 (TiO ₂ NTs) 0.071 (TiO ₂ -PtPd NTs)	¹
BiOCl-Bi ₂ O ₃ micropillars	400 W λ > 400 nm	0.004 Rhodamine B	0.009	²
TiO ₂ -Fe ₃ O ₄ particles	36 W, λ < 400 nm	0.04 Phenol	0.025	³
TiO ₂ -Fe ₃ O ₄ particles	Xenon lamp, 400 W λ > 420 nm	0.02 RhB	0.001 (P25) 0.014 (TiO ₂ -Fe ₃ O ₄)	⁴
Ag ₂ WO ₄ -Fe ₃ O ₄	300 W Xe lamp, λ > 400 nm	Fast Green	0.0016 (Fe ₃ O ₄ -Ag ₂ WO ₄)	⁵
Ag ₃ PO ₄ /NiFe ₂ O ₄	300 W Xe lamp λ > 420 nm	0.04 Methyl Orange	0.03 (Ag ₃ PO ₄) 0.06 (Ag ₃ PO ₄ -NiFe ₂ O ₄)	⁶
Fe ₃ O ₄ /ZnO/BiOI/PANI	50 W LED lamp λ > 420 nm	- RhB	0.022 (Fe ₃ O ₄ /ZnO /BiOI/PANI) 0.0003 (Fe ₃ O ₄ /ZnO)	⁷

Table S1. Comparison of organic pollutant degradation performance of other magnetic photocatalysts' with our work.

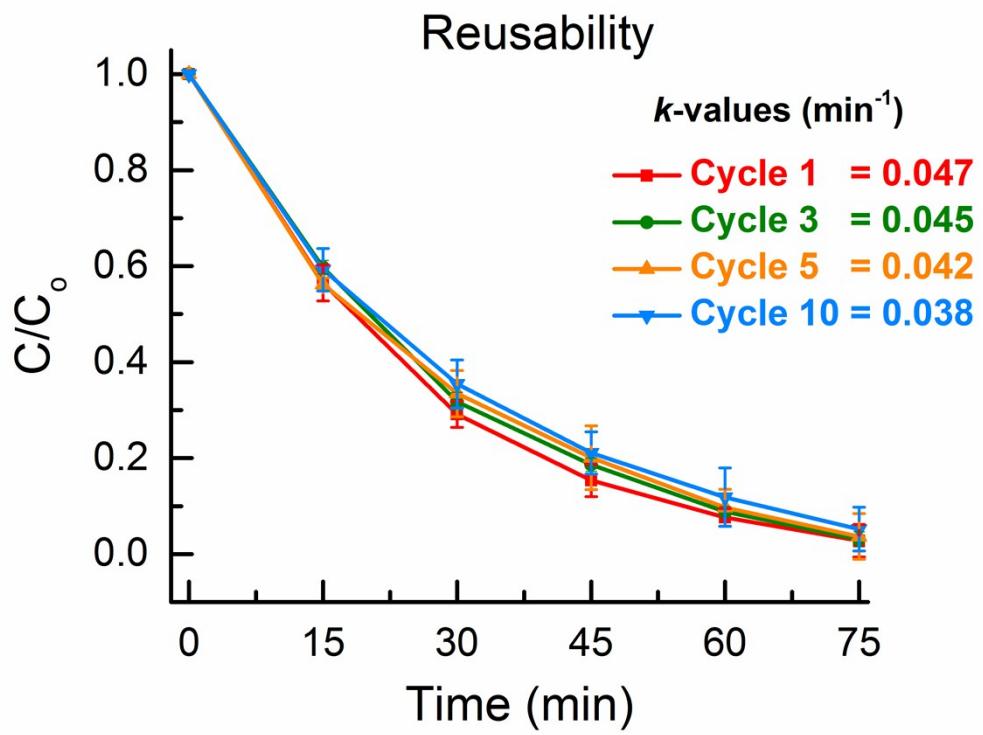


Figure S7: Plot showing results obtained under 10 consecutive cleaning runs using hybrid helices and UV-visible light. From here we can observe that the hybrids displayed a good stability and reusability over multiple runs.

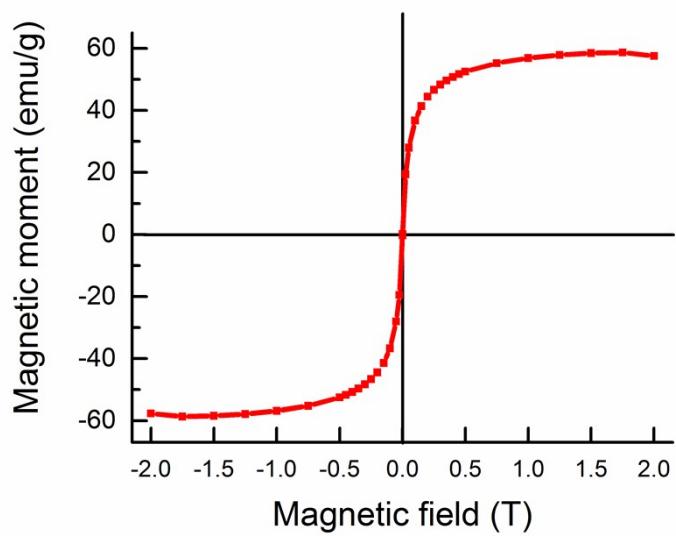


Figure S8: Magnetic hysteresis loop obtained for hybrid microhelices.

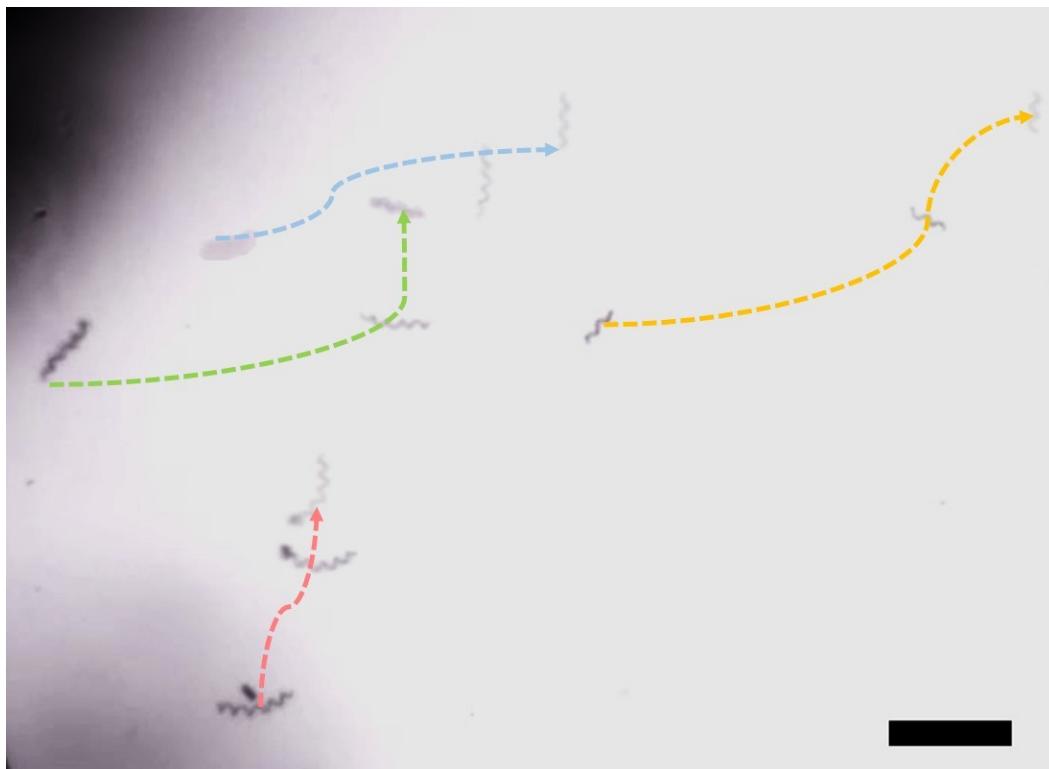


Figure S9: Time-lapse image obtained for a swarm of hybrid microhelices showing their precise propulsion and steering under 10 mT and 12 Hz rotating magnetic fields.

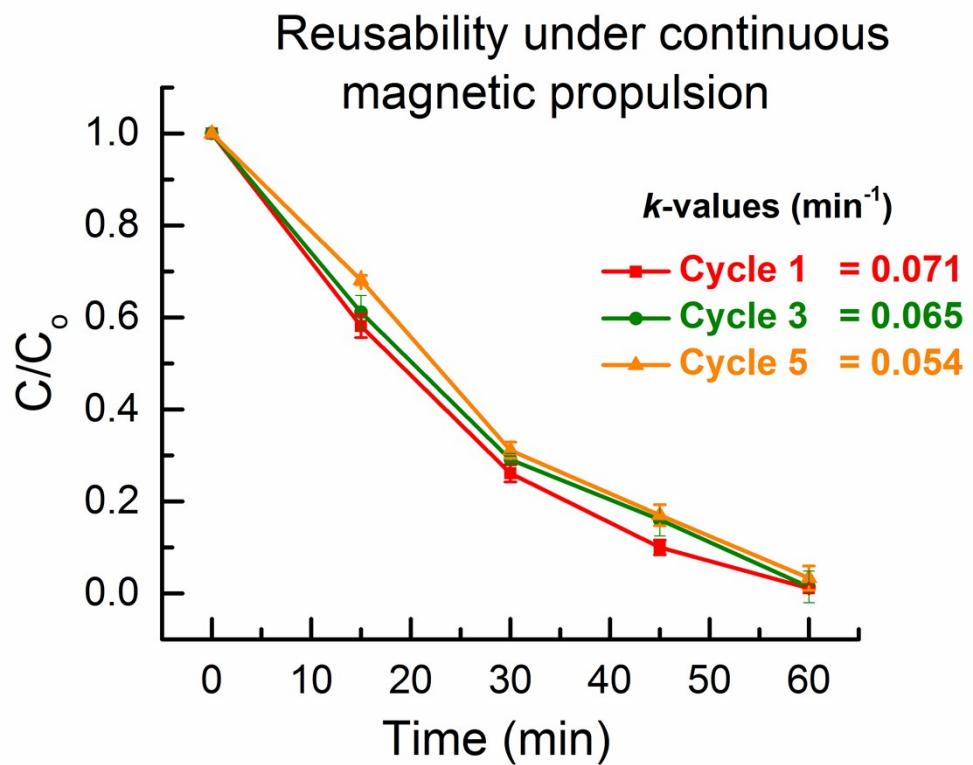


Figure S10. Plot showing results obtained under 5 consecutive cleaning runs using hybrid helices and UV-visible light, under continuous magnetic propulsion.

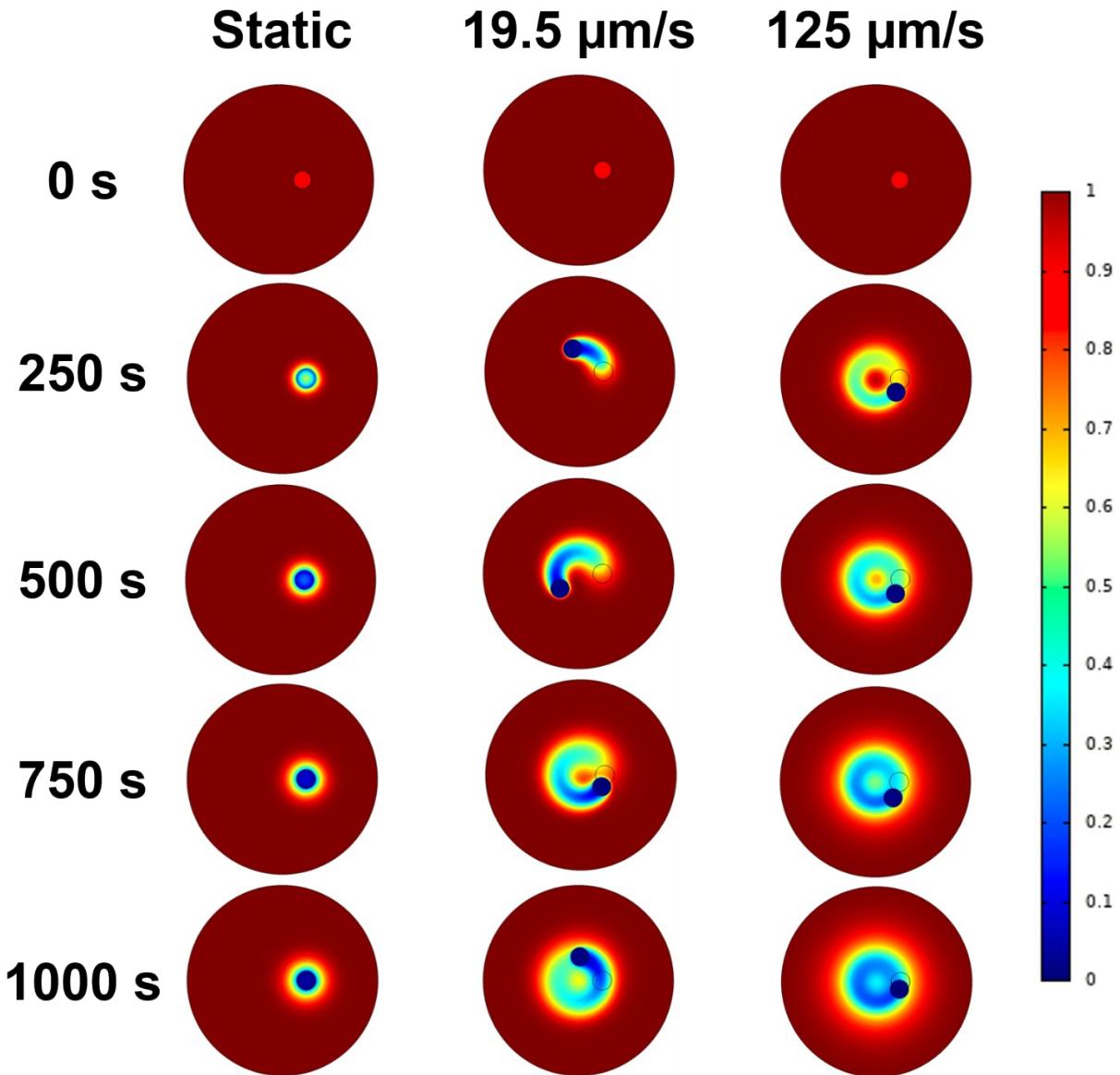


Figure S11: Time-lapse images obtained from COMSOL simulations showing the degradation of organic pollutant obtained under different swimming speeds over 1000 s. The color scale represents the pollutant degradation rates (C/C_0), where maroon color represents $C/C_0=1$ i.e. 100% organic pollutant concentration and dark blue represents complete degradation of organic pollutant.

1. Mushtaq, F.; Asani, A.; Hoop, M.; Chen, X.-Z.; Ahmed, D.; Nelson, B. J.; Pané, S. Highly Efficient Coaxial TiO₂-PtPd Tubular Nanomachines for Photocatalytic Water Purification with Multiple Locomotion Strategies. *Advanced Functional Materials* 2016, 26, 6995-7002.
2. Mushtaq, F.; Guerrero, M.; Sakar, M. S.; Hoop, M.; Lindo, A. M.; Sort, J.; Chen, X.; Nelson, B. J.; Pellicer, E.; Pane, S. Magnetically driven Bi₂O₃/BiOCl-based hybrid microrobots for photocatalytic water remediation. *Journal of Materials Chemistry A* 2015, 3, 23670-23676.
3. Chang, J.; Zhang, Q.; Liu, Y.; Shi, Y.; Qin, Z. Preparation of Fe₃O₄/TiO₂ magnetic photocatalyst for photocatalytic degradation of phenol. *Journal of Materials Science: Materials in Electronics* 2018, 29, 8258-8266.
4. Hong, T.; Mao, J.; Tao, F.; Lan, M. Recyclable Magnetic Titania Nanocomposite from Ilmenite with Enhanced Photocatalytic Activity. *Molecules* 2017, 22, 2044.
5. Rajamohan, S.; Kumaravel, V.; Muthuramalingam, R.; Ayyadurai, S.; Abdel-Wahab, A.; Sub Kwak, B.; Kang, M.; Sreekantan, S. Fe₃O₄-Ag₂WO₄: facile synthesis, characterization and visible light assisted photocatalytic activity. *New Journal of Chemistry* 2017, 41, 11722-11730.
6. Huang, S.; Xu, Y.; Zhou, T.; Xie, M.; Ma, Y.; Liu, Q.; Jing, L.; Xu, H.; Li, H. Constructing magnetic catalysts with in-situ solid-liquid interfacial photo-Fenton-like reaction over Ag₃PO₄@NiFe₂O₄ composites. *Applied Catalysis B: Environmental* 2018, 225, 40-50.
7. Habibi-Yangjeh, A.; Shekofteh-Gohari, M. Synthesis of magnetically recoverable visible-light-induced photocatalysts by combination of Fe₃O₄/ZnO with BiOI and polyaniline. *Progress in Natural Science: Materials International* 2019, 29, 145-155.