Graphene-based Janus Micromotors for Dynamic Removal of Pollutants

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Supporting Information

Videos

Video S1. SiO_2@rGO-Pt micromotors motion *vs* Brownian motion.

Video S2. Effect of H_2O_2 concentration on the micromotors motion.

Video S3. Micromotors magnetic properties. The video is presented in slow motion, at 40% of the real speed.

Video S4. Micromotors motion in a seawater sample.

Experimental Section

Synthesis of Janus micromotors. 1 ml of 1.3 mg ml^{-1} SiO_2 magnetic microparticles provided by Beata Anna Zasońska and Daniel Horák from Institute of Macromolecular Chemistry (Czech Republic),[1] were washed three times with water and then, 800 µl water were added to the microparticles, followed by 200 µl of a 0.5 wt.% graphene (GO) solution (Angstron materials). The mixture was stirred at 650 rpm for 2h. The resultant SiO_2@GO microparticles were washed three times with water before suspend them in 1 ml of 0.3 mgml^{-1} ascorbic acid solution for reduction of the GO-wrapped microparticles. The mixture was left stirring at 1200 rpm for 48 h, washed 3 times with deionized water and resuspended in 1 ml of water. To obtain the Pt hemispheric Janus micromotors, the as-prepared SiO_2@rGO microparticles were dissolved in 500 µl isopropanol (Sigma-Aldrich) and 150 µl of the solution was placed on top of a glass slide and left them dry at room temperature. Sputtering of Pt was carried out on a Leica EM ACE600. Current intensity (deposition rate) *i.e.* 30, 60 and 90 mA (0.1, 0.23 and 0.46 nm s^{-1}), respectively and thickness of the layer (20, 40 and 60 nm) were tuned to get optimal motion of the micromotors. In order to obtain a uniform Janus half-shell coating, the sample slides were set-up in parallel to the Pt target. Optimal conditions were set at 30 mA current, 60 nm Pt layer and a rotation speed of ~18 rpm. Some volume of water were then placed on top of the SiO_2@rGO-Pt microparticles and the glass slide placed in a sonication bath for short periods of time until most of the particles got released from the surface. The particles were collected in an eppendorf and concentrated up to 10 million of particles ml^{-1}. Particle number was estimated by direct counting (5 times) the number of motors present in a pre-defined area of a 0.5 µl aliquot of micromotors (under the microscope) and later extrapolated to 1 ml (**reviewer 2, comment 12**).

Propulsion of Janus micromotor. The propulsion of micromotors was tested under the microscope. Aqueous solutions of micromotors, sodium cholate (NaCh, Sigma-Aldrich) and H_2O_2 (Sigma-Aldrich), 2 µl each, were added consecutively on top of a glass slide. Optimal concentration was studied by varying the concentration of H_2O_2 from 1.5 to 10 %. For testing propulsion of the micromotors in real samples 33% of a seawater sample was used. Videos were captured by an inverted optical microscope (Olympus IX71) coupled with 4X, 20X and 40X objectives, at 20 frames s^{-1} and Cellsens software were used for capturing movies and photos. The micromotors speed was tracked using Fiji (ImageJ2) software.

Removal experiments. First, a calibration curve for PBDEs and Triclosan was done using a magnetic particle enzyme-linked immunoassay (ELISA) kit (Abraxis).[2] 1 ppm Stock solutions of PBDEs (AccuStandard) and 10 ppm stock solution of Triclosan (Sigma-Aldrich) were prepared by diluting the as-received reagents in ethanol and methanol (from Sigma-Aldrich), respectively and stored at 4 ºC when not in use. Standard solutions of 0 to 1 ppb of either PBDEs or Triclosan were prepared and the calibration curves obtained by plotting the natural logarithm of the absorbance relative to the absorbance of the blank *vs* the natural logarithm of the PBDEs or triclosan concentrations, respectively. Date fit with straight lines with equations: $y = -0.23 \ln[\text{PBDEs}] - 1.03$ ($R^2 = 0.996$) and $y = -0.31 \ln[\text{triclosan}] - 1.26$ ($R^2 = 0.991$). Solutions for the remediation experiments were prepared to have final concentrations of 10 ppb of PBDEs (or triclosan), 10^6 motors ml^{-1}, 3 wt. % of NaCh and 1.5 wt. % of H_2O_2, in a total volume of 500 µl. Remediation experiments were performed by adding the micromotors solution at the bottom of a glass container, already containing the before mentioned solutions (except for the fuel solution). Then, once the fuel is added, the motors were let to propel in the PBDEs (or triclosan) contaminated solution for 10 min. To prevent the inactivation that H_2O_2 can produce on the HRP enzyme (from the enzymatic kit) an aliquot of 20 µl of the remediation solution was placed into 80 µl of 325 mM sodium bisulphite (Sigma-Aldrich) solution to eliminate the H_2O_2 remaining in the remediation solution. Sodium bisulphite must be in at least double molar ratio respect to the expected H_2O_2 remaining concentration.[3] Afterwards, the samples were diluted with deionized water to get a concentration of 0.4 ppb; and concentration of PBDEs (or triclosan) pollutant was estimated before and after the remediation process, following the steps detailed in the Abraxis kits.

Removal experiments in real samples. To study the micromotor-based removal extend either 10 ppb of PBDEs or a mixture of 5 ppb PBDEs and 5 ppb triclosan were spiked in a seawater sample, collected form Icaria shorts, Barcelona (Spain). Quantification of only PBDEs, and of PBDEs and triclosan coexisting in the sample were separately achieved by using the corresponding kits, as explained in the previous section. As both kits are based on the same immunodetection principle and they have shown to interfere with one another, we first estimated the effect of triclosan over PBDEs quantification and later the one of PBDEs over the triclosan quantification. For this purpose we built a calibration curve with increasing concentrations of PBDEs in the presence of a 0.4 ppb fix concentration of triclosan interference and another one with increasing concentrations of triclosan with a 0.4 ppb fix concentration of PBDEs interference. By relating the curves obtained in the presence of interferences with those obtained without them, we found that PBDEs and triclosan quantification were overestimated in 1.20 and 1.15 factors, respectively when compared to each of the analytes quantified alone. Those factors are in agreement with those reported in the literature.[2,4] The corresponding spectra were then normalized respect the empirically found factors when coexisting both POPs in the same seawater sample.

Reusability experiments. To check the potential reusability of the SiO_2@rGO-Pt micromotors, we conducted some successive adsorption–desorption cycles. The micromotors were regenerated by solvent cleaning treatment, using isooctane (Sigma-Aldrich) as solvent. After the first cycle, the micromotors were magnetically separated from the seawater solution and washed twice with 100 μl ethanol before suspend them in 500 μl isooctane for desorption of PBDEs. After 30 min, the particles were separated and washed twice again with ethanol and then reused for the subsequent adsorption and desorption cycle.

Characterization. Micromotors scanning electron microscopy (SEM) images and EDS mapping were obtained with a scanning electron microscope FEI Quanta 650 F and the high-resolution images with a FEI Magellan 400 L. FTIR spectroscopy and surface charge properties were performed on a Bruker Tensor 27/PMA 50 Spectrometer and a Malven Zetasizer Nano analyzer, respectively.

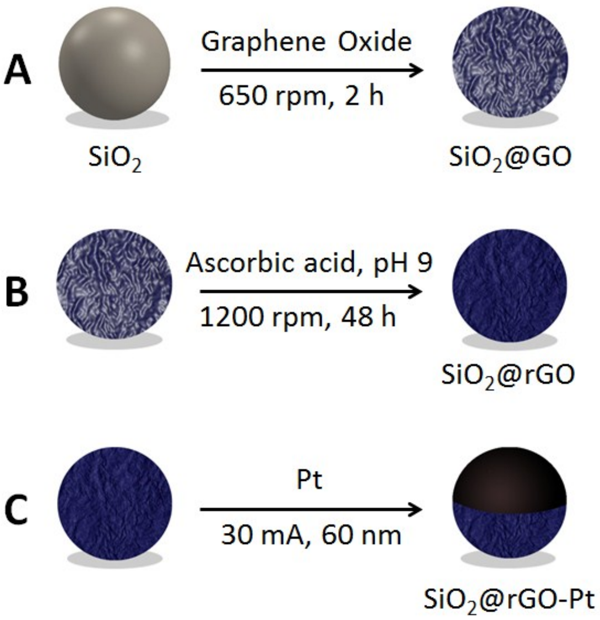

Figure S1. Schematic detailing the fabrication steps in the preparation of SiO_2@rGO-Pt micromotors.

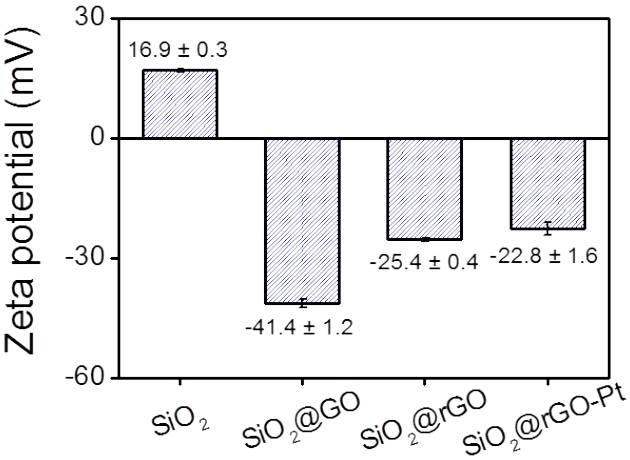

Figure S2. Zeta-potential values of SiO_2, SiO_2@GO, SiO_2@rGO and SiO_2@rGO-Pt, microparticles.

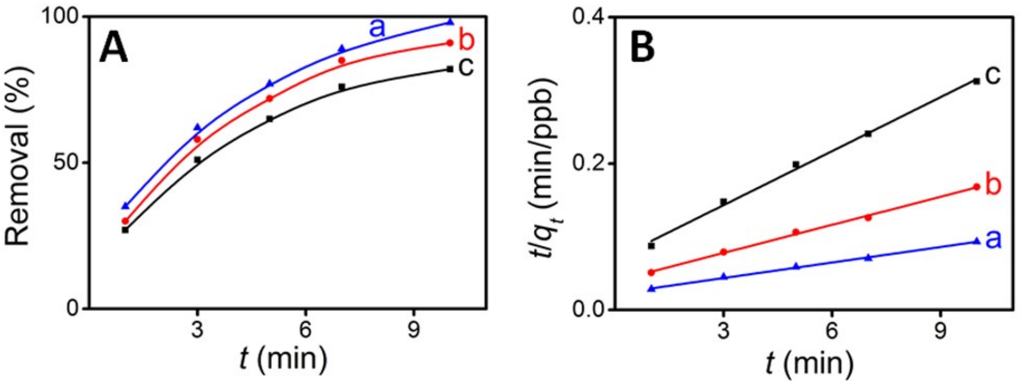

Figure S3. A) Adsorption and kinetic studies. Time dependence on the removal extent: 5 (a), 10 (b) and 20 (c) ppb of PBDEs contaminated solutions, by using SiO_2@rGO-Pt Janus micromotors; and B) corresponding pseudo-second-order kinetic model. Conditions: 10^6 micromotors in a total volume of 500 µl, 10 ppb PBDEs, 1.5 % H_2O_2 and 3% NaCh, 10 min reaction time.

Table S1. Rate constants and correlation coefficients of the pseudo-second-order kinetic model.

[PBDEs] (ppb)	q_e (mg g^{-1})	K_2 (g $mg^{-1}min^{-1}$)	V_0 (mg $g^{-1}min^{-1}$)*	R^2
5	40.7	0.009	14.4	0.9960
10	78.1	0.004	25.3	0.9974
20	140.8	0.002	44.6	0.9973

**The initial adsorption rate V_0 can be determined from the equation $V_0 = k_2 q_e^2$.*[5]

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