Electronic Supporting Information (ESI)

Graphene quantum dots based micromotors: a size matter

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Supporting videos

SI Video 1. Graphene quantum dots (GQDs)/Pt micromotor synthesis reproducibility.

SI Video 2. Partially reduced graphene oxide (rGO)/Pt micromotors synthesis reproducibility.

SI Video 3. GQDs micromotors speed dependence upon fuel concentration.

Supporting figures

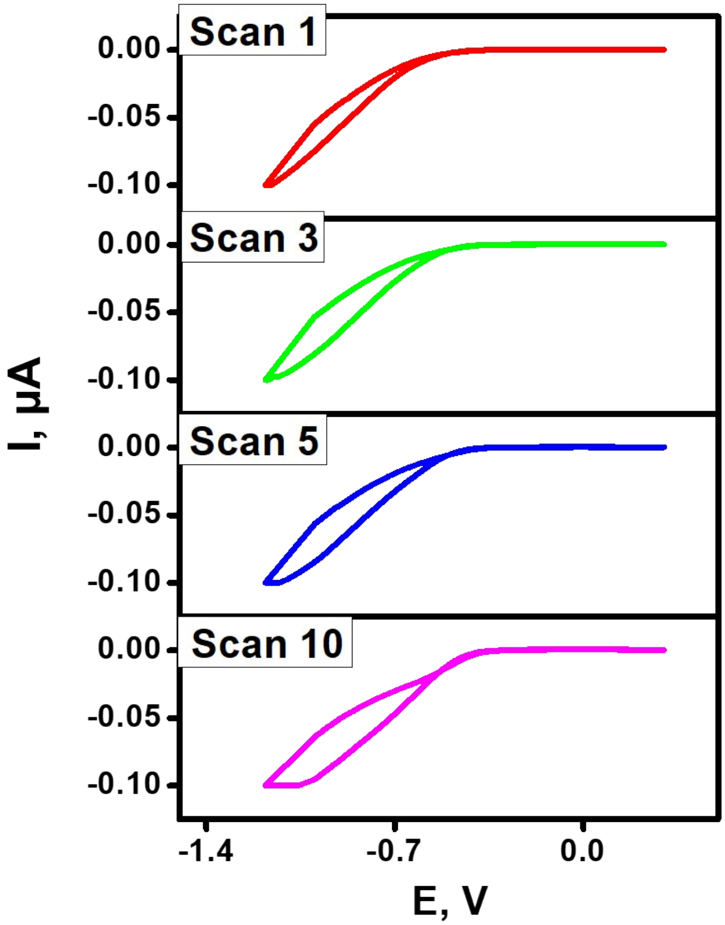

Figure S1. Cyclic voltammograms corresponding to the electrochemical reduction of GQDs.

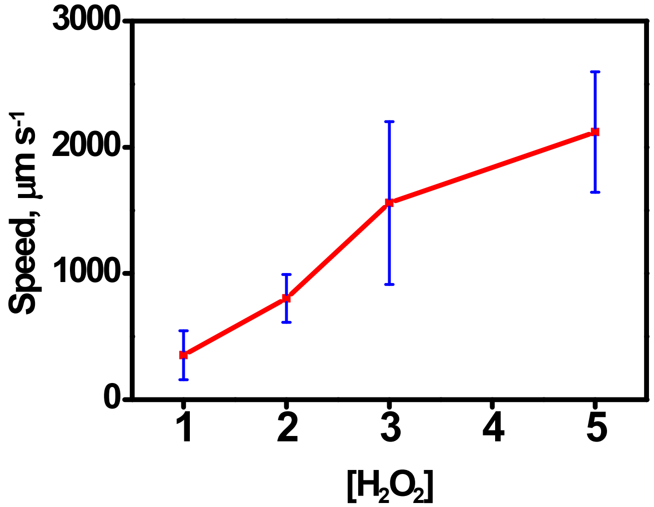

Figure S2. Influence of hydrogen peroxide concentration on GQDs/Pt micromotors speed.

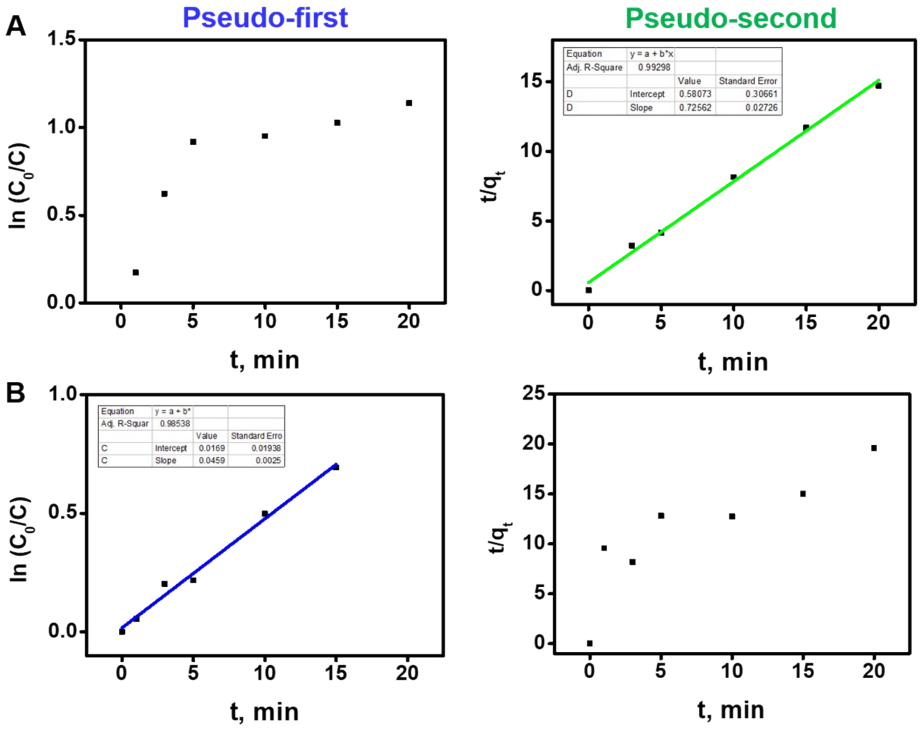

Figure S3. Pseudo-first and pseudo-second order kinetic of (A) GQDs/Pt and (B) rGO/Pt micromotors on the removal of Rhodamine 6B.

Experimental section

Equipments and reagents. All reagents, gold (III) chloride hydrate (cat. 254169), chloroplatinic acid hydrate (cat. 520896), sodium sulfate (cat. 204447), sodium cholate hydrate (cat. C9282), citric acid (251275), sodium hydroxide (cat. S5881), hydrochloric acid (cat. 320331), hydrogen peroxide (cat. 216763), boric acid (cat. B6768), potassium hexacyanoferrate (III) (cat. 244023) and hexacyanoferrate (II) trihydrate (cat. P3289) were obtained from Sigma-Aldrich (Germany). Partially reduced graphene oxide (rGO) was purchased from GRAPHENEA (Cambridge, MA, USA). All solutions were prepared by dilution in ultrapure water, 18.2 MΩ were obtained from Sigma-Aldrich and employed without further purification. Template electrochemical deposition of microtubes and electrochemical characterization was carried out using an Autolab PGSTAT 12 (Eco Chemie, Utrecht, The Netherlands). Scanning electron microscopy (SEM) images were obtained with a JEOL 6335 F instrument, using an acceleration voltage of 20 kV. Energy-dispersive X-ray mapping analysis was performed using a Bruker X flash 4010 EDX 6 detector attached to SEM instrument, using an acceleration voltage of 22 kV. Raman spectra was recorded using an Alpha 300 AR (WITec, Ulm, Germany) confocal Raman microscope. An inverted optical microscope (Nikon Eclipse Instrument Inc. Ti-S/L100), coupled with 4X, 10X, 20X and 40X objectives, and a Hamamatsu digital camera C11440 and NIS Elements AR 3.2 software, were used for capturing movies at a rate of 25 frames per second. The speed of the micromotors was tracked using a NIS Elements tracking module. The microscope includes an Epi-fluorescence attachment with a filter cube with a FTIC filter (530 ± 43 nm) use for fluorescence studies of Rhodamine 6G. Aqueous hydrogen peroxide solutions, with concentration of 0.5 to 5%, were used as the chemical fuel.

Graphene quantum dots synthesis. The quantum dots were synthetized by direct pyrolysis of citric acid and dispersion in alkaline solutions following a previous procedure.[1] The resulting GQDs have a round morphology with an average particle size of ~3 nm (by AFM) and strong fluorescence emission at 470 nm after excitation at 360 nm.[2]

Electrochemical synthesis of GQDs and rGO micromotors. Micromotors electrodeposition takes place into a 5 µm-diameter conical pores of a gold-sputtered polycarbonate membrane (Catalog No. 7060–2513; Whatman, New Jersey, USA). GQDs (0.01 mg mL^{-1}) or rGO (0.1 mg mL^{-1}) were dispersed in a solution containing 0.1 M H_2SO_4 and 0.5 M of Na_2SO_4. The simultaneous electrochemical reduction and deposition was carried out using cyclic voltammetry (CV, over +0.3 to –1.5 V vs Ag/AgCl (3 M), at 50 mV s^{-1} for forty and ten cycles, respectively), using a Pt wire as counter electrode. Subsequently, the inner PtNPs layer was amperometrically deposited at -0.4 V for 0.3 C from a solution containing 4 mM H_2PtCl_6 in 0.5 M boric acid. Gold layer was electrodeposited using a solution of $HAuCl_4$ 5 mM in H_2SO_4 0.1 M. The deposition was carried out by cyclic voltammetry over 0.0 to +0.85 V vs Ag/AgCl (3M) at 12.5 mV/s for 60 cycles. The sputtered gold layer was gently removed by hand polishing with 0.05 µm alumina slurry and dissolved in methylene chloride. Micromotors were then washed repeatedly with ethanol and dispersed in ultrapure water (18.2 Ω cm).

Electrochemical measurements. Linear sweep voltammograms were recorded a carbon electrode modified with the identical mass of each micromotor or deposited gold nanoparticles with a scan rate of 10 mV s^{-1} in 0.5 M N_2-saturated H_2SO_4. The reference electrode was Ag/AgCl and all potentials were referred to reversible HER electrode. Current densities were calculated taking into consideration the effective area of the electrode calculated from oxygen adsorption peak area, using as reference area of 390 µC cm^{-2} for polycrystalline Au.[3]

Impedance spectroscopy (EIS) was carried out using $K_3[Fe(CN)_6]/K_4[Fe(CN)_6]$ (1:1) (5 mM) in 0.01 M KCl solution and starting at open circuit potential using AC signals of amplitude 5 mV peak to peak in the frequency range of 109 to 104 Hz.

References

1 Y. Dong, J. Shao, C. Chen, H. Li, R. Wang, Y. Chi, X. Lin and G. Chen, *Carbon*, 2012, **50**, 4738-4743.
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