Graphene based microbots for toxic heavy metal removal and recovery from water

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Video S1. Tracking of microbots' trajectories at different times (0, 15, 30 and 60 min) during Pb(II) ions decontamination. (Initial experimental conditions: 1.5 % v/v H_2O_2 and 0.1% w/v of SDS).

Video S2. GOx-microbot controlled by magnetic guidance after the lead recovery process. (Experimental conditions: 1.5 % v/v H_2O_2 and 0.1% w/v of SDS).

Video S3. GOx-microbot controlled by magnetic guidance swimming in a PDMS microchannel as a prototype of microbots based water cleaning system. (Experimental conditions: 1.5 % v/v H_2O_2 and 0.1% w/v of SDS).

X-ray photoelectron spectroscopy (XPS) analysis of GOx-microbots

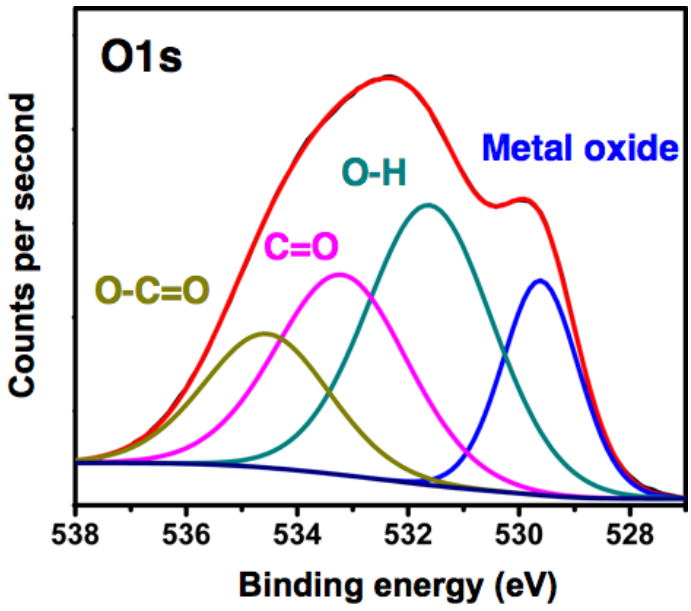

Figure S1. O1s high resolution XPS spectra of GOx-microbots.

Table S1. Various functional groups identified on the surface of GOx-microbots.

Spectra	Group	Position	%At
C 1s	C-C/C-H/C=C	284.68	48.638
C 1s	C-O	286.19	29.875
C 1s	C=O	288.09	17.099
C 1s	O-C=O	290.49	4.387
O 1s	Metal oxide	529.61	17.231
O 1s	O-H	531.61	37.207
O 1s	C=O	533.2	27.858
O 1s	O-C=O	534.55	17.703

Methods

Materials and reagents

Graphene oxide, sodium dodecyl sulfate (SDS), lead nitrate, nitrate acid, hydrochloric acid and sodium hydroxide were purchased from Sigma-Aldrich (Germany). Hydrogen peroxide 30%, potassium nitrate, methylene chloride and ethanol were purchased from Merck (Germany). Ultrapure water (Millipore Corporation, USA) was used for the preparation of all aqueous solutions.

Fabrication of graphene oxide-based multilayer microbots

The graphene oxide-based multilayer microbots were fabricated using a common template directed electrodeposition protocol. A cyclopore polycarbonate membrane, containing 5 μm maximum diameter conical-shaped micropores (Catalog no. 7060-2513; Whatman, Maidstone, UK), was employed as a template. A 80 nm gold film was first

sputtered (sputter system MED020 Bal-Tec) on one side of the porous membrane to serve as a working electrode using an evaporation and sputtering was performed at room temperature under vacuum of $5x10^{-2}$Torr, power 60 mA and Ar was flowed during 85s. A Pt wire and an Ag/AgCl with 3 M KCl were used as counter and reference electrodes, respectively. The membrane was then assembled in a plating cell with an aluminum foil serving as contact for the working electrode. A solution which contains 0.1mg/mL graphene oxide (GOx) in 0.5M of Na_2SO_4 and 0.1 M of H_2SO_4 was prepared from Sigma-Aldrich reagents[1]. The GOx of the solution was reduced by using cyclic voltammetry from -1.5V to 0.3V for five cycles. Then, the metallic layers were deposited from a Pt and Ni commercial solutions (Platinum TP; Technic Deutschland GmbH and nickel-100 semiplate; NB Technologies GmbH). Nickel solution was prepared by adding 0.0488 g l^{-1} SDS to the commercial Ni solution and sonicating using an ultrasound bath for 15 min. The first metallic layer, which uses a 1:1:1 Pt:Ni:water solution, was deposited galvanostatically at -2 mA for 300 s to provide a smooth surface and to improve the deposition of the next metallic layers. After washing three times with water, the Ni layer was deposited amperometrically at -1.0 V for 2.4 C to achieve the ferromagnetic properties that allows the microbot guidance by properly orienting the magnetic field created by a simple neodymium magnet. Finally, after other three washings, the catalytic inner Pt layer was deposited galvanostatically at -2 mA for 300 s. To release the GOx-microbots from the template, the sputtered gold layer was completely removed by mechanical hand polishing with 5 μm alumina slurry (Electron Microscopy Sciences, Hatfield, PA). The membrane was then dissolved in methylene chloride for 10 min to completely release the microtubes. Finally, the microbots were washed two times more

with methylene chloride, followed by ethanol and ultrapure water, two times of each, and collected by centrifugation at 9000 rpm (Eppendorf 3409) for 3 min after each wash.

Equipment

Template electrochemical deposition of microtubes was carried out with using a potentiostat (AUT50101, Metrohm Autolab B.V.). The software used for the electrochemical depositions was NOVA 1.10. An inverted optical microscope (Leica DMI3000B), coupled with a 10X, 20X, 40X and 63X objectives, along with a Leica digital camera DFC3000G with LAS V4.5 soft-ware, were used for capturing movies. Scanning electron microscope (E-beam-SEM Ultra 55 Zeiss) was used for the microbotss characterization. Energy dispersive X-ray analysis (EDX) was carried out using EDAX connected to Cryo-SEM Ultra 55 Zeiss EDAX. Raman analysis and mapping were carried out on a Thermo Scientific DXR^{TM} *Raman* Microscope with *Atlus* system. A 532 nm laser line with an output power of 5 W was used as the excitation source. The spectra were collected in ranges of 100 to 4000 cm^{-1} with exposure time of 1 second and 10× magnification. All Raman experiments were conducted at room temperature and ambient pressures. X-ray photoelectron spectroscopy (XPS) from SPECS system (Germany) was used to identify functional groups on the GOx-microbots surface. The instrument was equipped with XR50 duel anode source (Al operated at 150W) and a Phoibos MCD-9 detector. All measurements were done under the vacuum (pressure $5x10^{-9}$ mBar) and the hemispherical analyzer was set at the pass energy 25 eV while the high resolution spectra step size was set at 0.1 eV. Casa XPS program (Casa Software Ltd., UK) was used for the data analysis. Inductively coupled plasma optical emission spectrometry (ICP-OES), was employed as analytical

technique for the detection of Pb(II) ions. Origin Pro 9.0 and Microsoft Excel 2010 were employed for the analysis of the experimental data.

Experimental procedure

The GOx-microbots were characterized using different characterization techniques, such as, Raman, SEM and EDX. After characterization, the GOx-microbots fabricated were transferred together in a falcon tube and they were observed by using an inverted microscope for estimating the concentration of GOx-microbots in water. Once the GOx-microbots have been characterized and counted, they were used for decontamination experiments, which are carried out in a glass beaker containing total 3 ml of heavy metal polluted water consisted of 1ppm of lead (1µg/ml or 1000 ppb), hydrogen peroxide (1.5% v/v) and SDS (0.1 % w/v) at the pH (5.7). The assay was carried out by triplicate (n=3) for each time (5, 10, 30, 60 min and 24 hours) that the motors are swimming in the contaminated solution. Control experiments were also carried out by triplicate. Swimming of microbots was recorded at different time interval by inverted microscope and tracking was done by a custom made python script which used open CV libraries. Lead concentration was measured by ICP-OES and the GOx-microbots were kept in the glass beakers using a magnet due to their magnetic properties. Then, the GOx-microbots were washed once with water and characterized by SEM and EDX analysis. After that, they were exposed for 1 hour to different treatments, such as water presence, water[2] presence under low temperature, basic pH, acid pH by using HCl (pH=1)[3] and HNO_3 (pH=0.3)[4, 5], for the lead recovery and washed once with water. The supernatant from these different treatments were measured by ICP-OES to probe the lead content and thus, the lead recovery from the GOx-microbots. On the other hand, the GOx microbots were characterized by SEM and EDX and washed several times with

water for their reusability. Reusability experiments were carried out following the same conditions of the first lead decontamination and also by tripiclate for 1 hour. After that, the GOx-microbots were kept in the glass beakers using a magnet and the solutions were measured by ICP-OES.

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