Electronic Supporting Info

Microengine-assisted Electrochemical Measurements at Printable Sensor Strips

Stefano Cinti,^{ab} Gabriela Valdés-Ramírez,^a Wei Gao,^a Jinxing Li,^a Giuseppe Palleschi,^{*b} and Joseph Wang ^{*a}

E-mail: josephwang@ucsd.edu

E-mail: giuseppe.palleschi@uniroma2.it

a Department of Nanoengineering, University of California San Diego, La Jolla, California 92093-0448, United States

b Dipartimento di Scienze e Tecnologie Chimiche, Università di Roma Tor Vergata, Via della Ricerca Scientifica 1, 00133 Rome, Italy

1. Experimental Section

Reagents and Instrumentation

Potassium Chloride (Catalog #P217) was obtained from Fisher Chemical (Fair Lawn, NJ), Paraoxon Methyl (Pestanal, Catalog #46192) was purchased by Sigma-Aldrich (St. Louis, MO), Magnesium (Mg) microparticles (Catalog #465666, powder, 325 mesh, 99.5% trace metals basis Sigma-Aldrich, St Louis, MO) All the chemicals were used without further purification. Electrochemical measurements were performed at room temperature using a portable CH Instruments electrochemical analyzer (model 1232A, Austin, TX). The applied potentials in all measurements were versus the screen-printed pseudo Ag/AgCl reference electrode.

Screen-Printed Electrodes fabrication

Alumina plates (10 cm x 10 cm) were purchased from CoorsTek, Inc. (CA, USA). A Speedline Technologies (Franklin, MA) screen printer (MPM-SPM model TF-100) was used to fabricate the sensor. An Ag/AgCl-based ink (124-36, medical grade), was purchased from Creative Materials Inc. (MA, USA) and it was employed to define the conductive underlayer as well as the reference electrode. A carbon-based ink (Acheson E440B) from Henkel Corp. (Madison Heights, MI) was overlaid on the conductor to define working and counter electrodes. The contacts pads were insulated. The working electrode has a diameter of 3 mm.

Microengines fabrication

The Janus microengines have been made as reported in a previous work,²⁶ with a slight modification. Briefly, Mg microparticles were placed onto glass slide and coated with an 80 nm nickel layer and a 10 nm gold layer using Temescal BJD 1800 E beam Evaporator. The microengines were removed from the glass slide and dispersed into ethanol.

Development of sensing platform

2 μL of the Mg Janus microengine dispersion were drop casted onto the SPE's alumina substrate as displayed in Figure S1. The magnetic microparticles were disposed in 4 spots (0.20±0.02 mg)

sufficiently far from the working electrode area. In order to keep fixed the Mg Janus particles during the chemical reaction and electrochemical measurements, and external magnetic bar was positioned on the back of the microengine-modified electrode as shown in Figure S1.



Figure SI1. Magnesium-based Janus particle microengines coupled to a screen printed electrode as electrochemical sensing strip platform.

Nerve Agents detection

The electrode surface and Janus microengines were covered by a 50 μ L-drop of paraoxon prepared in 0.1 M KCl solution. Cyclic voltammetry and amperometry experiments were carried out after 4 minutes reaction, allowing microengine-driven degradation of the nerve agents. Cyclic voltammetry were performed from 0.3 to 1.2 V at 0.05 V s⁻¹ scan rate. Amperometric measurements were carried out by applying a potential step to +0.9 V for 60 s. Each measurement was performed by using a different electrode strips modified under the same conditions.

2. Results

OP degradation to *p*-nitrophenol

Cyclic voltammetry experiments were performed to verify the success of the degradation carried out by using Mg-based microengines. 20 mM of a solution of *p*-nitrophenol at differente pH were analyzed and compared with the signal due to the OP degradation, as illustrated in Figure S2.



Figure SI2. Cyclic Voltammetry of (a) 20 mM nitrophenol in 0.1 M KCl (pH=11) without microengines, (b) 20 mM paraoxon in 0.1M KCl with microengines, (c) 20 mM nitrophenol in 0.1

M KCl (pH=7) without Janus microengines and (d) 20 mM paraoxon in 0.1M KCl without microengines. Scan rate of 0.05 V/s.