Nanoscale

ROYAL SOCIETY OF CHEMISTRY

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Magnetic control of electrochemical processes at electrode surface using iron-rich graphene materials with dual functionality

Chee Shan Lim,[a] Adriano Ambrosi,[a] Zdeněk Sofer[b] and Martin Pumera*[a]

Cite this: *Nanoscale*, 2014, **6**, 7391

Metal-doped graphene hybrid materials demonstrate promising capabilities in catalysis and various sensing applications. There also exists great interest for on-demand control of the selectivity of many electrochemical processes. In this work, an iron-doped thermally reduced graphene oxide (Fe–TRGO) was prepared and used to investigate the possibility of a reproducible, magnetically controlled method to modulate electrochemical reactivities through a scalable method. We made use of the presence of both magnetic and electrocatalytic properties in the Fe–TRGOs to induce attraction and removal of the Fe–TRGO material onto and off the working electrode surfaces magnetically, thereby controlling the electrochemical oxidation and reduction processes. The outstanding electrochemical performance of the Fe–TRGO material was evident, with enhanced current signals and lower peak potentials observed upon magnetic activation. Reversible and reproducible cycles of activation and deactivation were obtained as the peak heights and peak potentials remained relatively consistent with no apparent carryover between every step. Both components of Fe–TRGO play an electrocatalytic role in the electrochemical sensing. In the cases of the oxygen reduction reaction and reduction of cumene hydroperoxide, the iron oxide plays the role of an electrocatalyst, while in the cases of ascorbic acid, the enhanced electroactivity originates from the high surface area of the graphene portion in the Fe–TRGO hybrid material. The feasibility of this magnetically switchable method for on-demand sensing and energy production thus brings about potential developments for future electrochemical applications.

Received 12th April 2014
Accepted 2nd May 2014

DOI: 10.1039/c4nr01985g

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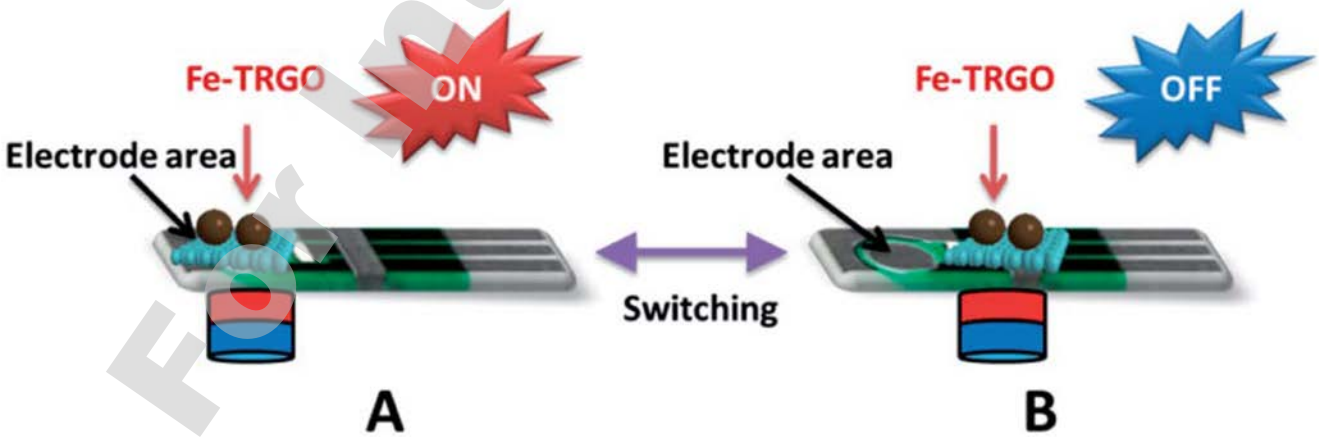

Fig. 3 Experimental setup for (A) activation and (B) deactivation of the electrochemical process.

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Cite this: *Analyst*, 2015, **140**, 7195

Analyst

ROYAL SOCIETY OF CHEMISTRY

Received 6th July 2015,
Accepted 8th September 2015

DOI: 10.1039/c5an01358e

www.rsc.org/analyst

Electrochemically monitoring the antibiotic susceptibility of *Pseudomonas aeruginosa* biofilms†

Thaddaeus A. Webster, Hunter J. Sismaet, I-ping J. Chan and Edgar D. Goluch*

The condition of cells in *Pseudomonas aeruginosa* biofilms was monitored *via* the electrochemical detection of the electro-active virulence factor pyocyanin in a fabricated microfluidic growth chamber coupled with a disposable three electrode cell. Cells were exposed to 4, 16, and 100 mg L^{-1} colistin sulfate after overnight growth. At the end of testing, the measured maximum peak current (and therefore pyocyanin concentration) was reduced by approximately 68% and 82% in *P. aeruginosa* exposed to 16 and 100 mg L^{-1} colistin sulfate, respectively. Samples were removed from the microfluidic chamber, analyzed for viability using staining, and streaked onto culture plates to confirm that the *P. aeruginosa* cells were affected by the antibiotics. The correlation between electrical signal drop and the viability of *P. aeruginosa* cells after antibiotic exposure highlights the usefulness of this approach for future low cost antibiotic screening applications.

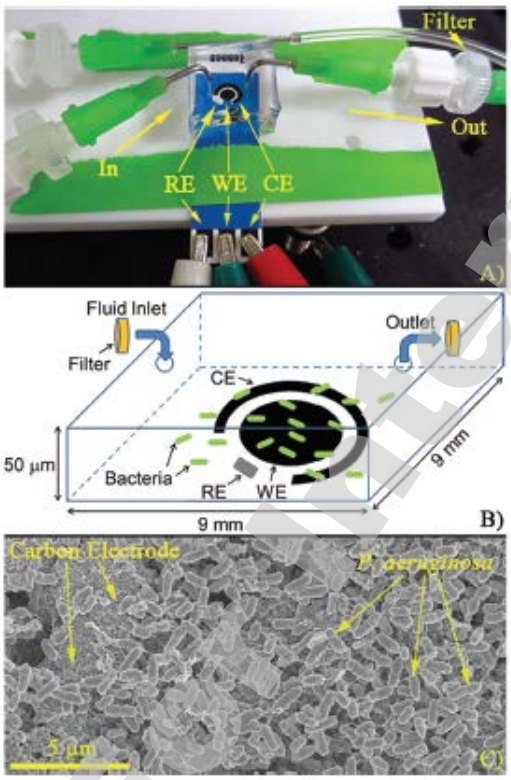


Fig. 1 Experimental apparatus. (A) Finished device connected to a potentiostat. Inlets and outlets contain filters (pore size 0.2 µm) to prevent PA14 from leaving the channels. (B) Schematic of the sensor covered with a microfluidic chamber (not to scale). Bacteria are trapped in the chamber while fluid moves in and out. (C) Scanning electron micrograph (SEM) of PA14 grown on top of the carbon working electrode after overnight growth under stagnant conditions. Reference, Working, and Counter Electrodes (RE, WE, and CE, respectively).

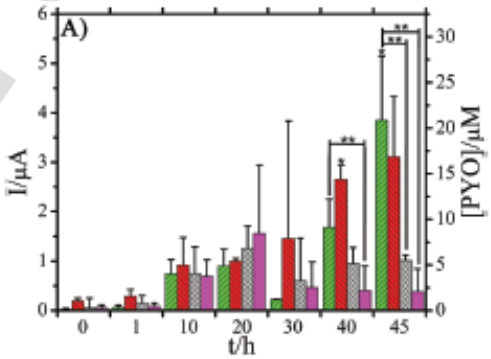
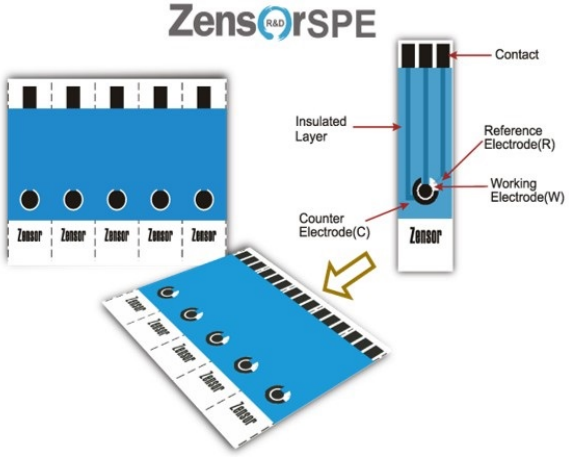


Fig. 3 (A) Response of PA14 biofilms at selected time points during the 48 hour experiments. (BL = Bacteria loaded into the chamber). Left axis: average peak current (blank subtracted) measured over time in PA14 cultures exposed to colistin sulfate at 0 (green right slash), 4 (red left slash, low MIC), 16 (blue crosses, High MIC), and 100 mg L^{-1} (pink no slash lines). Right axis: approximate pyocyanin concentration based on calibration curve. * indicates time points where only two replicates were used. ** indicates $P < 0.05$ from ANOVA analysis of the 16 and 100 mg L^{-1} antibiotic concentrations against the control.



SCIENTIFIC REPORTS

Fluorographene based Ultrasensitive Ammonia Sensor

Kiran Kumar Tadi, Shubhadeep Pal & Tharangattu N. Narayanan

Single molecule detection using graphene can be brought by tuning the interactions *via* specific dopants. Electrostatic interaction between the most electronegative element fluorine (F) and hydrogen (H) is one of the strong interactions in hydrogen bonding, and here we report the selective binding of ammonia/ammonium with F in fluorographene (FG) resulting to a change in the impedance of the system. Very low limit of detection value of ~0.44 pM with linearity over wide range of concentrations (1 pM–0.1 μM) is achieved using the FG based impedance sensor, andthisscreen printed FG sensor works in both ionized (ammonium) and un-ionized ammonia sensing platforms. The interaction energies of FG and NH_3/NH_4^+ are evaluated using density functional theory calculations and the interactions are mapped. Here FGs with two different amounts of fluorinecontents —~5 atomic% ($C_{39}H_{16}F_2$) and ~24 atomic% ($C_{39}H_{16}F_{12}$) - are theoretically and experimentally studied for selective, high sensitive and ultra-low level detection of ammonia. Fast responding, high sensitive, large area patternable FG based sensor platform demonstrated here can open new avenues for the development of point-of-care devices and clinical sensors.

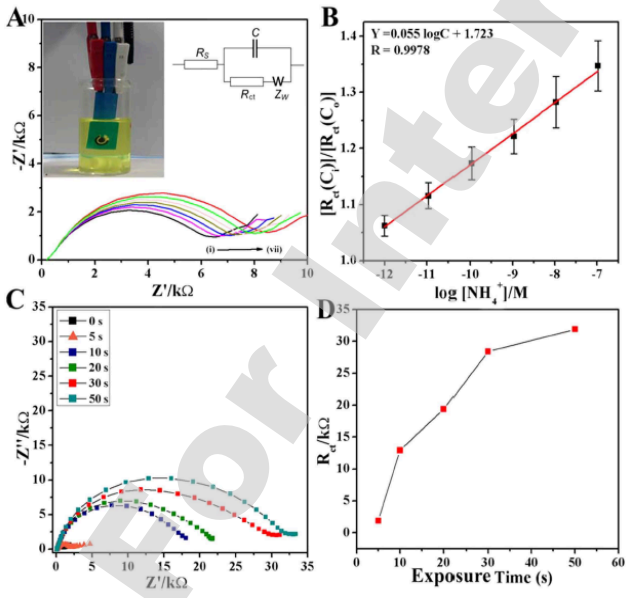
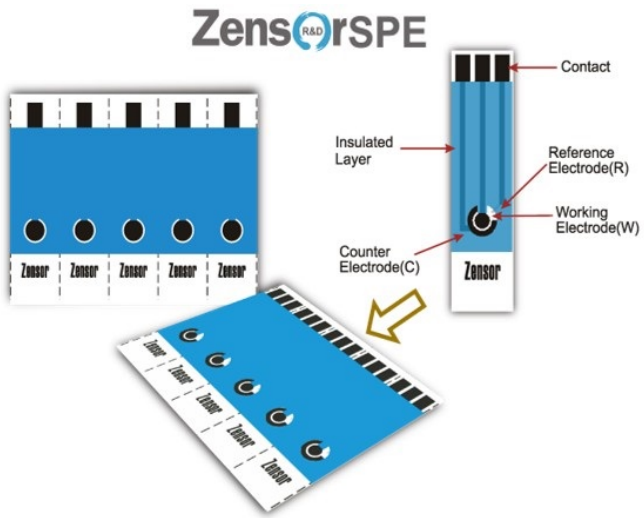


Figure 4. (A) Nyquist plots of FG coated electrode on SPE sensor for varying ammonium ion (NH_4^+) concentrations (i. blank, ii. 1 pM, iii. 10 pM, iv. 100 pM, v. 1 nM, vi. 10 nM, and vii. 0.1 μM), (inset) the photograph of an FG coated SPE sensor, (B) normalized charge transfer resistance for various ammonium ion concentrations, (C) Nyquist plots showing increased impedance with increase in direct NH_3 exposing time, (D) R_{ct} values with varying direct NH_3 exposures.



SCIENTIFIC REPORTS | 6:25221

nature COMMUNICATIONS

ARTICLE

Received 20 May 2015 | Accepted 8 Jul 2015 | Published 18 Aug 2015

DOI: 10.1038/ncomms9050 OPEN

Adhesive curing through low-voltage activation

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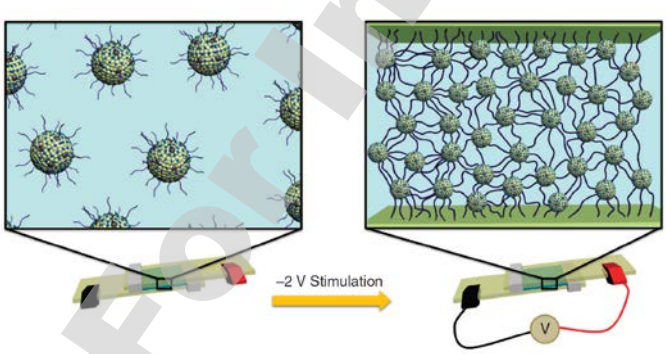
Instant curing adhesives typically fall within three categories, being activated by either light (photocuring), heat (thermocuring) or chemical means. These curing strategies limit applications to specific substrates and can only be activated under certain conditions. Here we present the development of an instant curing adhesive through low-voltage activation. The electrocuring adhesive is synthesized by grafting carbene precursors on polyamidoamine dendrimers and dissolving in aqueous solvents to form viscous gels. The electrocuring adhesives are activated at −2 V versus Ag/AgCl, allowing tunable crosslinking within the dendrimer matrix and on both electrode surfaces. As the applied voltage discontinued, crosslinking immediately terminated. Thus, crosslinking initiation and propagation are observed to be voltage and time dependent, enabling tuning of both material properties and adhesive strength. The electrocuring adhesive has immediate implications in manufacturing and development of implantable bioadhesives.



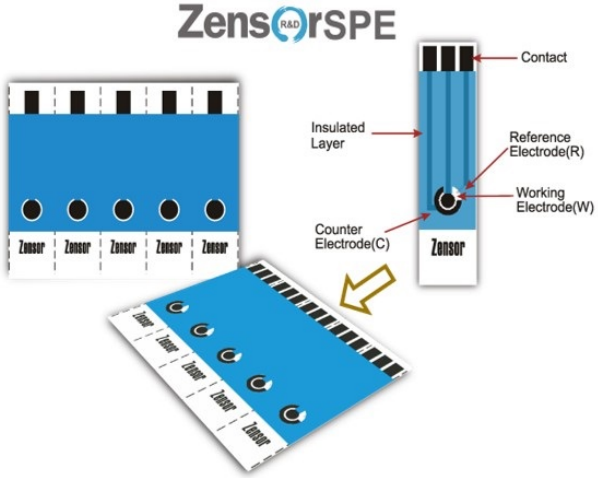


Figure 1 | Concept of electrocuring adhesive. Low-voltage activation allows polymer and substrate crosslinking.

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Cite this: *RSC Adv.*, 2015, **5**, 4286

Bismuth oxide nanoparticles as a nanoscale guide to form a silver–polydopamine hybrid electrocatalyst with enhanced activity and stability for the oxygen reduction reaction†

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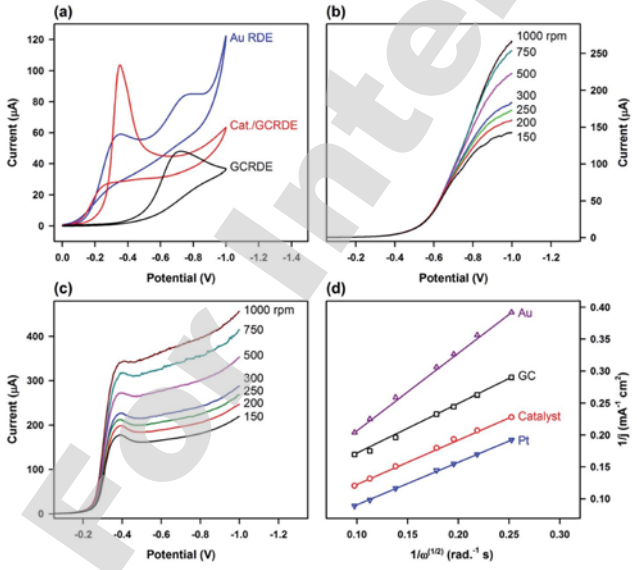
Received 23rd October 2014
Accepted 5th December 2014

DOI: 10.1039/c4ra12989j

www.rsc.org/advances

Highly dispersed Ag nanoparticles (Ag NPs) were successfully synthesized on functionalized polydopamine (PDA)@Bi_2O_3 NPs for use as an electrocatalyst. In the proposed method, a uniform layer of PDA was first coated on Bi_2O_3 NPs. The surface of the PDA@Bi_2O_3 can then be used as a nanoscale guide to deposit Ag NPs and hence for the formation of Ag–PDA@Bi_2O_3 hybrid nanocatalysts. It was found that Ag NPs enhanced the electrocatalytic ability on PDA@Bi_2O_3 by a synergetic effect for direct $4e^-$ transfer in the oxygen reduction reaction (ORR) with a low overpotential. The surface morphology and lattice fringes of Ag NPs of crystalline nature of the obtained Ag–PDA@Bi_2O_3 hybrid nanocatalysts were examined through HR-TEM and SAED patterns. The material's purity and chemical functional groups were identified by FT-IR analysis. This strategy provides new opportunities to design and optimize heterogeneous nanocatalysts with tailored size, morphology, chemical configuration and supporting substrates for metal-catalyzed reactions.



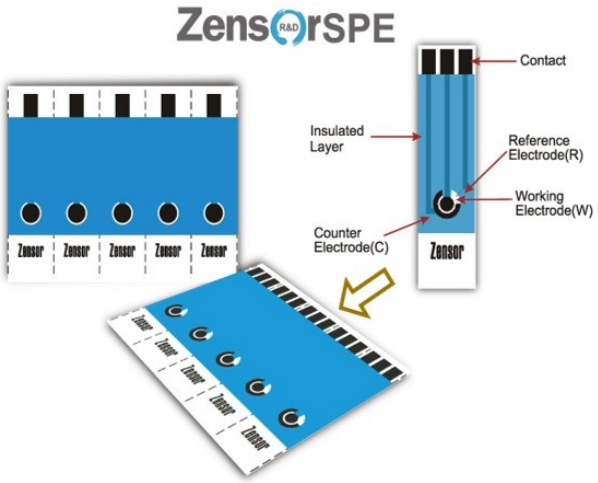


Fig. 5 (a) Cyclic voltammograms for ORR at different RDEs. RDE voltammetry curve for ORR on GCRDE (b) and Ag–PDA@Bi_2O_3-modified GCRDE (c) in 0.1 M O_2-saturated PBS (pH 7.4) at various rotation rates. (c) RDE diffusion curve of different electrodes (GC at −0.9 V, Ag–PDA@Bi_2O_3 at −0.38 V). (d) K–L plots.

THE JOURNAL OF PHYSICAL CHEMISTRY C

Article

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Electrochemical Synthesis and Deposition of Surface-Enhanced Raman Scattering-Active Silver Microstructures on a Screen-Printed Carbon Electrode

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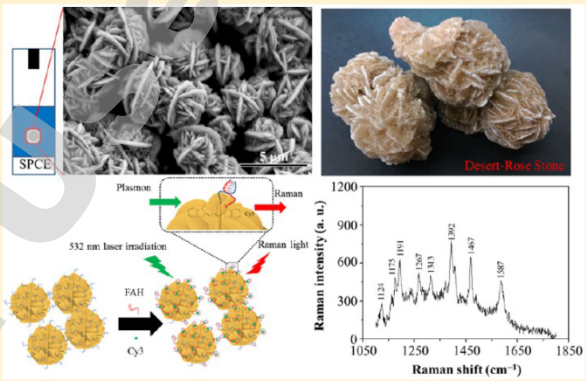
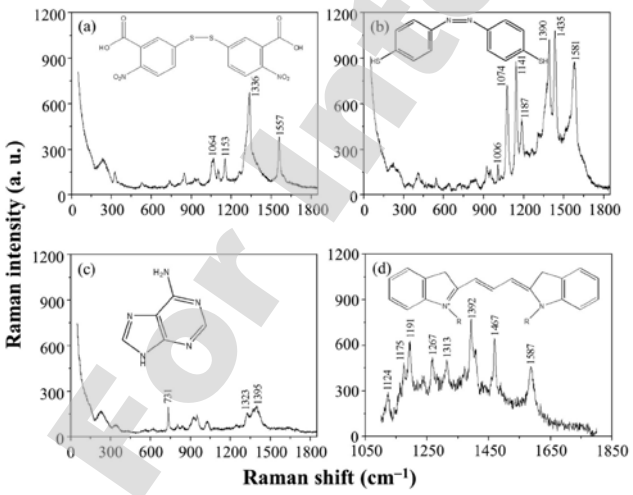
Supporting Information

ABSTRACT: We demonstrated a series of Ag microstructures with controlled morphologies directly deposited on a screen-printed carbon electrode by using electrochemical procedures in the presence of different electrolytes. Scanning electron microscopy, transmission electron microscopy, energy-dispersive X-ray spectroscopy, and high-resolution X-ray diffractometry were used for characterizing as-prepared Ag substrates. Thereafter, the potential of the flower-like Ag microstructures for use in surface-enhanced Raman scattering (SERS) applications was investigated. The flower-like Ag microstructures provided a more intense SERS signal because of extremely intense local electromagnetic fields. The enhancement factor value was approximately 1.2×10^6 for 4-mercaptobenzoic acid molecules. The percentage of relative standard deviation of SERS signals was lower than 2.1%. Determining the SERS spectra of 4,4′-dimercapto-azobenzene, 5,5′-dithiobis-2-nitrobenzoic acid, adenine, and single-stranded DNA (fumarylacetoacetate hydrolase gene) was straightforward. Furthermore, the thermal stability and aging behavior of the microstructures were improved. The present substrate fabrication process is facile and has excellent SERS-active properties and reproducibility and thus provides opportunities for quantitative analysis by using flower-like Ag microstructures.





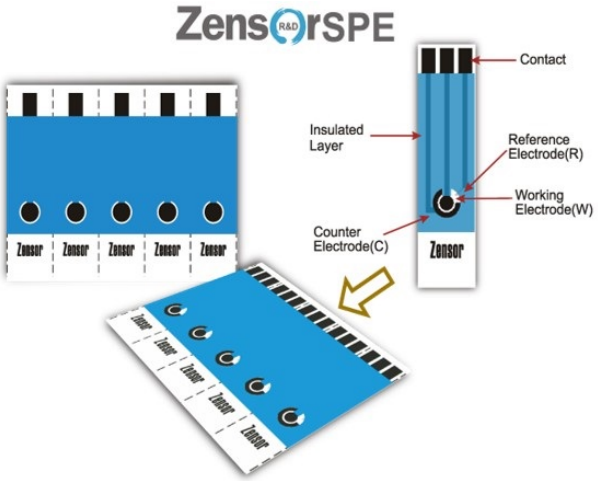


Figure 7. SERS spectra of (a) DTNB, (b) 4-ATP, (c) adenine, and (d) Cy3 from dsDNA adsorbed on substrate 2.

J. Phys. Chem. C 2015, 119, 24865−24874

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Cite this: *Phys. Chem. Chem. Phys.*, 2015, **17**, 26997

Impact electrochemistry: colloidal metal sulfide detection by cathodic particle coulometry†

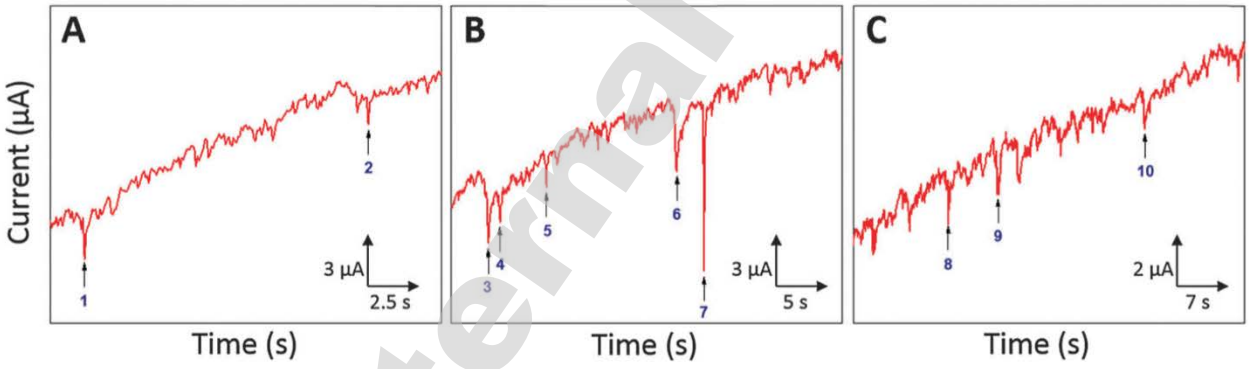
Chee Shan Lim and Martin Pumera*

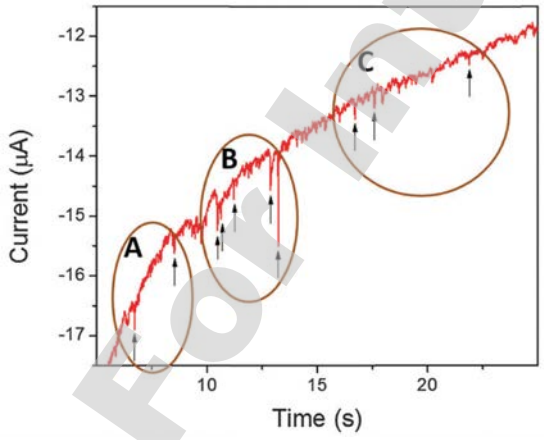
Received 22nd August 2015,
Accepted 8th September 2015

DOI: 10.1039/c5cp05004a

www.rsc.org/pccp

The determination of the size and concentration of colloidal nano and microparticles is of paramount importance to modern nanoscience. Application of the particle collision technique on metal and metal oxide nanoparticles has been intensively explored over the past decade owing to its ability to determine the particle size and concentration *via* reactions including the inherent oxidation or the reduction of nanoparticles as well as surface reactions catalysed by the nanoparticles. Transition metal dichalcogenide particles were previously quantified using the anodic (oxidative) particle coulometry method. Here we show that cathodic (reductive) particle coulometry can be favorably used for the detection of metal sulfide colloidal particles. The detection of sulfides of cobalt and lead was performed using the particle collision technique in this work. The presence of spikes confirmed the viability of detecting new and larger particles from compounds using reductive (cathodic) potentials. Such an expansion of the impact particle coulometry method will be useful and applicable to the determination of concentration and size of colloidal metal sulfide nanoparticles in general.





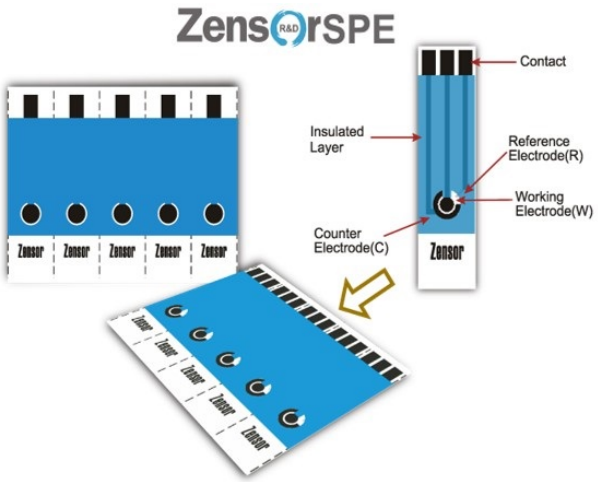


Fig. 3 Spikes selected for size determination study of CoS.

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Short communication

Susceptibility of FeS_2 hydrogen evolution performance to sulfide poisoning

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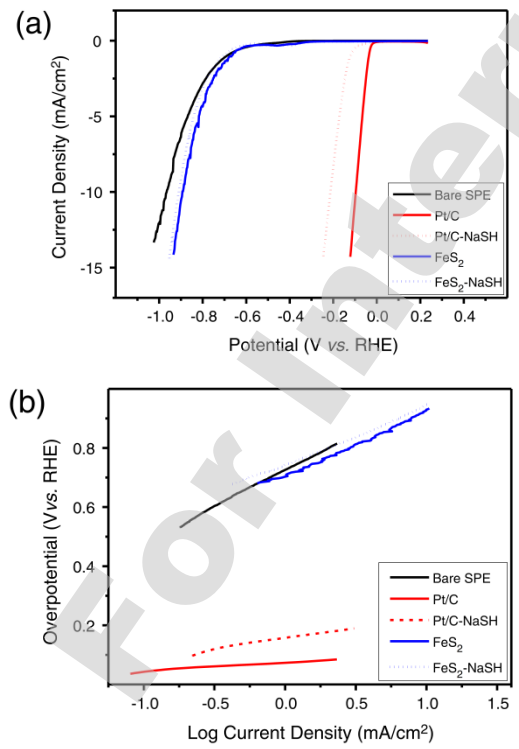
ARTICLE INFO

Article history:
Received 1 May 2015
Received in revised form 22 May 2015
Accepted 27 May 2015
Available online 3 June 2015

Keywords:
Hydrogen evolution reaction
Iron pyrite
Sulfide
Poisoning

ABSTRACT

The imminent depletion of fossil fuels raises concern over the need for next-generation clean energy. Of numerous alternatives, electrochemical water splitting is a promising method to store energy in the form of hydrogen. In order to benefit from this system, technological advancement in the development of affordable and efficient electrocatalysts for hydrogen evolution reaction is necessary. Transition-metal electrocatalysts composing of earth-abundant elements, specifically natural FeS_2, has demonstrated excellent performance for hydrogen evolution reaction. However, previous studies on platinum surfaces highlighted the detrimental effect toward hydrogen evolution performance upon poisoning of the active sites. In this work, we examine the susceptibility of natural FeS_2 toward sulfide poisoning. Our findings showed that the degradation effect from the introduction of sulfide to natural FeS_2 was not as severe as that observed on platinum. The overpotential (at a current density of 10 mA/cm^2) for natural FeS_2 and platinum increased by approximately 20 and 110 mV, respectively.



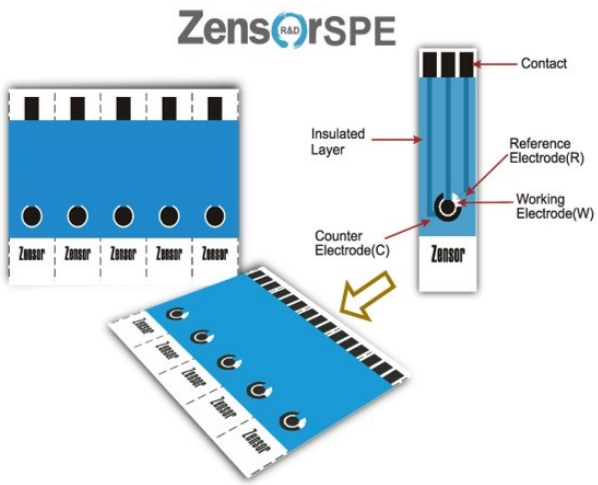


Fig. 3. Electrochemical characterization of bare screen printed electrode, Pt/C, poisoned Pt/C, FeS_2 and poisoned FeS_2 toward hydrogen evolution reaction. (a) Polarization curves of current density against potential. (b) Tafel-analysis of overpotential against the log of current density.

Electrochemistry Communications 58 (2015) 29–32