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Polyacrylamide-lithium chloride polymer electrolyte and its applications in electrochemical capacitors

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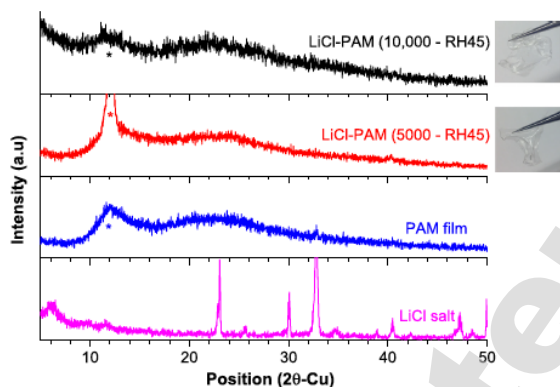
Neutral pH electrolyte

Polymer electrolyte

ABSTRACT

A neutral polymer electrolyte containing lithium chloride (LiCl) and polyacrylamide (PAM) was developed. The LiCl-PAM electrolyte film had an amorphous structure and an ionic conductivity $> 10 \text{ mS cm}^{-1}$. The addition of LiCl to the polyacrylamide did not alter the chemical bonding of PAM. Symmetric double layer capacitors (EDLC) were constructed using CNT-graphite electrodes. The solid EDLC retained approximately 85% of the capacitance achieved with a baseline cell in a LiCl aqueous solution. The solid EDLC devices demonstrated a wide voltage window (1.5 V), good cycle life ($> 10,000$ cycles), and excellent rate capability (up to 5 V s^{-1}).

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*: silicon vacuum grease

Fig. 2. XRD patterns of LiCl-PAM film vs. its components indicating the amorphous nature of the LiCl-PAM electrolyte. Inset: film appearance for both concentrations.

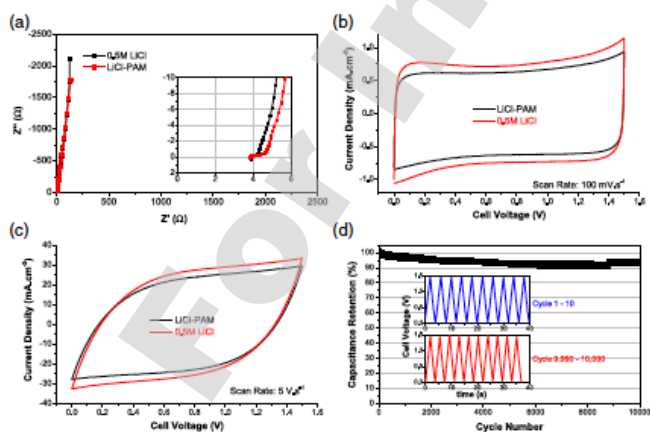


Fig. 4. Solid cell performance of CNT-graphite with LiCl-PAM(10000) electrolyte (—) vs. 0.5 M LiCl liquid electrolyte (---): (a) EIS spectra, inset at high frequency; (b) CV at 5 V s^{-1} ; (c) CV at 5 V s^{-1} ; and (d) capacitance retention up to 10,000 cycles with galvanostatic charge/discharge at 5 A g^{-1} current load, insets cycling profiles for first and last 10 cycles.

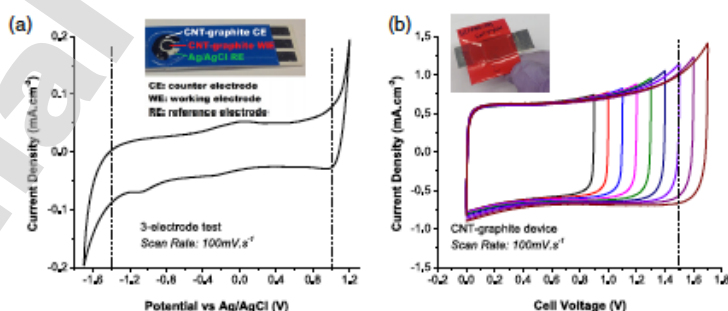
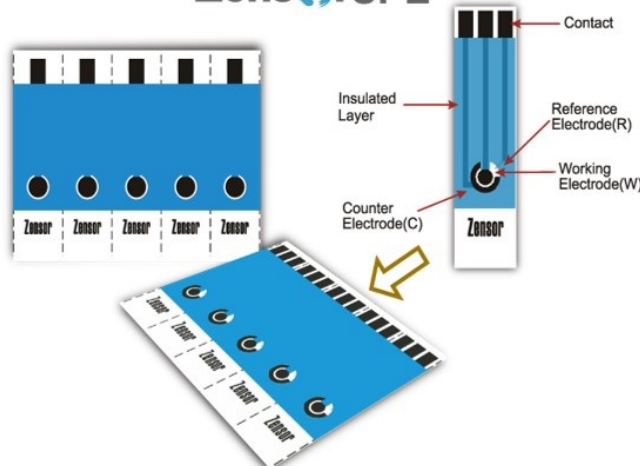


Fig. 3. LiCl-PAM(10000) electrochemical stability window with CNT-graphite electrode in (a) 3-electrode screen-printed and (b) incremental CV of symmetric cell; inset showing actual device.

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Highly active nanostructured water oxidation catalyst electrodeposited from Co(cyclam) complex

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Oxygen evolution reaction

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Cobalt complex

Modified electrode

Water splitting

ABSTRACT

The water soluble molecular complex $[\text{Co}(\text{cyclam})(\text{ClO}_4)]\text{ClO}_4$ (cyclam = 1,4,8,11-tetraazacyclotetradecane) is utilized as a precursor for deposition of highly active cobalt based nanostructured material on the electrode surface upon electrooxidation. The electrolysis of the complex at +1.1 V vs Ag/AgCl in 0.1 M potassium phosphate at pH 12 leads to the formation of a nanoporous Co(II) hydroxide/phosphate thin film on the printed carbon electrode. The deposited surface was characterized by scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDX), and X-ray photoelectron spectroscopy (XPS). The modified electrode (Co-PCE-12) is stable for more than 34 h during the continuous electrolysis. The modified electrode exhibits a high water oxidation catalytic activity of 6.5 mA cm^{-2} at an overpotential of 580 mV (0.9 V vs Ag/AgCl (3 M KCl) at pH 12) with 98% Faradaic yield.

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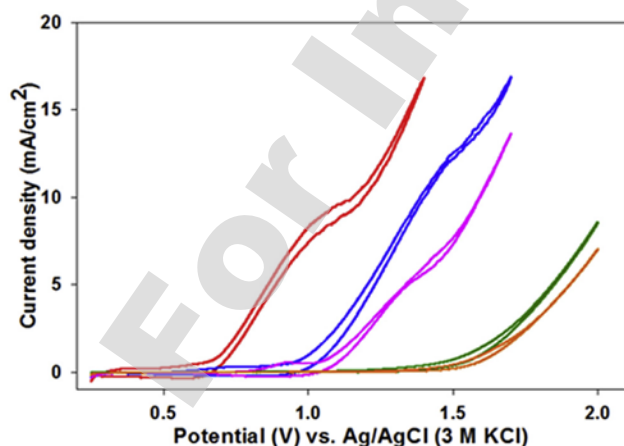
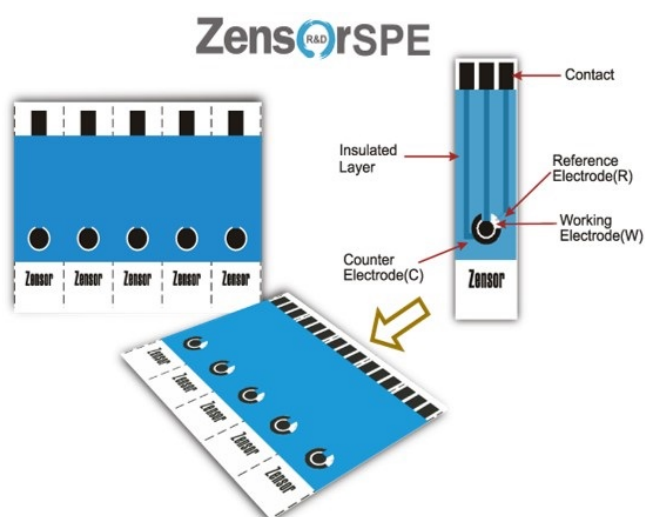


Fig. 5 – Cyclic voltammograms of Co-PCE-12 in 0.1 M KPi solutions with different pH values (12, 9, 7, 5.5, and 2, from left to right) under an Ar atmosphere. $v = 5 \text{ mV/s}$.





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Li_2SO_4 -polyacrylamide polymer electrolytes for 2.0 V solid symmetric supercapacitors

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ABSTRACT

A neutral polymer electrolyte comprised of lithium sulfate (Li_2SO_4) and polyacrylamide (PAM) was developed. The Li_2SO_4 -PAM electrolyte film shows an ionic conductivity up to 10 mS cm^{-1} in 45%RH conditions. Solid double layer capacitors were demonstrated using CNT-graphite electrodes and Li_2SO_4 -PAM solid electrolytes. The voltage window of the solid cell was about 2.0 V, identical to that of a Li_2SO_4 liquid cell used as baseline. The demonstrated voltage window is significantly larger than that reported for proton- or hydroxyl-conducting electrolytes, suggesting that the Li_2SO_4 -PAM electrolyte is a promising system for high energy density supercapacitors. The solid device also demonstrated excellent rate capability (up to 5 V s^{-1}) and good cycle life (beyond 10,000 charge/discharge cycles).

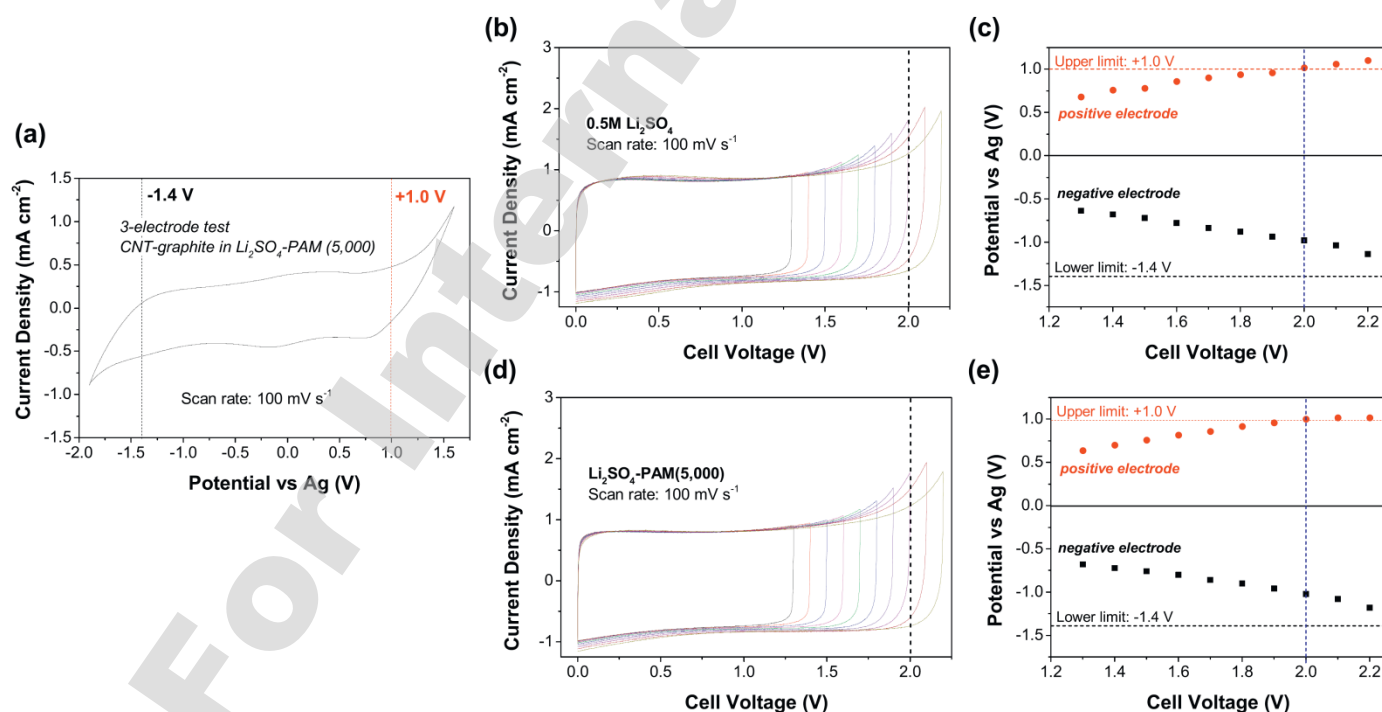


Fig. 1. Voltage window determined by (a) the full-range stability window with 3-electrode test of CNT-graphite electrodes in Li_2SO_4 electrolytes, along with cyclic voltammetry and simultaneous electrode polarizations of CNT-graphite cells with (b-c) 0.5 M Li_2SO_4 liquid electrolytes and (d-e) Li_2SO_4 -PAM(5000) solid electrolytes.

Surface modified catalytically grown carbon nanofibers/MnO₂ composites for use in supercapacitor

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ABSTRACT

We have reported a fast and eco-friendly method to synthesize the MnO₂ on catalytically grown carbon nanofiber (CGCNF). The CGCNF was functionalized by acid treatment under various H₂SO₄/HNO₃ ratios. A microwave-assisted hydrothermal method was then used to synthesize MnO₂/CGCNF composites at a very short time of 5 min. We demonstrated that the surface modification has significant effect on the MnO₂ deposition and the electrochemical performance of the resulting MnO₂/CGCNF composites. Electrical impedance spectroscopy analysis and cyclic voltammetry showed that O-functional group controls the electrical conductivity and the electrochemical performance of both CGCNF and CGCNF/MnO₂ composites, respectively. It was found that C=O bond assists the MnO₂ deposition. CGCNF/MnO₂ composite showing specific capacitance (C_{sp}) of 257 F/g at a scan rate of 5 mV/s and electrical resistance of 19 Ω was demonstrated.

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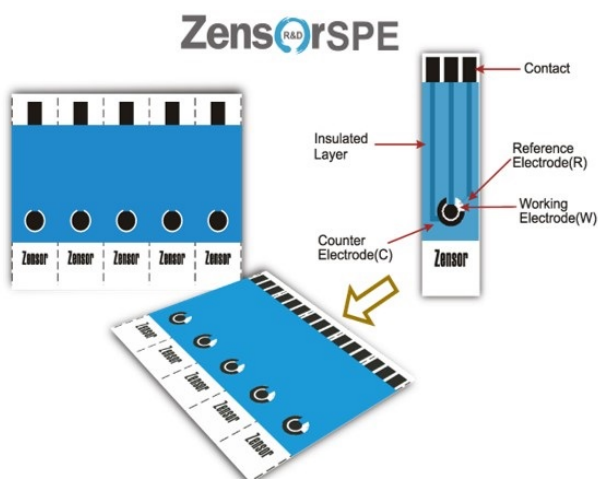
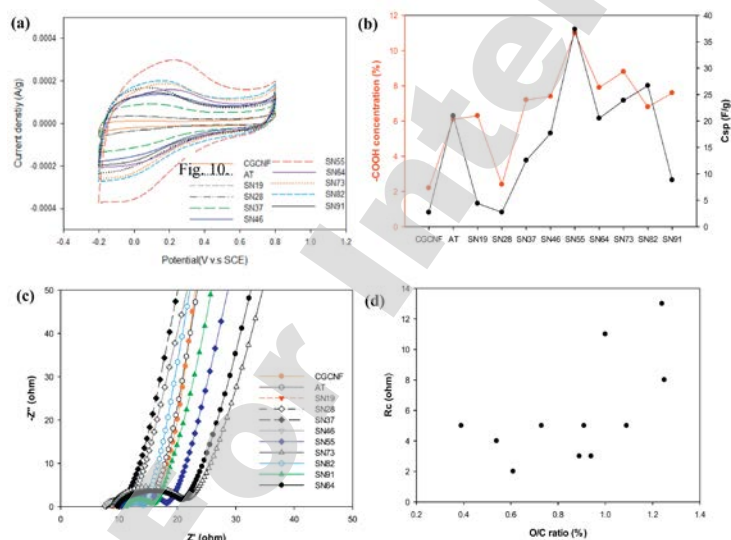


Fig. 9. (a) CV curves of CGCNF. (b) Variations of -COOH concentration and C_{sp} from sample to sample. (c) Nyquist plots of CGCNF. (d) R_c increases with the O/C ratio.

Electroactive Biofilm Serving as the Green Synthesizer and Stabilizer for *in Situ* Fabricating 3D Nanopalladium Network: An Efficient Electrocatalyst

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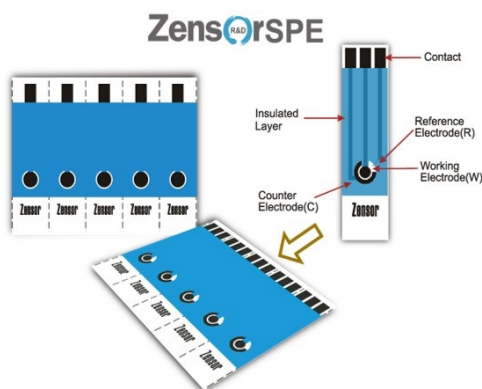
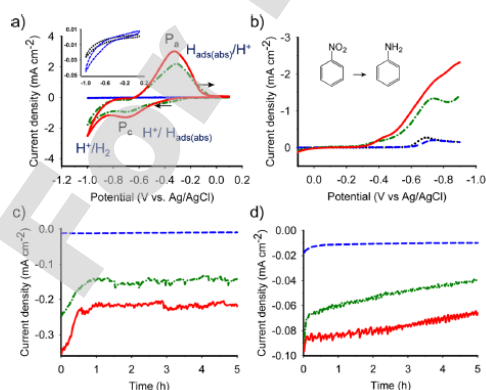
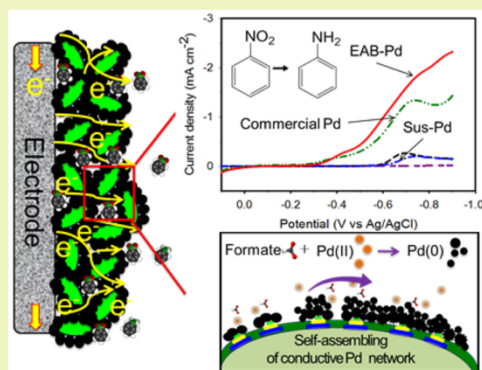
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Supporting Information

ABSTRACT: Biogenetic nanopalladium (bio-Pd) has attracted increasing attention recently due to its economical and environmental friendly synthesis route. However, traditional bacteria suspensions formed palladium (Sus-Pd) is limited to be the electrochemical catalyst owing to the poor conductivity of bacterial cells. Herein, we demonstrated Pd nanoparticles, synthesized by electroactive *Geobacter* biofilm, can form a three-dimensional conductive network (EAB-Pd) that is beneficial to the electrons transfer. As a result, the EAB-Pd delivered an over 5-fold increase of current compared to the Sus-Pd in hydrogen evolution and the reductive degradation of nitro-, azo- and chloroaromatics. Superior performance of EAB-Pd was also observed in comparison with the commercial Pd catalyst. A good stability of EAB-Pd has been further confirmed under electrochemical and mechanical stresses as well as through the reuse after over 3 months of storage. This novel proposed method enables the direct electrochemical application of bio-Pd without the previous required cell carbonization and chemical binders.

KEYWORDS: Nanopalladium, Electroactive biofilm, Conductive 3D network, *In situ* fabrication, Reductive catalysis



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A $\text{H}_5\text{BW}_{12}\text{O}_{40}$ –polyvinyl alcohol polymer electrolyte and its application in solid supercapacitors

Han Gao† and Keryn Lian*

A polymer electrolyte comprised of $\text{H}_5\text{BW}_{12}\text{O}_{40}$ (BWA) and cross-linked polyvinyl alcohol (BWA–XLPVA) has been developed and characterized for solid supercapacitors. The performance of this polymer electrolyte was compared to that of a known polymer electrolyte based on $\text{H}_4\text{SiW}_{12}\text{O}_{40}$ (SiWA). An enhanced proton conductivity was observed for BWA–XLPVA compared to its SiWA counterpart, especially under low humidity conditions (5% RH). Dielectric analyses revealed an increase of proton density and proton mobility in the BWA-based electrolyte. A solid-state ^1H NMR study showed that all protons in the BWA-based electrolyte were hydrated in the low humidity environment. This indicated that BWA had more crystallized water content than SiWA, resulting in higher proton mobility in the PVA matrix. An *in situ* tracking of electrode potential in solid supercapacitors was utilized to identify the reactions and the factors limiting solid supercapacitor cell voltage for both BWA- and SiWA-based polymer electrolyte systems. A solid device leveraging the BWA-based polymer electrolyte achieved a cell voltage of 1.3 V, 0.2 V wider than that of a SiWA-based device.

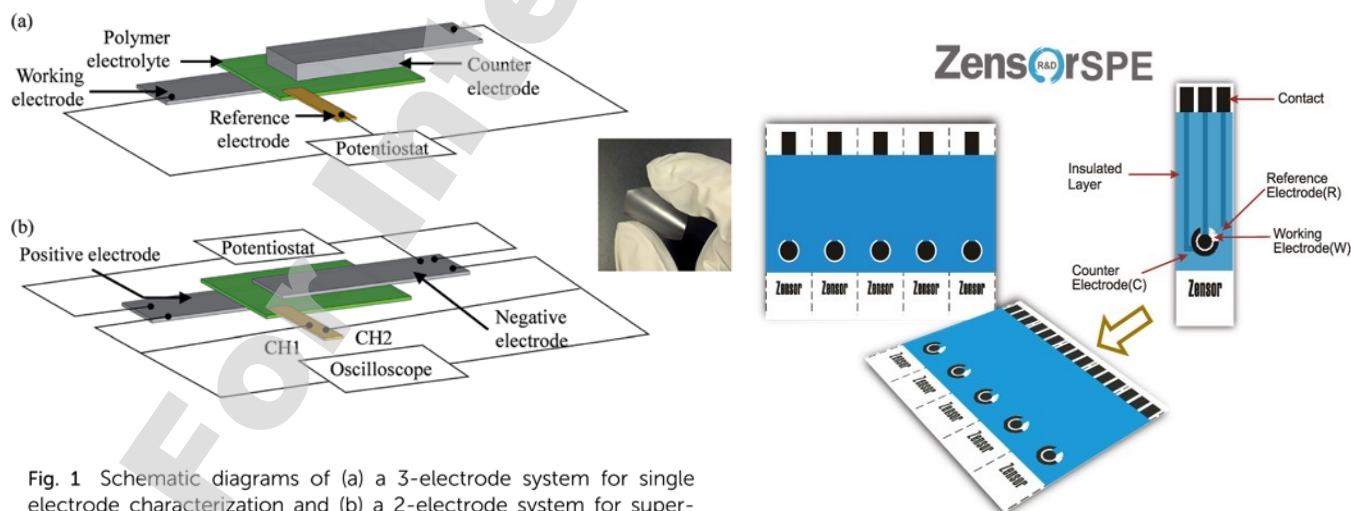


Fig. 1 Schematic diagrams of (a) a 3-electrode system for single electrode characterization and (b) a 2-electrode system for supercapacitor device characterization with *in situ* potential tracking (the inset shows a photograph of a polymer electrolyte film).

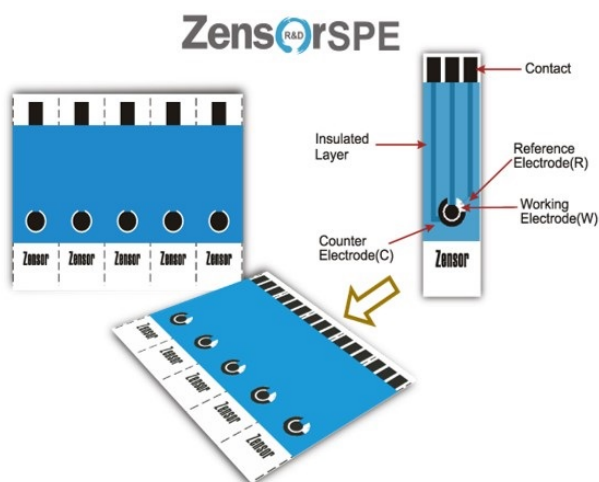
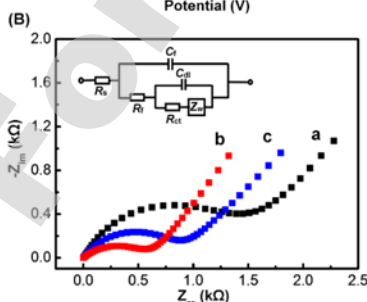
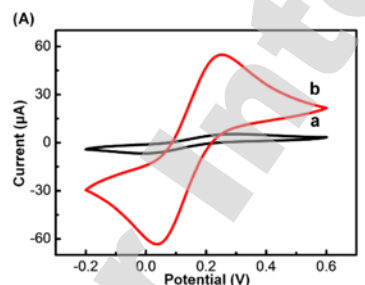
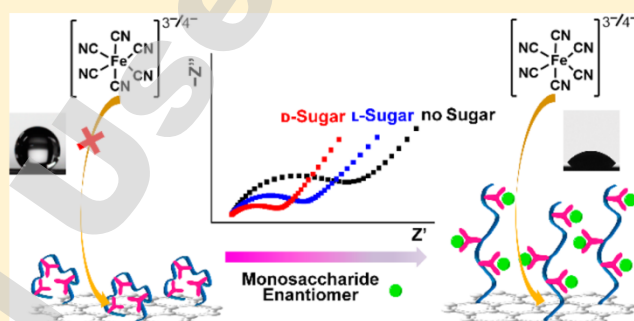
Wettability Switching of Electrode for Signal Amplification: Conversion of Conformational Change of Stimuli-Responsive Polymer into Enhanced Electrochemical Chiral Analysis

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Supporting Information

ABSTRACT: Signal amplification of chiral interaction is a much needed task for sensing of enantiomers due to nearly identical chemical and physical properties of the chiral isomers. In this article, we established an electrochemical chiral sensing method with high sensitivity and selectivity for monosaccharides based on the stimuli-responsive copolymer/graphene hybrid-modified screen-printed carbon electrodes. The hybrid synthesized by the “grafting from” atom transfer radical polymerization (ATRP) process not only acted as a chiral recognition element but also provided a chiral signal amplification strategy. This occurs due to high sensitivity of conformational transition of copolymer on graphene to the weak chiral interactions that greatly facilitating the diffusion of electroactive probes and monosaccharides to the electrode surface. The described method can quantify monosaccharides, even the concentration of one enantiomer is as low as 1 nM. Apart from the demonstrated chiral distinguish ability, good selectivity toward monosaccharides in comparison to potential interference molecules was also observed. The electrodes with significant analytical performance were successfully applied for discriminating glucose enantiomers in live cells and studying their different transport mechanism. Together, the results show that the coupling of amplification-by-wettability switching concept with electrochemical method offers great promises in providing a sensitive, facile, and cost-effective solution for chiral recognition of molecules in biological process.



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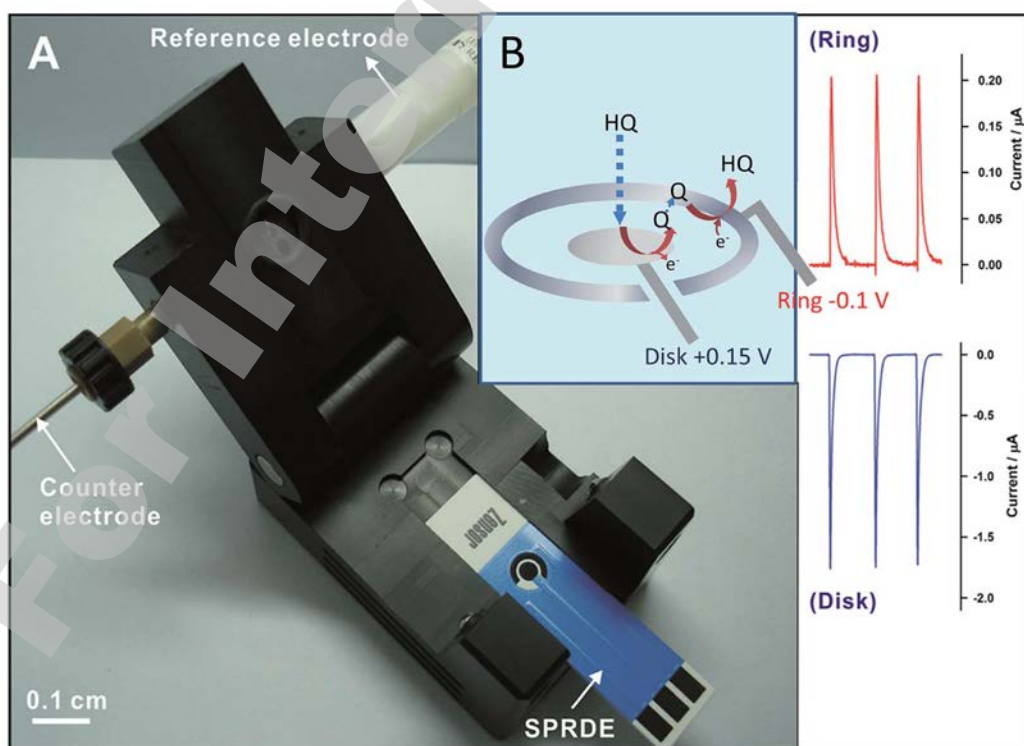
Self-validated detection of hydroquinone in medicated cosmetic products using a preanodized screen-printed ring disk carbon electrode

Hsueh-Hui Yang,^{*a} Hsiao-Han Ting^b and Ying Shih^{*b}

An anodically pretreated screen-printed ring disk carbon electrode (SPRDCE*) coupled with a flow injection analysis system was developed as a simple, rapid, sensitive, and self-validated hydroquinone (HQ) sensor. HQ was electrocatalytically oxidized at the preanodized disk electrode and the oxidized product *para*-benzoquinone was then electrocatalytically reduced to HQ at the preanodized ring electrode. A well-defined and quasireversible redox peak couple was observed. The amount of HQ could be determined by using the catalytic current from the SPRDCE*. Besides, it is also worth noting that the performance of this system could be validated directly by using the redox current ratio (the reduction current at the ring electrode divided by the oxidation current at the disk electrode). Under optimized conditions, a linear range for HQ at the disk electrode was in the range of 0.25–160 ppm with 0.999 and 0.024 ppm for the correlation coefficient and the detection limit ($S/N = 3$), respectively. Using this method, HQ in cosmetic products was successfully quantified without any pre-treatment with recoveries between 97.76% and 103.74%.

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Scheme 1 Schematic representation for monitoring of HQ using the SPRDCE* coupled with FIA.

Digital pH Test Strips for In-Field pH Monitoring Using Iridium Oxide-Reduced Graphene Oxide Hybrid Thin Films

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Supporting Information

ABSTRACT: While pH test strips are not decimally accurate and only semiquantitative, the more accurate and automated laboratory-based pH meters lack disposability and portability. Benefiting from advantages of both sides and filling the gap of unmet needs in between, we integrated a miniaturized paper-fluidic electrochemical pH platform coupled with a portable pH device powered by consumer batteries to make digital pH test strips for truly in-field measurements. To overcome the inability to form the smooth and uniform pH-sensitive iridium oxide thin films (AEIROFs), reduced graphene oxide was used as substrate for synthesis of homogeneous metal oxide–nanocarbon hybrid thin films, IrO₂-reduced graphene oxide (IrO₂-rGO), as the sensing moiety with strong substrate adhesion. A hydrophobic barrier-patterned paper micropad (μ PAD) with programmed flow rates can locally accelerate linear wicking speed to boost delivery and response time. IrO₂-rGO shows slightly super-Nernstian linear responses from pH 2 to 12 with small hysteresis, fast response time, reproducible performances, and low sensitivities to interfering ionic species and dissolved oxygen. A miniaturized portable pH device made of high-impedance buffer amplifier and off-the-shelf digital multimeter provides results consistent with those of a commercial pH meter equipped with a glass electrode. Our system combines the accuracy of pH meters with the low-cost and convenience of pH strips, making it ideal for resource-limited settings.

KEYWORDS: iridium oxide, graphene, paper-fluidic, potentiometric sensor, pH sensor, electrochemistry, programmed flow rate, hydrophobic patterning

