Nanostructured electrodes have garnered a great amount of interest in the field of electrochemistry due to their interesting and sometimes superior properties compared to bulk analogs. Nanomaterials have been widely used for the preparation of energy storage and conversion devices as well as sensors, biosensors, and bioelectronics. Such applications have largely been driven by the advantageous properties of nanomaterials, such as their large surface areas, electrocatalytic capabilities, and/or abilities to facilitate electron transport between bulk materials and electrochemically active biological materials.

One simple and widely used technique for preparing nanostructured electrodes, called the layer-by-layer (LbL) method, involves adsorption of successive layers or films of different materials onto an underlying conductive bulk surface. Adjacent layers usually associate through electrostatic interactions between materials of opposite charge. Film stability can also be affected by other intermolecular forces such as hydrogen bonding, hydrophobic interactions, and Van der Waal’s forces. LbL-constructed nanostructured electrodes have found use in the preparation of supercapacitors and proton-exchange membrane fuel cells (PEMFCS) as well as chemical sensors and biosensors.

Sensors and biosensors prepared by LbL methods often employ ionic polymers like poly(diallyldimethylammonium chloride) (PDDA) and/or polystyrene sulfonate (PSS) to facilitate adsorption of metal, semiconductor, or carbon-based nanoparticles (e.g., nanospheres, nanorods, nanotubes or graphene sheets) typically onto a bulk carbon or gold electrode. In addition to conventional disk-shaped glassy carbon, pyrolytic carbon, and gold electrodes, screen-printed electrodes have also found wide use as platforms for LbL-based sensors and biosensors. Screen printing enables low-cost, customizable sensor design and provides opportunities to tailor electrode properties through ink formulation and pattern geometry.

Inks for preparing screen-printed electrodes typically consist of conductive particles distributed with one or more polymeric binders (e.g., poly(vinyl chloride), poly(vinyl acetate), etc.) in a solvent (e.g., cyclohexanone, mesitylene, etc.). Manual, semi-automatic, or automatic screen-printing may be employed using inks prepared from raw materials or purchased from commercial sources. Pre- and custom-designed screen-printed electrodes are also available from several manufacturers.

Application of LbL methods to screen-printed carbon electrodes (SPCEs) provides a relatively simple, cost-effective, and versatile strategy for producing nanomaterial-modified electrodes. When employed as platforms for sensing and biosensing, such electrodes reportedly exhibit improved electrochemical properties (e.g., enhanced response and/or superior electron-transfer kinetics over bare SPCEs). One benefit provided by nanoparticles that is typically asserted as important in rationalizing the augmented response of nanomaterial-modified SPCEs over bare SPCEs is the increase in electroactive surface area provided by the inclusion of nanomaterials on the electrode surface. The electroactive surface area, A, is often determined (in cm²) through voltammetric studies of common redox probes by employing the Randles–Ševčik equation (at 25°C):

$$i_p = \frac{2.69 \times 10^5 n^{1/2} A D^{1/2} C v^{1/2}}{\gamma}$$

where $i_p$ is the peak current in amperes, $n$ is the number of electrons involved in the electrode reaction, $D$ is the diffusion coefficient (in cm² s⁻¹) of the electroactive species (redox probe), $C$ is the bulk concentration of the electroactive species (in mol cm⁻³), and $v$ is the scan rate (in V s⁻¹). Using this method with Fe(CN)₆⁴⁻/₃⁻ as the redox probe, a previous report established that the electroactive surface area of SPCEs can be increased by 102% by employing an LbL strategy to modify the electrode surface with glutathione-capped gold nanoparticles (AuNPs).

Recent studies with highly ordered pyrolytic graphite (HOPG) and graphene-modified electrodes have indicated that characterization of carbon electrodes through use of the Fe(CN)₆³⁻⁻/₄⁻ redox couple can result in misinterpretation of their electrochemical properties. For example, the cyclic voltammetric (CV) response of HOPG electrodes using 1 mM Fe(CN)₆³⁻ in 0.1 M KCl was found to depend on time. Freshly cleaved HOPG surfaces exhibited voltammetric peak-to-peak separation ($\Delta E_p$) values near 59 mV as expected for an electrochemically reversible process, while aged HOPG surfaces produced much larger $\Delta E_p$ values and lower peak currents for the Fe(CN)₆³⁻⁻/₄⁻ redox couple that are suggestive of poorer electron transfer kinetics. In contrast, similar experiments with Ru(NH₃)₆³⁺/²⁺ did not indicate any significant difference between the electrochemical behaviors of freshly cleaved and aged HOPG electrodes. CV studies of graphene-modified electrodes using Fe(CN)₆³⁻⁻, Ru(NH₃)₆³⁺, and ferrocene methanol (FcMeOH) produced similar results, with Fe(CN)₆³⁻⁻ exhibiting sensitivity to supporting electrolyte solution and electrode surface conditions that were not observed with either Ru(NH₃)₆³⁺ or FcMeOH.

Overall, these studies suggest that the Fe(CN)₆³⁻⁻/₄⁻ redox couple may be a poor choice for the electrochemical characterization of some carbon-based electrodes due to its somewhat unique surface sensitivity.
compared to other common outer-sphere redox probes. This sensitivity can result in complicated, non-ideal, and unpredictable behavior. Variations in the response of the Fe(CN)$_6^{3-/-4-}$ redox couple on HOPG and graphene-modified electrodes have been used to help explain the wide disparities in reported electrochemical behaviors of carbon nanotubes and graphene as well as the perceived dependence of electrochemical properties of carbon materials on edge and basal plane surfaces and defects.21–23 Such observations suggest that care must be taken when employing Fe(CN)$_6^{3-}$ as a redox probe to characterize the electrochemical properties of carbon-based electrodes.21

While the electrochemical characteristics of SPCEs have been widely reported, many of these studies have relied on interpretation of SPCE response with the Fe(CN)$_6^{3-/-4-}$ redox couple.13,17,18,25,26 Furthermore, the improvement in electroactive surface area previously reported for LbL construction of AuNP-modified SPCEs was based on differences between the CV responses of Fe(CN)$_6^{3-/-4-}$ on AuNP-modified and bare SPCEs.17,18 Here, we investigate the electrochemical responses of Fe(CN)$_6^{3-/-4-}$ and other redox probes (Ru(NH$_3$)$_6^{3+/-4+}$ and FeCMeOH) using bare and LbL-modified SPCEs to determine the importance and role of AuNPs in improving electrochemical properties of modified SPCEs. The extent of AuNP coverage and effect of AuNPs on the electroactive surface area of modified SPCEs are also addressed. The results of these studies may have wider implications to other types of modified SPCEs that are used as sensing platforms and the characterization of their electrochemical properties.

Experimental

Materials.—Potassium ferricyanide and sodium borohydride were obtained from Fisher Scientific. Ferrocene methanol and 20 wt% poly(diallyldimethylammonium chloride) (PDDA) solution (average MW 200,000-350,000) in water were obtained from Sigma-Aldrich. Hexaamineterminthium (III) chloride was purchased from Strem Chemicals. Hydrogen tetrachlorouraque (III) hydrate and L-glutathione were obtained from Alfa Aesar. All solutions were prepared using 18.2 MΩ·cm ultrapure water prepared by passing deionized water through a Millipore Synergy UV purification system. Screen-printable carbon graphite (C2050106D7) and Ag/AgCl (C2051014P10) inks were supplied by Gwent Electronic Materials Ltd (Pontypool, UK).

Fabrication of screen-printed carbon electrodes (SPCEs).—Electrodes were prepared from graphite and Ag/AgCl inks by manual screen printing using a 200 mesh screen coated with diazo photo emulsion. Patterns that define electrodes, conductive paths, and contact pads were printed on acetate tracing paper using an inkjet printer and placed under an 8 in. × 10 in. piece of glass on top of the photo emulsion-coated screen. Patterns were transferred to the screen by exposure using a 150 W clear incandescent bulb at a height of 18" above the screen for 7 min.

Using a squeegee, graphite ink was forced through the screen and transferred onto a cellulose acetate sheet (transparency film) to produce contact pads, conductive paths for electrode connection, and working and counter electrodes. The pattern that defined graphite ink designs featured three 2 mm × 5 mm (w × l) contact pads each connected to a 1 mm × 20 mm conductive path, a circular 2 mm diameter working electrode connected to the center conductive path, and a 2 mm-wide arc-shaped counter electrode (inner arc radius 2 mm) connected to one of the outer conductive paths (Figure 1). Ink was cured in an oven for 30 min at 60 °C. Ag/AgCl ink was forced through a 2 mm-wide arc-shaped pattern (inner arc radius 1 mm) on the screen to form the reference electrodes on top of the third conductive path. After Ag/AgCl ink deposition, curing was again carried out for 30 min at 60 °C. Kapton tape was placed over printed conductive paths for insulation and to help define working electrode area. Geometric areas of working electrodes were measured from digital photographic images using ImageJ.27 The average geometric area of the working electrodes used in electrochemical studies was 2.52 ± (0.29) × 10⁻² cm² (n = 10).

Figure 1. Exploded view of design (a) and photographic image (b) of screen-printed electrode.

Synthesis of glutathione-capped gold nanoparticles.—Glutathione (GSH)-capped gold nanoparticles (AuNPs) were prepared according to previous reports.17,19 Briefly, 19.7 mg hydrogen tetrachlorouraque hydrate and 7.7 mg L-glutathione were dissolved in a mixture of methanol and acetic acid (86:14 by vol%). The solution was rapidly stirred using a magnetic stirrer, and 1.5 mL of a 0.53 mM sodium borohydride solution was added dropwise. Addition of the sodium borohydride solution was immediately accompanied by a change in color of the solution from bright yellow to brown. After 2 hours of continued stirring, the suspension was filtered through 50 kDa MW cutoff filter centrifuge tubes by centrifugation at 2150×g for 8 minutes. Particles were resuspended in 20 mM HEPES buffer, pH 8.0, and centrifugation was repeated four times followed by final resuspension in HEPES buffer. UV-Vis spectra of 10-fold diluted particle suspension exhibited a characteristic absorbance peak at 515 nm. Estimation of particle size from UV-Vis absorbance28 indicated particle diameter of 4–5 nm, which is in agreement with similarly prepared particles in previous reports.17,19

Layer-by-layer deposition of AuNPs on SPCEs.—Screen-printed carbon electrodes (SPCEs) were pretreated by performing a linear voltammetric sweep from −1.2 to +1.5 V vs. Ag/AgCl at 100 mV s⁻¹.25 After pretreatment, electrodes were rinsed with ultrapure water and dried. AuNPs were deposited on the SPCE via a previously reported layer-by-layer deposition technique.17,19 A micropipette was used to deliver 2 μL of 2 mg mL⁻¹ PDDA in 50 mM NaCl to the working electrode. After 20 minutes, the PDDA-modified electrode was rinsed with ultrapure water and dried. 2 μL of AuNP suspension was then added to the working electrode surface. After 20 minutes, the AuNP/PDDA-modified electrode was rinsed with ultrapure water to remove any excess AuNPs.

Electrochemical measurements.—All electrochemical measurements were performed using a CHI 400 operating in potentiostatic mode. Bare, PDDA-modified, and AuNP/PDDA-modified electrodes were placed in a 10 mL beaker filled with potassium ferricyanide, hexaamineterminthium (III) chloride, or ferrocene methanol (FcMeOH) in 0.1 M KCl, and cyclic voltammetry (CV) was performed at 10–200 mV s⁻¹. Measured currents were converted to current densities by normalization with the geometric area for each electrode.

Results

Cyclic voltammetry of common redox probes using bare and modified SPCEs.—Among the three redox probes used in these studies, the largest differences between bare and modified SPCEs were exhibited through use of Fe(CN)$_6^{3-/-4-}$ (Figure 2). For the Fe(CN)$_6^{3-/-4-}$ redox couple, bare SPCEs presented smaller peak current densities (jₚ = iₚ/Aₑ) (Table I) and larger ΔEₛ (Table II) compared to PDDA and AuNP/PDDA-modified SPCEs. While all ΔEₛ values are significantly larger than 59 mV that is indicative of an electrochemically reversible process, 217 (+ 49) mV for Fe(CN)$_6^{3-/-4-}$ determined in these studies using bare SPCEs is comparable to the value found with analogous measurements (234 mV) using SPCEs that exhibited edge plane-like properties.29
There were no significant differences between \( j_p \) and \( \Delta E_p \) for the Fe(CN)\(_6^{3−/4−}\) redox couple between PDDA- and AuNP/PDDA-modified SPCEs at the 95% confidence level. However, PDDA-modified SPCEs typically displayed post-reduction and pre-oxidation waves or peaks (Figure 2a) that were not present in CVs using AuNP/PDDA-modified electrodes. Post- and pre-peak waves for the Fe(CN)\(_6^{3−/4−}\) redox couple were evident for 70% (7 out of 10) of the PDDA-modified electrodes used in these studies. Even without this behavior, PDDA-modified electrodes still produced Fe(CN)\(_6^{3−/4−}\) peak currents that were similar to those obtained using AuNP/PDDA-modified SPCEs (Figure 2b). In contrast to the Fe(CN)\(_6^{3−/4−}\) redox couple, the Ru(NH\(_3\))\(_6^{3+/2+}\) and FcMeOH/FcMeOH\(^+\) redox couples exhibited no significant differences for \( j_p \) or \( \Delta E_p \) between bare, PDDA-modified, and AuNP/PDDA-modified electrodes at the 95% confidence level. However, \( j_p \) varied by as much as 15%, and \( \Delta E_p \) varied by as much as 27% among electrodes with like surface modifications. These differences in \( j_p \) and \( \Delta E_p \) as well as those in CVs of PDDA-modified electrodes may result from variations in the distribution of edge plane, basal plane, and polymeric domains\(^{30}\) in the SPCEs due to ink inhomogeneity or inconsistencies in the manual screen printing process.

### Table II. Peak separation (\( \Delta E_p \)) for various redox couples in 0.1 M KCl with bare and modified SPCEs using voltammetric scan rate of 100 mV s\(^{-1}\).

| SPCE Modification | 1 mM Fe(CN)\(_6^{3−}\) | 0.5 mM FcMeOH/FcMeOH\(^+\) | 1 mM Ru(NH\(_3\))\(_6^{3+/2+}\) |
|-------------------|-----------------|-----------------|-----------------|
| None (Bare)       | 217 (±49)       | 90 (±17)        | 109 (±29)       |
| PDDA              | 133 (±30)       | 94 (±17)        | 113 (±25)       |
| AuNP/PDDA         | 136 (±34)       | 102 (±18)       | 117 (±32)       |

The rate parameter \( \Lambda \) is related to the parameter \( \psi \) that is used to estimate the electron transfer rate constant \( k_0 \) (in cm s\(^{-1}\)) from CV measurements via the Nicholson method:\(^{20,32}\)

\[
\Lambda = \frac{n^{1/2}}{D_0 D_n^0 f n v} \quad (3)
\]

where \( D_0 \) and \( D_n^0 \) are the diffusion coefficients of the oxidized and reduced forms of the redox probe, respectively, and \( v \) corresponds to...
The ratio of electroactive to geometric surface area (\( R_A = A/A_{geo} \)), also called the roughness factor, has been previously used to characterize SPCEs as a means to describe the extents of these electroactive and inactive domains.\(^{13,33} \) Upon converting this ratio to a percentage for bare SPCEs, results with FcMeOH and Ru(NH\(_3\))\(_6^{3+}\) indicated \( R_A \) to be 113 (±5)% and 110 (±10)% respectively. In contrast, an \( R_A \) value of 71(±10)% was obtained using the electroactive surface area determined from Fe(CN)\(_6^{3-}\) experiments. Similar measurements for various commercially available SPCEs ranged from 39–79% using Fe(CN)\(_6^{3-}\).\(^{13} \)

**Electron transfer kinetics.**—Heterogeneous electron transfer rate constants \( k_0 \) were determined through the Nicholson method using the linear relationship between \( \psi \) and \( \nu^{-1/2} \) (Eq. 3). The same literature values listed above for \( D \) in Eq. 2 were used for \( D_0 \) for Fe(CN)\(_6^{3-}\) and Ru(NH\(_3\))\(_6^{3+}\) and \( D_0 = D_0 \) for Fe(CN)\(_6^{3-}\) in Eq. 3. Literature values of 6.5 × 10\(^{-6}\) and 1.19 × 10\(^{-5}\) cm\(^2\) s\(^{-1}\) were used for \( D_0 \) of Fe(CN)\(_6^{3-}\) and Ru(NH\(_3\))\(_6^{3+}\), respectively.\(^{20,38} \) Surface modification did not appear to have an effect on \( k_0 \) for Fe(CN)\(_6^{3-}\)/FcMeOH or Ru(NH\(_3\))\(_6^{3+}/2+\), as there were no differences between rate constants obtained with bare, PDDA-, and AuNP/PDDA-modified SPCEs. Rate constants for FeMeOH/FeMeOH\(^+\) and Ru(NH\(_3\))\(_6^{3+}/2+\) were found to be 6.8 (±2.1) × 10\(^{-3}\) and 4.1 (±1.7) × 10\(^{-3}\) cm\(^2\) s\(^{-1}\) respectively. Using Fe(CN)\(_6^{3-}\), there was no significant difference between \( k_0 \) values obtained with PDDA- and AuNP/PDDA-modified SPCEs. The average \( k_0 \) for Fe(CN)\(_6^{3-}\)/FeMeOH using modified electrodes was found to be 2.8 (±1.2) × 10\(^{-3}\) cm\(^2\) s\(^{-1}\), while a value of 1.20 (±0.25) × 10\(^{-3}\) cm\(^2\) s\(^{-1}\) was determined for \( k_0 \) for the same system with bare SPCEs. Electron transfer rate constants between 1.67 × 10\(^{-3}\) and 8.2 × 10\(^{-3}\) cm\(^2\) s\(^{-1}\) have been reported for Fe(CN)\(_6^{3-}\)/FcMeOH using other SPCEs.\(^{13,25,36,37} \)

**Evaluation of AuNP surface coverage.**—Voltammograms of AuNP/PDDA-modified SPCEs in 0.5 M H\(_2\)SO\(_4\) exhibited characteristic peaks at +1.25 (±0.010) V and +0.66 (±0.025) V corresponding to the oxidation and subsequent reduction of AuNPs, respectively (Figure 4).\(^{36,39} \) Surface areas attributed to AuNPs for AuNP/PDDA-modified SPCEs were estimated using the charge associated with the reduction peak at +0.66 (±0.025) V.\(^{36,40} \) For a monolayer of gold, the integration of this reduction peak results in a charge of 400 \( \mu \)C cm\(^{-2}\).\(^{40} \) The surface area of AuNP/PDDA-modified SPCEs determined from voltammetry in this way was 1.69 (±0.34) × 10\(^{-3}\) cm\(^2\), which corresponds to a surface area of 67 (±9)% of the electroactive surface area determined for AuNP/PDDA-modified correlates to 62 (±12)% of the electroactive surface area determined from studies with Fe(CN)\(_6^{3-}\), FcMeOH/FcMeOH\(^+\), and Ru(NH\(_3\))\(_6^{3+}/2+\) redox couples, confirming the presence of electroactive sites distributed within an electro-inactive matrix.
ing that, though AuNPs were able to participate in electron transfer processes, their presence did not significantly improve the electroactive surface area of SPCEs.

Discussion

An increase of 102% in electroactive surface area has been reported when AuNPs are deposited on SPCEs using a PDDA-based LbL electrostatic adsorption method.17 However, the improvement in surface area was determined from voltammetric studies that employed Fe(CN)₆³⁻/⁴⁺ as the redox probe. Difficulties using Fe(CN)₆³⁻/⁴⁺ as a redox couple for the characterization of some other carbon electrodes have been previously documented. For example, it has long been known that the electron transfer kinetics of Fe(CN)₆³⁻/⁴⁺ are dependent on the presence and charge state of surface carboxylate groups as well as the surface history for glassy carbon and carbon paste electrodes.31,42 Recent studies have drawn similar conclusions about the surface sensitivity of the electrochemical response of Fe(CN)₆³⁻/⁴⁺ on HOPG and graphene-modified electrodes.21–23 Here, we report evidence that suggests caution must also be practiced when characterizing SPCEs using Fe(CN)₆³⁻/⁴⁺.

Previous work with AuNP/PDDA-modified carbon electrodes17,19 did not seem to address the possible role of PDDA in the observed peak current increase and attributed the enhancement in voltammetric signal over bare electrodes entirely to the presence of AuNPs. In studies here, voltammetric responses of PDDA-modified SPCEs were comparable to both bare and AuNP/PDDA-modified SPCEs when Fe₃O₄ or Ru(NH₃)₆³⁺ was used as the redox probe. The only significant differences between the bare and modified SPCEs were found when Fe(CN)₆³⁻/⁴⁺ was used as the redox probe, with bare SPCEs exhibiting larger ∆Eₚ and smaller iₚ than PDDA- and AuNP/PDDA-modified SPCEs. Similarly large ∆Eₚ values for the Fe(CN)₆³⁻/⁴⁺/⁴⁻ redox couple have been previously reported for commercially available SPCEs,12,25,29,36 as well as HOPG21 and graphene-modified2,23 electrodes. The response of boron-doped diamond electrodes modified with carboxylate-functionalized graphene was found to depend on electrolyte pH with pH < 8 corresponding to larger ∆Eₚ and smaller iₚ for the Fe(CN)₆³⁻/⁴⁺ redox couple.25 Comparison of the electrochemical behavior of Fe(CN)₆³⁻/⁴⁺ with SPCEs prepared from graphite and graphene inks showed larger ∆Eₚ for electrodes with more basal plane-like composition and lower content of oxygenated species.29

Interestingly, gold30 and platinum31 screen-printed electrodes also reportedly exhibit larger ∆Eₚ for the Fe(CN)₆³⁻/⁴⁺/⁴⁻ redox couple. ∆Eₚ for the Fe(CN)₆³⁻/⁴⁺ redox couple decreased from 330 to 90 mV by electrodeposition of an additional layer of gold nanoparticles onto gold screen-printed electrodes,43 perhaps suggesting that conductive particle distribution in the cured ink and/or binder composition is also important in determining the electrochemical response of screen-printed electrodes. Indeed, ∆Eₚ for the Ru(NH₃)₆³⁺/²⁺ redox couple with SPEC prepared from custom-formulated inks was found to depend on the ratio of poly(vinyl chloride) binder to conductive pyrolytic graphite particles, with inks that featured lower percentages of binder producing smaller ∆Eₚ.30 Surface treatments, such as exposure to organic solvents18,31 and mechanical polishing,18,31 have also been found to affect ∆Eₚ for common redox couples. Peak currents for Fe(CN)₆³⁻/⁴⁺ increased by ~8x for SPCEs after mechanical polishing using an agate lapping hammer.18 In a separate study, polishing SPCEs with alumina had no significant effect on electroactive surface area determined by outer-sphere redox probe Ru(NH₃)₆³⁺/²⁺ but improved electrochemical activity toward nitrite by two-fold.31 Treatment of SPCEs with N,N-dimethylformamide was reported to increase the electroactive surface area to 57-fold over the geometric area based on measurements with Fe(CN)₆³⁻/⁴⁺.28 However, this drastic improvement was challenged based on more modest improvements (<1.38-fold) found for the response of similarly treated SPCEs toward Ru(NH₃)₆³⁺/²⁺, capsaicin, and dihydronicotinamide adenine dinucleotide.44

In studies reported here, PDDA-modified SPCEs exhibited voltammetric peak currents that were comparable to those obtained with AuNP/PDDA-modified SPCEs using Fe(CN)₆³⁻/⁴⁺, Fe₃O₄, and Ru(NH₃)₆³⁺ as redox probes. However, PDDA-modified SPCEs typically produced extra voltammetric waves for Fe(CN)₆³⁻/⁴⁺. These waves are similar to those that were reported for PDDA-modified glassy carbon electrodes and may be attributed to Fe(CN)₆³⁻/⁴⁺ confined in the polymer layer at the electrode surface.46 While CVs for AuNP/PDDA-modified SPCEs in sulfuric acid confirmed the presence of gold, the electroactive surface area that could be attributed to gold was less than the geometric surface area of the bare SPCEs and the electroactive surface areas of AuNP/PDDA-modified SPCEs that were measured using Fe(CN)₆³⁻/⁴⁺, Fe₃O₄, and Ru(NH₃)₆³⁺ as redox probes. Overall, these results suggest that modifying the electrode surface with AuNPs by electrostatic adsorption on PDDA does not result in an increase in electroactive surface area as previously reported. Rather, the surface areas of bare, PDDA-, and AuNP/PDDA-modified electrodes are all similar, and any perceived increase in surface area is likely the result of sub-optimal behavior of Fe(CN)₆³⁻/⁴⁻ as a redox probe21–23 for the characterization of bare SPCEs.

Conclusions

LbL-modification of SPCEs provides a simple, cost-effective route to prepare nanomaterial-modified electrodes; however, care must be taken when characterizing the role and benefits of the resulting composite platforms in terms of electrochemical properties. While AuNPs immobilized on the electrode surface using an LbL strategy have been shown here to provide no improvement in the electroactive surface area over bare SPCEs, modification of SPCEs with such nanomaterials can still have advantages. Nanomaterials like AuNPs can allow ease of control of surface functionality, may be engineered to offer abundant sites for conjugation of the desired species on the electrode surface, and can exhibit catalytic properties toward some analytes and substrates. The similarities between PDDA- and AuNP/PDDA-modified SPCEs suggest that the increased Fe(CN)₆³⁻/⁴⁺ peak currents observed for AuNP/PDDA-modified SPCEs compared to bare SPCEs, which have previously been attributed to the increase in surface area expected to result from the introduction of AuNPs, may be more appropriately ascribed to the effect PDDA has on making the SPCE surface more amenable for electron transfer with Fe(CN)₆³⁻/⁴⁻.

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References

1. J. J. Gooding, L. M. H. Lai, and I. Y. Goon, in Chemically Modified Electrodes, Vol. 11, eds R. C. Alkire, D. M. Kolb, J. Lipkowski, and P. N. Ross, pp. 1, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany (2009).
2. A. Mantiriam, A. V. Murugan, A. Sarkar, and T. Muraligandh, Energy Environ. Sci., 1, 621 (2008).
3. G. Wang, L. Zhang, and Z. Jiang, Chem. Soc. Rev., 41, 797 (2012).
4. Y. Xiang, S. Lu, and S. P. Jiang, Chem. Soc. Rev., 41, 7291 (2012).
5. G. Rydzek, Q. Ji, M. Li, P. Schaar, J. P. Hill, F. Boulmedais, and K. Arega, Nano Today, 10, 138 (2015).
6. R. M. Lost and F. N. Crespolho, Biosens. Bioelectron., 31, 1 (2012).
7. J. F. Rusling, G. W. Bishop, N. M. Doan, and F. Papadimitriakopoulos, J. Mater. Chem. B, 2, 12 (2014).
8. G. W. Bishop and J. F. Rusling, in Nanoelectrochemistry, eds M. V. Mirkin and S. Amenniya, pp. 469, CRC Press Taylor & Francis Group, LLC, Boca Raton, FL (2015).
9. G. Decher, Science, 277, 1232 (1997).
10. J. F. Metters, R. O. Kadara, and C. E. Banks, Analyst, 136, 1067 (2011).
11. M. Li, Y.-T. Li, D.-W. Li, and Y.-T. Long, Anal. Chim. Acta, 734, 31 (2012).
12. R. A. S. Couto, J. L. F. C. Lima, and M. B. Quinaz, Talanta, 146, 801 (2016).
13. R. O. Kadara, N. Jenkinson, and C. E. Banks, Analyst, 7291 (2012).
14. S. Miserere, S. Ledra, N. Ruillé, S. Griveau, M. Boujitta, and F. Bedinou, Electrocchem. Commun., 8, 238 (2006).
15. O. Bagel, B. Limoges, B. Schollhorn, and C. Degrand, Anal. Chem., 69, 4688 (1997).
16. S. Sánchez, M. Pumera, E. Cabrera, and F. Fábregas, Analyst, 132, 142 (2007).
17. B. V. Chikvaurevath, V. Manti, V. Patel, J. S. Guindt, and J. F. Rusling, Biosens. Bioelectron., 26, 4477 (2011).
18. M. Yan, D. Zang, S. Ge, L. Ge, and J. Yu, Biosens. Bioelectron., 38, 355 (2012).

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19. V. Mani, B. V. Chikkaveeraiah, V. Patel, J. S. Gutkind, and J. F. Rusling, *ACS Nano*, 3, 585 (2009).
20. A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, 2nd Ed., John Wiley & Sons, Inc., New York (2001).
21. A. N. Patel, M. G. Collignon, M. A. O’Connell, W. O. Y. Hung, K. McKelvey, J. V. Macpherson, and P. R. Unwin, *J. Am. Chem. Soc.*, 134, 20117 (2012).
22. M. M. Lounasvuori, M. Rosillo-Lopez, C. G. Salzmann, D. J. Caruana, and K. B. Holt, *Faraday Discuss.*, 172, 293 (2014).
23. M. M. Lounasvuori, M. Rosillo-Lopez, C. G. Salzmann, D. J. Caruana, and K. B. Holt, *J. Electroanal. Chem.*, 753, 28 (2015).
24. R. L. McCreery and M. T. McDermott, *Anal. Chem.*, 84, 2602 (2012).
25. A. Morrin, A. J. Killard, and M. R. Smyth, *Anal. Lett.*, 36, 2021 (2003).
26. A. P. Wash, P. Lozano-Sánchez, D. Bejarano-Nosas, and I. Petrii, *Electrochim. Acta*, 91, 166 (2013).
27. C. A. Schneider, W. S. Rasband, and K. W. Eliceiri, *Nat. Methods*, 9, 671 (2012).
28. W. Haiss, N. T. K. Thanh, J. Aveyard, and D. G. Fernig, *Anal. Chem.*, 79, 4215 (2007).
29. E. P. Randviir, D. A. C. Brownson, J. P. Metters, R. O. Kadara, and C. E. Banks, *Phys. Chem. Chem. Phys.*, 16, 4598 (2014).
30. A. Erlenkötter, M. Kottbus, and G.-C. Chemnitius, *J. Electroanal. Chem.*, 481, 82 (2000).
31. L. R. Cumba, C. W. Foster, D. A. C. Brownson, J. P. Smith, J. Iniesta, B. Thakur, D. R. do Carmo, and C. E. Banks, *Analyst*, 141, 2791 (2016).
32. R. S. Nicholson, *Anal. Chem.*, 37, 1351 (1965).
33. H. Matsuda and Y. Ayabe, *Z. Elektrochem.*, 59, 494 (1955).
34. P. Sun and M. V. Mirkan, *Anal. Chem.*, 78, 6526 (2006).
35. Y. Wang, J. G. Limon-Petersen, and R. G. Compton, *J. Electroanal. Chem.*, 652, 13 (2011).
36. P. Fanjul-Bolado, D. Hernández-Santos, P. J. Lamas-Ardisana, A. Martín-Pernía, and A. Costa-García, *Electrochim. Acta*, 53, 3635 (2008).
37. J. Wang, M. Pedrero, H. Sakslund, O. Hammerich, and J. Pingarrón, *Analyst*, 121, 345 (1996).
38. N. Alexeyeva and K. Tammeveski, *Anal. Chim. Acta*, 618, 140 (2008).
39. K. L. Adams, B. K. Jena, S. J. Percival, and B. Zhang, *Anal. Chem.*, 83, 920 (2011).
40. S. Trasatti and O. A. Petrii, *Pure Appl. Chem.*, 63, 711 (1991).
41. M. R. Deakin, K. J. Stutts, and R. M. Wightman, *J. Electroanal. Chem.*, 182, 113 (1985).
42. K. K. Cline, M. T. McDermott, and R. L. McCreery, *J. Phys. Chem.*, 98, 5314 (1994).
43. J. Krejci, Z. Sajdlova, V. Nedela, E. Flodrova, R. Sejnohova, H. Vranova, and R. Picka, *J. Electrochem. Soc.*, 161, B147 (2014).
44. A. Erlenkötter, M. Kottbus, and G.-C. Chemnitius, *J. Electroanal. Chem.*, 481, 82 (2000).
45. E. Blanco, C. W. Foster, L. R. Cumba, D. R. do Carmo, and C. E. Banks, *Analyst*, 141, 2783 (2016).
46. M. Maizels, W. R. Heineman, and C. J. Seliskar, *Electroanalysis*, 12, 241 (2000).