

Electrosynthesis of polyphenylpyrrole coated silver particles at a liquid–liquid interface

Christoffer Johans^a, Jason Clohessy^b, Sebastien Fantini^b, Kyösti Kontturi^a,
Vincent J. Cunnane^{b,*}

^a *Laboratory of Physical Chemistry and Electrochemistry, Helsinki University of Technology, Finland*

^b *Materials and Surface Science Institute, University of Limerick, Limerick, Ireland*

Received 19 December 2001; received in revised form 10 January 2002; accepted 10 January 2002

Abstract

This communication reports the production of polyphenylpyrrole coated silver nanoparticles at the liquid/liquid interface by an EC-type mechanism. In the electrochemical step of the reaction *N*-phenylpyrrole facilitates the transfer of the silver ion from an aqueous to an organic phase. This step is followed by a slow homogeneous electron transfer reaction from the *N*-phenylpyrrole to the silver ion followed by polymerization and metal cluster growth. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Nanoparticles; Conducting polymer; ITIES; Facilitated ion transfer; Liquid–liquid

1. Introduction

During the last two decades nanosized materials have been studied intensively mainly for their potential use in catalysis and electronics [1]. A lot of interest has focused on tailoring the properties of these materials by changing their surface properties [2]. This change in surface properties is commonly achieved by surrounding the nanoparticle by another material, resulting in a so called nanocompound.

Conducting polymers have also been studied for their electronic properties. Recently, Cunnane and Evans [3,4] have shown that it is possible to electrochemically generate conducting polymers at the interface between two immiscible electrolyte solutions (ITIES). Furthermore, Schiffrin et al. [5,6] have electrodeposited metal particles at the ITIES. In this study we combine these two fields of conducting polymers and electrodeposition of metal particles to produce a nanocompound. Similar novel but single phase type reactions have been carried out by Selvan et al. [7–10]

between chloroauric acid and pyrrole in a copolymer matrix forming 7–9 nm large gold particles surrounded by a 24 nm shell of polypyrrole. Recently, Youk et al. [11] prepared gold nanoparticles from a single phase polyelectrolyte complex solution of terthiophene amphiphiles.

2. Experimental

Li₂SO₄ (99.9%, Fluka) and Ag₂SO₄ (99.9%, Aldrich) were used as the aqueous reagents with Millipore MQ water with a resistivity of > 18 Ω cm used throughout. *N*-Phenylpyrrole (Aldrich, 99%) and Tetraphenylarsonium tetrakis (pentafluorophenyl) borate (TPAsTPBF₂₀) were used as the organic reagents. 1,2-dichloroethane (1,2-DCE) (Fluka, 99.5%) was used as the organic solvent in all experiments. The TPAsTPBF₂₀ was prepared from TPAsCl (Fluka) and LiTPBF₂₀ (Boulder Scientific), as described previously [12]. All chemicals were used as received. A Solartron 1287A electrochemical interface connected to a PC was used throughout. A conventional four-electrode electrochemical cell was used [13]. The electrochemical cells are chemically described as follows:

* Corresponding author. Tel.: +353-61-202308; fax: +353-61-202568.
E-mail address: vincent.cunnane@ul.ie (V.J. Cunnane).

Cell 1

Ag|AgCl|1 mM TPAsCl(w)|10 mM TPAsTPBF₂₀(o)||
10 mM Li₂SO₄(w) + 0.25 mM Ag₂SO₄(w)|AgCl|Ag

Cell 2

Ag|AgCl|1 mM TPAsCl(w)|10 mM TPAsTPBF₂₀(o)
+ 100 mM *N*-Phenylpyrrole(o)||10 mM Li₂SO₄(w)
+ 0.25 mM Ag₂SO₄(w)|AgCl|Ag

where || denotes the polarizable liquid/liquid interface. The reaction was studied by cyclic voltammetry. Prior to each single sweep the applied potential was held at 100 mV for 120 s. The potential was then swept to 440 mV and back to 100 mV. Scan rates of 80–0.1 mV/s were used.

Since the sweep rates are very slow tetraethyl ammonium ion (TEA⁺) was transferred at similar conditions to ensure that natural convection does not lead to a decrease in the return peak. A solution of 0.5 mM TEACl (Aldrich) in 10 mM of Li₂SO₄ was used for this purpose. The organic phase was the same as used previously.

UV–VIS measurements were performed with a Hewlett-Packard 8451A diode array spectrophotometer. Partitioning ions were used to set the potential in order to drive the transfer of Ag⁺ from the aqueous phase [14]. 1.5 mM LiTPBF₂₀(o) was added to the organic phase; Li⁺ was the partitioning ion. The cell is chemically described below (Cell 3). For the blank measurement an aqueous solution of 10 mM of Li₂SO₄ was used, the organic solution was as Cell 3. Three millilitres of organic phase was contacted with 3 ml of the aqueous phase. The reaction was allowed to proceed for 24 h. The organic phase was then placed in a quartz cuvette and the spectrum was recorded with an acquisition of 25 s.

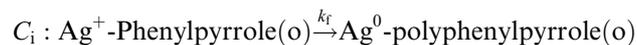
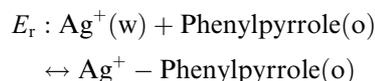
Cell 3

10 mM TPAsTPBF₂₀(o)
+ 100 mM *N*-Phenylpyrrole(o)
+ 1.5 mM LiTPBF₂₀(o)||10 mM Li₂SO₄(w)
+ 0.25 mM Ag₂SO₄(w)

The potentials reported throughout have been corrected to the Galvani scale by assuming a standard ion transfer potential of 44 mV for TEA⁺ [15] between water and 1,2-DCE.

3. Theory

The reaction considered consists of a reversible facilitated ion transfer step followed by a slow irreversible chemical reaction:



In the system studied phenylpyrrole is present in excess and it can be assumed that its concentration remains unchanged in the reaction layer. This assumption reduces the mathematics of the mass transfer problem to that of a simple $E_r C_i$ -mechanism, and hence, the criteria for $E_r C_i$ -mechanisms [16] can be used. The peak ratio of the forward and return peaks was calculated from [17]:

$$\frac{i_{\text{return}}}{i_{\text{forward}}} = \frac{(i_{\text{return}})_0}{i_{\text{forward}}} + \frac{0.485(i_{\text{sp}})_0}{i_{\text{forward}}} + 0.086, \quad (1)$$

where i_{return} and i_{forward} are the peak current densities of the return and forward scans. $(i_{\text{return}})_0$ is the uncorrected return peak current and $(i_{\text{sp}})_0$ is the current at the switching potential.

4. Results and discussion

In Fig. 1 the potential window for the system is shown in the absence and in the presence of *N*-phenylpyrrole. In the absence of *N*-phenylpyrrole a region of low current density is seen where no ion or electron transfer occurs. This region is limited by the transfer of TPAs⁺ from the organic to the aqueous phase at negative potentials and the transfer of Ag⁺ from the aqueous phase to the organic phase at positive potentials. In the presence of *N*-phenylpyrrole however, a charge transfer wave occurs at $E_{1/2} = 336$ mV. This is attributed to the transfer of Ag⁺ facilitated by the *N*-phenylpyrrole. The scanned potential region is also extended to the onset of Li⁺ transfer at the positive end.

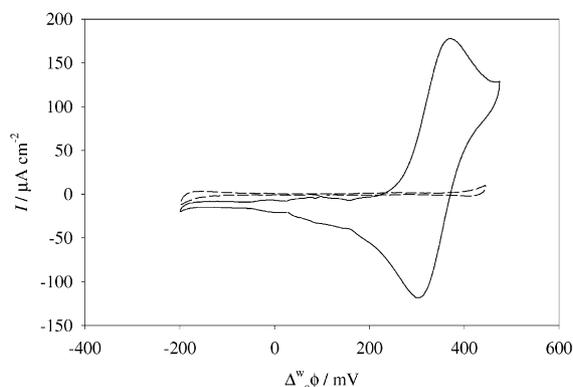


Fig. 1. Potential windows of 10 mM TPAsTPBF₂₀(o), 0.25 mM Ag₂SO₄(w) and 10 mM Li₂SO₄(w): (---) without *N*-phenylpyrrole(o) (Cell 1), (—) 100 mM *N*-phenylpyrrole(o) (Cell 2).

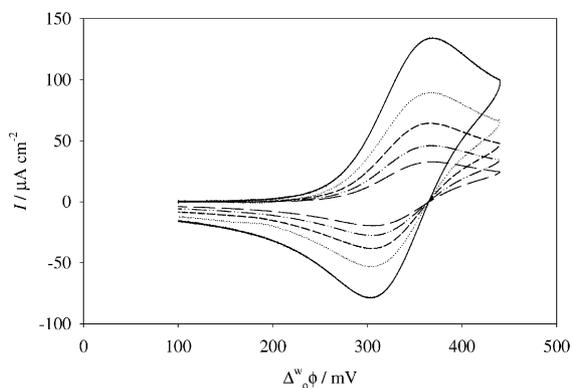


Fig. 2. Sweep rate dependence of Cell 2: (—) 80 mV/s, (·····) 40 mV/s, (---) 20 mV/s, (- · - ·) 10 mV/s and (- -) 5 mV/s.

In Fig. 2 single sweep voltammograms at high sweep rates are shown. The charge transfer reaction appears reversible with a 60 mV peak separation.

As the sweep rate is lowered the return peak gradually disappears (see Fig. 3). This is typical for an E_rC_i -mechanism. The peak current ratio of the forward and return scans is shown as a function of $k_f\tau$ in Fig. 4, where τ is the time between $E_{1/2}$ and the switching potential and k_f is the heterogeneous forward rate constant. The peak currents were calculated as described above. The solid line corresponds to that predicted by theory [16]. From the fit of the solid line a k_f of $0.8 \times 10^{-3} \text{ s}^{-1}$ was obtained.

The slow reaction rate obtained here is a direct consequence of the high redox potential of the 1-phenylpyrrole monomer. The chemical reaction between Ag^+ and 1-phenylpyrrole proceeds by an initial charge transfer step followed by polymerization with other monomers or polymers. We do not believe that the driving force for the overall reaction is very high due to the high oxidation potential of the phenylpyrrole. However it is felt that the additive contributions of the potential for the reduction of silver in 1,2-DCE and the facilitated transfer potential plus the energy gained from

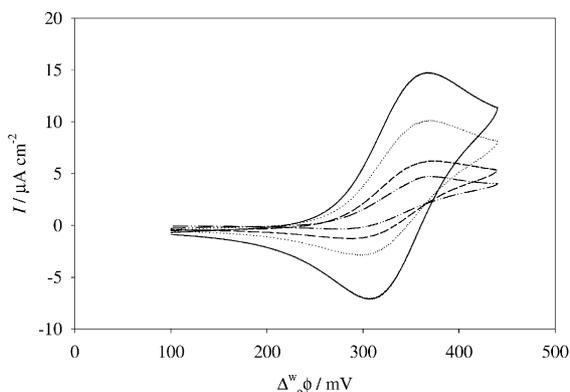


Fig. 3. Sweep rate dependence of Cell 2: (—) 1 mV/s, (·····) 0.5 mV/s, (---) 0.25 mV/s and (- · - ·) 0.1 mV/s.

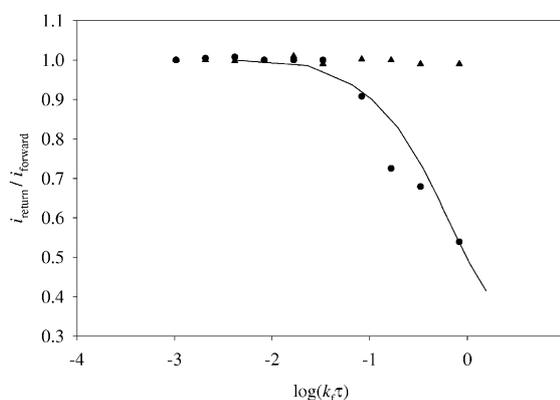


Fig. 4. Plot of peak current ratio vs. $\log(k_f\tau)$ (●) experimental data and (—) theoretical fit. (▲) peak ratio of TEA^+ transfer at corresponding sweep rates.

the chemical step are sufficient to drive the reaction to the extent witnessed by the presence of silver colloids and oligomeric species in solution (shown later).

The diffusion coefficient for $\text{Ag}^+(\text{w})$ was calculated from the forward scan peak currents and a value of $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was obtained, see Fig. 5. This value is in accordance with that found in the literature, $1.65 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, for Ag^+ at infinite dilution and 25 °C [18].

The duration of the slow sweeps is much longer than the general recommended “rule of thumb” of 300 s for diffusion controlled electrochemical measurements. To ensure that the reaction studied was an E_rC_i -mechanism and not natural convection due to density gradients or vibrations, TEA^+ ion transfer was carried out under similar conditions. No decay in the peak current ratio was observed. The peak ratios obtained from this experiment are also shown in Fig. 4.

The UV–VIS difference spectrum between the prepared sample (Cell 3) and the blank is shown in Fig. 6. In this experiment Li^+ transfers from the organic phase to the aqueous phase with the simultaneous transfer of

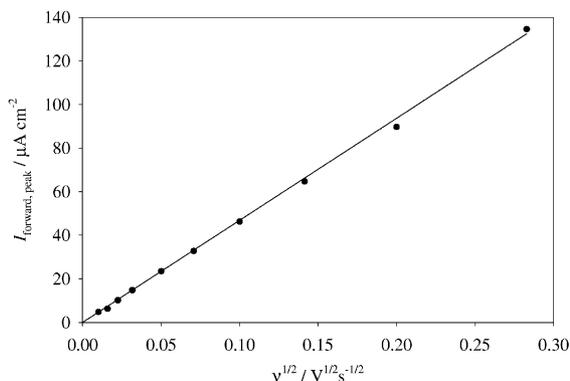


Fig. 5. Peak current of forward scan vs. square root of sweep rate: (●) experimental data and (—) linear fit to the experimental data.

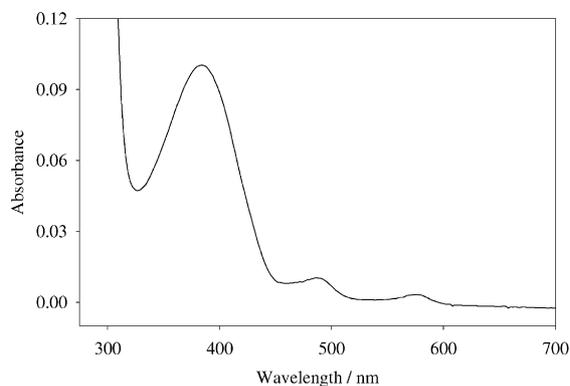


Fig. 6. UV–VIS spectrum of the organic phase after 24 h of contact of 3 ml of Cell 3.

Ag^+ from the aqueous phase to the organic phase since the Galvani potential established by the partition of Li^+ , approximately 450 mV as anticipated from the voltammogram in Fig. 1, is more positive than that of 1-phenylpyrrole facilitated transfer of Ag^+ , 336 mV. The distinct absorption peak of colloidal silver is seen at 390 nm. The absorption peak of silver particles in the size ranges 3–20 nm in water is 380 nm [19]. For particles in 1,2-DCE the adsorption peak is shifted towards longer wavelengths. From the dispersion relation of silver [20] and the refractive index of 1.444 for 1,2-DCE the adsorption peak of silver particles in the 3–20 nm size range can be calculated, as outlined in reference [19], to occur at 398 nm. Shorter wavelengths are expected for smaller particles. The *N*-phenylpyrrole monomer absorbs at 260 nm when dissolved in 1,2-DCE. A sharp peak has also appeared at 300 nm. Unfortunately, both the phenyl rings of the TPAs^+ and TPBF_{20}^- ions and *N*-phenylpyrrole (260 nm [3]) also absorb in the region below 300 nm, and therefore this peak is difficult to characterize. However, it may correspond to the formation of oligo- and polyphenylpyrrole [21]. The absorption peaks at 480 and 580 nm are indicative of higher oligomer forms of pyrrole [22]. A golden brown colour was also observed in the organic phase.

5. Conclusions

In this communication the electrochemical properties of the liquid/liquid interface have been used to synthesize silver nanoparticles and polypyrrole by transferring the silver metal ion from the aqueous phase to the organic phase, where it reacts with the pyrrole monomer. Whilst there is no direct evidence for the formation of polymer coated silver colloids we believe that due to the facilitated transfer and, as such, the shorter reaction

distances that polymer coated colloids are the most likely outcome. The reaction was studied by conventional cyclic voltammetry using very slow sweep rates. Fitting the data to the theory for E_rC_i -mechanisms presented by Nicholson and Shain [16] gave an apparent rate constant for the chemical step of $0.8 \times 10^{-3} \text{ s}^{-1}$. A diffusion coefficient of $1.2 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ was obtained for Ag^+ in water. UV–VIS measurements were carried out to confirm the formation of colloidal silver and polyphenylpyrrole.

Acknowledgements

Financial support from the European Union under project No. ERB-FMRX-CT96-0078 (ODRELLI TMR network) and the National Technology Agency (Finland) is greatly acknowledged.

References

- [1] G. Schmid, M. Bäuml, M. Geerkens, I. Heim, C. Osemann, T. Sawitowski, *Chem. Soc. Rev.* 28 (1999) 179–185.
- [2] R. Gangopadhyay, A. De, *Chem. Mater.* 12 (2000) 608–622.
- [3] V.J. Cunnane, U. Evans, *Chem. Commun.* (1998) 2163–2164.
- [4] K. Gorgy, F. Fusalba, U. Evans, K. Kontturi, V.J. Cunnane, *Synth. Met.* 125 (2002) 365–373.
- [5] Y.F. Cheng, D.J. Schiffrin, *J. Chem. Soc. Faraday Trans.* 92 (1996) 3865–3871.
- [6] C. Johans, R. Lahtinen, K. Kontturi, D.J. Schiffrin, *J. Electroanal. Chem.* 488 (2000) 99–109.
- [7] S.T. Selvan, *Chem. Commun.* (1998) 351–352.
- [8] S.T. Selvan, T. Hayakawa, M. Nogami, M. Moller, *J. Phys. Chem. B* 103 (1999) 7441–7448.
- [9] S.T. Selvan, M. Nogami, *J. Mater. Sci. Lett.* 17 (1998) 1385–1388.
- [10] S.T. Selvan, J.P. Spatz, H.A. Klok, M. Moller, *Adv. Mater.* 10 (1998) 132.
- [11] J.H. Youk, J. Locklin, C.J. Xia, M.K. Park, R. Advincula, *Langmuir* 17 (2001) 4681–4683.
- [12] D.J. Fermin, H.D. Duong, Z.F. Ding, P.F. Brevet, H.H. Girault, *Phys. Chem. Chem. Phys.* 1 (1999) 1461–1467.
- [13] Z. Samec, V. Marecek, J. Koryta, M.W. Khalil, *J. Electroanal. Chem.* 83 (1977) 393.
- [14] V.J. Cunnane, D.J. Schiffrin, C. Beltran, G. Geblewicz, T. Solomon, *J. Electroanal. Chem.* 247 (1988) 203–214.
- [15] J. Czapkiewicz, B. Czapkiewicz-Tutaj, *J. Chem. Soc. Faraday Trans.* 76 (1980) 1663–1668.
- [16] R. Nicholson, I. Shain, *Anal. Chem.* 36 (1964) 706–723.
- [17] R. Nicholson, *Anal. Chem.* 37 (1965) 1351–1355.
- [18] J. Heyrovsky, J. Kuta, *Instrumental Techniques in Electrochemistry*, Academic Press, New York, 1966.
- [19] J.A. Creighton, D.G. Eadon, *J. Chem. Soc. Faraday Trans.* 87 (1991) 3881–3891.
- [20] P.B. Johnson, R.W. Christy, *Phys. Rev. B* 6 (1972) 4370–4379.
- [21] N. Rohde, M. Eh, U. Geissler, M.L. Hallensleben, B. Voigt, M. Voigt, *Adv. Mater.* 7 (1995) 401–404.
- [22] D.J. Fermin, B.R. Scharifker, *J. Electroanal. Chem.* 357 (1993) 273–287.