

Cite this: *Analyst*, 2012, **137**, 4693

www.rsc.org/analyst

PAPER

# Facile *in situ* characterization of gold nanoparticles on electrode surfaces by electrochemical techniques: average size, number density and morphology determination

Ying Wang,<sup>a</sup> Eduardo Laborda,<sup>a</sup> Chris Salter,<sup>b</sup> Alison Crossley<sup>b</sup> and Richard G. Compton<sup>\*a</sup>

Received 1st August 2012, Accepted 30th August 2012

DOI: 10.1039/c2an36050k

A fast and cheap *in situ* approach is presented for the characterization of gold nanoparticles from electrochemical experiments. The average size and number of nanoparticles deposited on a glassy carbon electrode are determined from the values of the total surface area and amount of gold obtained by lead underpotential deposition and by stripping of gold in hydrochloric acid solution, respectively. The morphology of the nanoparticle surface can also be analyzed from the “fingerprint” in lead deposition/stripping experiments. The method is tested through the study of gold nanoparticles deposited on a glassy carbon substrate by seed-mediated growth method which enables an easy control of the nanoparticle size. The procedure is also applied to the characterization of supplied gold nanoparticles. The results are in satisfactory agreement with those obtained *via* scanning electron microscopy.

## 1. Introduction

The particular surface and electronic features of nanosized materials are very advantageous in many scientific fields such as electroanalysis,<sup>1,2</sup> catalysis,<sup>3,4</sup> medicine<sup>5</sup> and material science.<sup>6</sup> The synthesis and characterization of nanoparticles are two essential aspects to any study given that their reactivity and properties are defined by their composition, size and morphology.

Scanning electron microscopy (SEM),<sup>7–10</sup> transmission electron microscopy (TEM),<sup>11,12</sup> atomic force microscopy (AFM),<sup>13</sup> scanning tunnelling microscopy (STM) and X-ray diffraction (XRD)<sup>14</sup> are usually employed for the characterization of nanoparticles. However, these techniques have some limitations which are particularly unfavourable when examining nanoparticle-modified electrodes. Thus, the inefficiency in cost and time and the sample preparation restrictions prevent the analysis of modified electrodes immediately before or after each experiment. Moreover, the results obtained may not be representative of the whole sample.

The aim of this work is to find a simple and time-efficient *in situ* characterization method for nanoparticles on electrode surfaces. The approach proposed is based on routine electrochemical experiments that can be carried out in any electrochemistry laboratory. This enables the estimation of average values of the

size and number of gold nanoparticles together with the different surface sites.<sup>15</sup> The particles are deposited on a glassy carbon electrode and the total gold surface area is extracted from the charge associated with lead underpotential deposition on gold.<sup>16</sup> The voltammograms corresponding to lead deposition and stripping also informs about the surface sites on the nanoparticle. Next, the total amount of gold is obtained from its anodic stripping in chlorhydric acid medium.<sup>17</sup> From the values of the total surface area and amount of gold, the average size of the gold particles can be easily calculated.

The suitability of the electrochemical characterization procedure is tested by comparison with the results obtained in SEM for a glassy carbon electrode modified with gold nanoparticles of different size *via* seed-mediated growth method.<sup>11,12,14,18–20</sup> The methodology is also applied to the study of supplied gold nanoparticles with satisfactory results.

## 2. Experimental

### 2.1 Chemical reagents

Sodium borohydride (98%, NaBH<sub>4</sub>), gold(III) chloride trihydrate (>99%, HAuCl<sub>4</sub>·3H<sub>2</sub>O), trisodium citrate (>99.0%), hexadecyltrimethylammonium bromide (CTAB), hydrochloric acid (37%, HCl), L-ascorbic acid (>99.0%), sodium hydroxide (>97%, NaOH) and lead(II) nitrate (>99.5%, Pb(NO<sub>3</sub>)<sub>2</sub>) were all purchased from Sigma-Aldrich and used as received without further purification. Citrate-capped gold nanoparticles were provided by Mintek (Randburg, South Africa). All the solutions were prepared using deionised water with a resistivity 18.2 MΩ cm (25 °C).

<sup>a</sup>Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, OX1 3QZ, UK. E-mail: richard.compton@chem.ox.ac.uk; Fax: +44 (0)1865 275 410; Tel: +44 (0)1865 275 413

<sup>b</sup>Department of Materials, Oxford University, Begbroke Science Park, Sandy Lane, Yarnton, OX5 1PF, UK

## 2.2 Instrumentation

Electrochemical experiments were performed using a three-electrode system with an Autolab PGStat 20 computer-controlled potentiostat (Eco-Chemie, Utrecht, Netherlands). Platinum wire was employed as counter electrode and the reference electrode was a saturated calomel electrode (SCE, Radiometer, Copenhagen). A bare or modified glassy carbon (GC) electrode (3 mm diameter, BAS, Technical, UK) was used as working electrode. The GC electrode was polished before use with diamond paste (Kent, UK) of decreasing size (3.0, 1.0 and 0.1  $\mu\text{m}$ ) and sonicated in ultrasound bath.

Scanning electron microscope (SEM) images were obtained on a JEOL 6500F FEGSEM.

## 2.3 Electrode modification with gold nanoparticles

Seed-mediated growth method was used to modify a glassy carbon electrode.<sup>11,12,14,18–20</sup> The polished GC electrode was immersed in the gold seeding solution containing 18 mL water, 0.5 mL (0.01 M) trisodium citrate, 0.5 mL  $\text{HAuCl}_4$  (0.01 M) and 0.5 mL freshly prepared ice-cold  $\text{NaBH}_4$  (0.10 M). After immersing in the seeding solution for 30 minutes, the electrode was sequentially rinsed by water and dried with nitrogen. Then the seeded electrode was immersed in the growth solution containing 18 mL CTAB (0.10 M), 0.5 mL  $\text{HAuCl}_4$  (0.01 M) and 0.1 mL ascorbic acid (0.10 M) solutions for 2, 10 and 30 min to reach different degrees of coverage. SEM results (not shown) pointed out that the use of longer growing times resulted in a higher degree of agglomeration of particles which compromised the accuracy of the characterization method here presented. The modified electrode was rinsed thoroughly with deionized water and dried under nitrogen atmosphere before electrochemical experiments.

## 2.4 Electrochemical characterization

The modified electrode was first immersed into 1 mM  $\text{Pb}(\text{NO}_3)_2$ , 0.1 M NaOH solution to run cyclic voltammetry at 50  $\text{mV s}^{-1}$  in the range of  $-0.20$  to  $-0.73$  V (vs. SCE). After the experiments with lead the modified electrode was rinsed with distilled water and transferred into 0.1 M HCl. Stripping experiments in hydrochloric acid were carried out by scanning between 0.70 and 1.30 V (vs. SCE). All the solutions were deoxygenated by purging with nitrogen gas for about 30 minutes and the experiments were carried out under  $\text{N}_2$  atmosphere.

## 3. Results and discussion

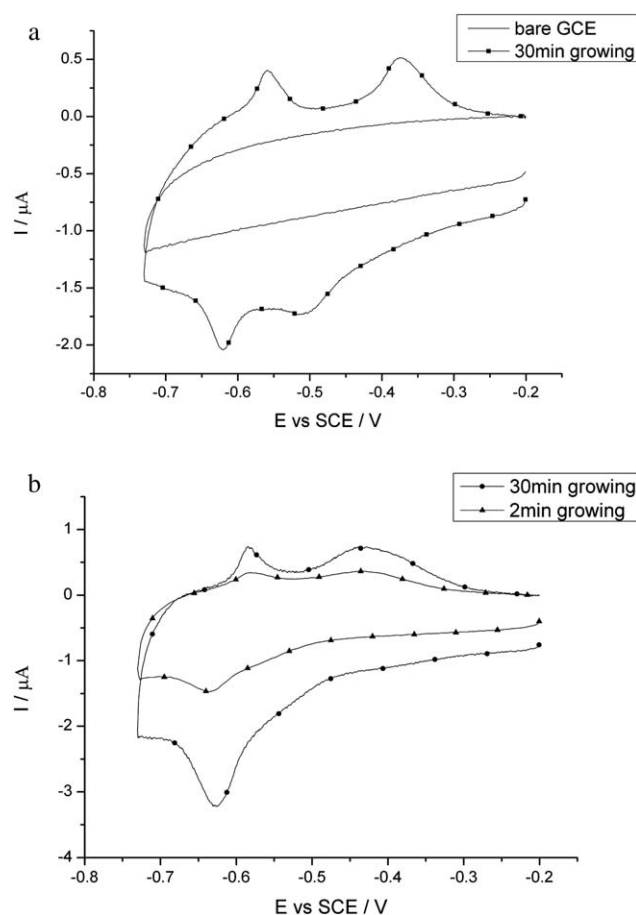
### 3.1 Electrochemical characterization

Underpotential deposition (UPD) of metals as well as adsorption/desorption processes are surface-sensitive and they enable selective examination of the characteristics of metal substrates. In the case of gold surfaces, electrooxidation in 0.5 M sulphuric acid medium is a commonly used approach for the determination of the surface area by integration of the cathodic peak.<sup>13</sup> However, the use of this method for quantitative analysis can be inappropriate given that the gold oxide growth is a function of the number of scans as a result of the formation of monolayer and multilayer oxidized products.<sup>21–23</sup> This effect was found in

preliminary experiments of this work (not shown) such that the reduction peak shifts towards less positive potentials in successive scans as reported in the literature.<sup>23</sup>

Underpotential deposition is well known to be highly sensitive to the surface structure of the electrode, the process being dependent on the particular interactions between the surface and the depositing atoms.<sup>24</sup> Hernandez *et al.*<sup>16</sup> have proved lead UPD in alkaline solution to be a suitable system for the estimation of the surface area and surface structure of gold nanoparticles (NPs). Thus, lead forms a layer on gold surface at a slightly positive potential than bulk lead deposition<sup>25</sup> which is dissolved at different potentials depending on the facets of the gold nanocrystals. As shown below, the voltammograms corresponding to the lead deposition/stripping on gold provide better accuracy and reproducibility as well as further insights into the gold surface sites.

The voltammetric profiles of bare and gold nanoparticle-modified (Au/GCE) glassy carbon electrodes in 1 mM  $\text{Pb}(\text{NO}_3)_2$ , 0.1 M NaOH solution are shown in Fig. 1a. Whereas no signal is observed on the bare GC, the peaks corresponding to the deposition and subsequent stripping of lead are recorded after the modification with gold nanoparticles.

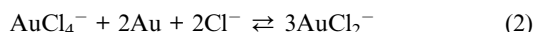
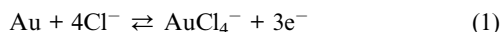


**Fig. 1** (a) Comparison of the cyclic voltammogram corresponding to lead deposition on gold nanoparticles on GC electrode and bare GC electrode in 1 mM  $\text{Pb}(\text{NO}_3)_2$  and 0.1 M NaOH solution. Scan rate: 50  $\text{mV s}^{-1}$ . (b) Cyclic voltammograms of gold nanoparticle-modified GC electrodes with different growing times in 1 mM  $\text{Pb}(\text{NO}_3)_2$  and 0.1 M NaOH solution. Scan rate: 50  $\text{mV s}^{-1}$ .

In the seed-mediated growth method employed here the size of the nanoparticles (and so the total surface area) can be increased by immersing the seeded electrode in the growing solution for longer periods of time. Fig. 1b shows the “fingerprint” in lead solution corresponding to 2 and 30 min, the charge of lead deposition/stripping clearly increasing with the length of the growing step.

From the results obtained with single-crystal electrodes<sup>16</sup> it is known that Au(111), Au(100) and Au(110) have well-defined deposition/stripping peaks at different potentials. Thus, structural information is available along with the quantitative determination of the surface area of nanoparticles. The sharp stripping peak at  $-0.58$  V (vs. SCE) in Fig. 1 is associated with the Au(111) domain and a lead UPD charge of  $380 \mu\text{C cm}^{-2}$  (ref. 16 and 25). Au(110) facet contributes to the broader stripping peak at  $-0.38$  V (vs. SCE) with a deposition charge associated of  $330 \mu\text{C cm}^{-2}$  (ref. 16). No relevant contribution of (100) domains is observed in the voltammograms shown in Fig. 1. Therefore, additionally to the determination of the gold surface area, lead UPD peaks enable us to identify the different surface sites on the NP surface and their relative areas. This is connected to the size and shape of the nanoparticles and it is essential to evaluate their suitability for a given application.

The quantification of the amount of gold deposited on the glassy carbon surface has been carried out by anodic stripping of the nanoparticles in  $0.1$  M hydrochloric acid.<sup>17</sup> According to studies on macro gold electrodes<sup>26,27</sup> the resulting species are the complexes  $\text{AuCl}_2^-$  and  $\text{AuCl}_4^-$  according to the following equilibria:<sup>17,26,27</sup>



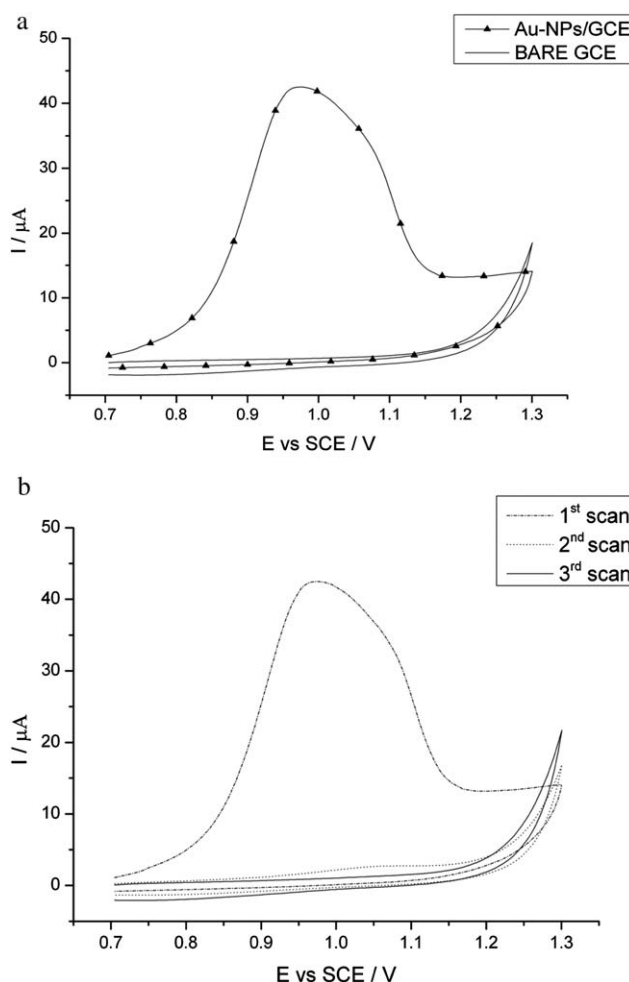
Recent work in our group has extended the study to nano-gold,<sup>17</sup> the results showing that the charge of the stripping is quantitatively related to the loading of gold nanoparticles with a value of  $1.9 \pm 0.1$  electrons transferred per gold atom. Thus, the electro-oxidation of gold nanoparticles was carried out *via* cyclic voltammetry in the potential range  $0.70$ – $1.30$  V (vs. SCE). As can be observed in Fig. 2a, no signal is recorded on bare glassy carbon electrode which confirms that the stripping charge is all due to gold nanoparticles. After several scans (typically 3 scans, see Fig. 2b) the gold deposit is completely removed and the charge under the peaks enables the calculation of the total amount of gold deposited on the glassy carbon surface.

By combining the values of the surface area ( $S$ ) determined by lead UPD and the amount of gold ( $Q$ ) from anodic stripping in HCl the radius and number of nanoparticles on the GC electrode can be easily calculated from the following relationships:

$$S = x\pi r^2 \times N \quad (3)$$

$$Q = 1.9 \times e \times \frac{x}{3} \pi r^3 \rho_{\text{Au}} \times N_{\text{A}} \times N \quad (4)$$

where  $x = 2$  for hemispherical and  $x = 4$  for spherical nanoparticles,  $e$  is the electronic charge,  $r$  the average radius of the nanoparticles,  $N$  the number of particles,  $\rho_{\text{Au}}$  the density of gold,  $M_{\text{Au}}$  the molar mass of gold and  $N_{\text{A}}$  is the Avogadro constant.



**Fig. 2** (a) Comparison of cyclic voltammograms obtained with gold nanoparticle-modified GC electrode and bare GC electrode in  $0.1$  M HCl. Scan rate:  $100 \text{ mV s}^{-1}$ . (b) Successive cyclic voltammograms obtained with gold nanoparticle-modified GC electrodes in  $0.1$  M HCl. Scan rates:  $100 \text{ mV s}^{-1}$ .

Thus, from the ratio  $Q/S$  the radius of the nanoparticles can be determined:

$$r = \frac{3M_{\text{Au}}}{1.9e\rho_{\text{Au}}N_{\text{A}}} \times \frac{Q}{S} \quad (5)$$

Once the radius is known, the number of particles can be extracted from eqn (3) or (4).

Following the above procedure the characteristics of the nanoparticles at the modified GC electrode have been examined for different growing times. The results are shown in Table 1. As expected, the values obtained for the diameter of the particles gradually increase with the growing time from *ca.*  $20 \text{ nm}$  for  $2 \text{ min}$  growing time up to *ca.*  $40 \text{ nm}$  for  $30 \text{ min}$ . Assuming a hemispherical shape for the particles, the mean value for the number of particles obtained is  $(4 \pm 2) \times 10^8$  NPs, which yields a value of particle density of *ca.*  $(6 \pm 3) \times 10^9 \text{ NP cm}^{-2}$ .

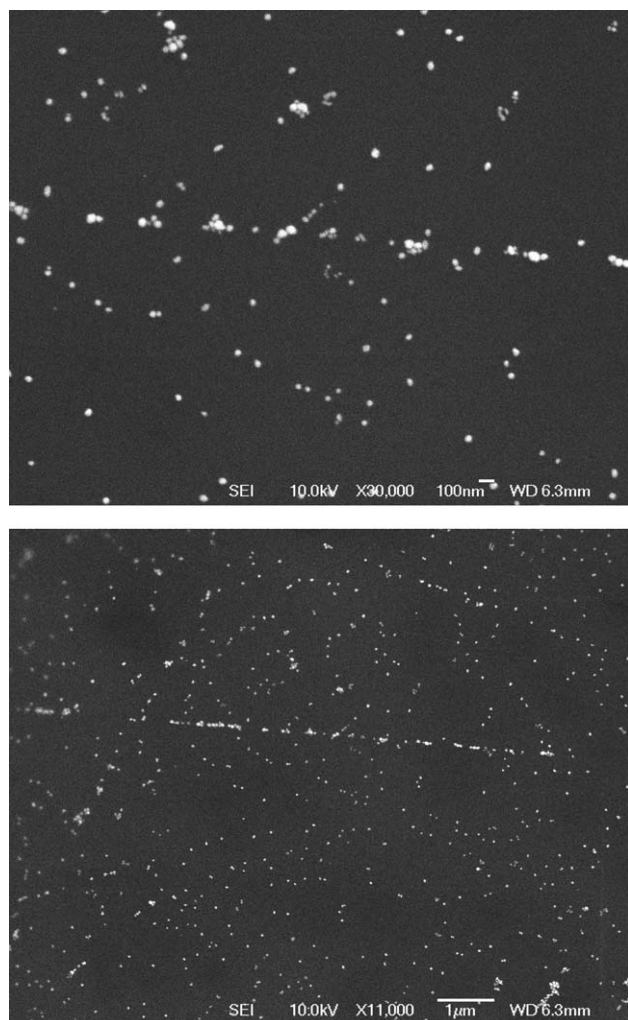
### 3.2 Scanning electron microscope (SEM) results

Scanning electron microscope (SEM) images of the surface of the modified GC electrodes were also obtained in order to evaluate



**Table 1** Values of the diameter ( $d$ ) and number ( $N$ ) of gold nanoparticles obtained through electrochemical characterization (*i.e.*, lead deposition and stripping in HCl solution). Different growing times in the modification of the electrode are considered

Growing time/min	$d/\text{nm}$	$N/(10^8 \text{ particles})$
2	$23 \pm 2$	$4 \pm 2$
10	$32 \pm 7$	
30	$39 \pm 3$	



**Fig. 3** Scanning electron microscopy images of a glassy carbon surface modified with gold nanoparticles by seed-mediated growth method with a growing time of 30 min.

the size and distribution of the nanoparticles and test the suitability of the electrochemical approach presented in Section 3.1. SEM images of Au/GC electrodes after growing times of 30 min are shown in Fig. 3. As can be observed, gold nanoparticles have a spherical shape, with an average size of *ca.* 40 nm diameter, which agrees very well with the results obtained with the electrochemical approach.

### 3.3 Application to supplied Au NPs

The electrochemical characterization method has also been tested by characterizing supplied nanoparticles (Mintek,

Randburg, South Africa). The glassy carbon electrode was modified with 5  $\mu\text{L}$  gold nanoparticles by drop-cast method. The electrochemical characterization approach yields an average diameter of *ca.* 22 nm. These results are in good agreement with those obtained by SEM and anodic particle coulometry which yielded a diameter of 20 nm and 21 nm, respectively.<sup>17</sup>

## 4. Conclusions

A simple electrochemical methodology has been presented for *in situ* characterization of gold nanoparticles. This can complement typically used imaging techniques since it provides faster and more representative results.

Gold nanoparticles under study are deposited on a glassy carbon electrode. First, the total surface area and structure of the particles are estimated from underpotential deposition of lead in alkaline medium. Next, the amount of gold is determined from the charge associated with the anodic stripping of gold in chlorhydric acid solution. Both measurements enable the extraction of the average size and number of nanoparticles as well as the estimation of the different surface sites.

The suitability of the method has been confirmed by examining glassy carbon electrodes modified with gold nanoparticles of different size by seed-mediated growth method. The results obtained with the electrochemical approach agree well with those derived from scanning electron microscopy. The new characterization procedure has also been applied to the study of supplied nanoparticles.

## Acknowledgements

The authors greatly thank Mintek (Dr J Pillay and Dr R Tshikhudo) for providing the citrate-capped gold nanoparticles. EL thanks the Fundación SENECA for financial support.

## References

- 1 S. Vaddiraju, I. Tomazos, D. J. Burgess, F. C. Jain and F. Papadimitrakopoulos, *Biosens. Bioelectron.*, 2010, **25**, 1553–1565.
- 2 F. W. Campbell and R. G. Compton, *Anal. Bioanal. Chem.*, 2010, **396**, 241–259.
- 3 *Nanoparticles and Catalysis*, ed. D. Astruc, Wiley-VCH, Weinheim, Germany, 2008.
- 4 M. T. M. Koper, *Nanoscale*, 2011, **3**, 2054–2073.
- 5 *Nanotechnology in Biology and Medicine: Methods, Devices and Applications*, ed. T. Vo-Dinh, CRC Press, Boca Raton, USA, 2007.
- 6 O. D. Velev and S. Gupta, *Adv. Mater.*, 2009, **21**, 1897–1905.
- 7 J. Zhang, M. Kambayashi and M. Oyama, *Electrochem. Commun.*, 2004, **6**, 683–688.
- 8 T. Horibe, J. Zhang and M. Oyama, *Electroanalysis*, 2007, **19**, 847–852.
- 9 M. Oyama, S. Yamaguchi and J. Zhang, *Anal. Sci.*, 2009, **25**, 249–253.
- 10 M. S. El-Deab, T. Sotomura and T. Ohsaka, *J. Electrochem. Soc.*, 2005, **152**, C1–C6.
- 11 T. K. Sau and C. J. Murphy, *J. Am. Chem. Soc.*, 2004, **126**, 8648–8649.
- 12 N. R. Jana, L. Gearheart and C. J. Murphy, *J. Phys. Chem. B*, 2001, **105**, 4065–4067.
- 13 X. Dai, O. Nekrassova, M. E. Hyde and R. G. Compton, *Anal. Chem.*, 2004, **76**, 5924–5929.
- 14 N. R. Jana, L. Gearheart and C. J. Murphy, *Langmuir*, 2001, **17**, 6782–6786.
- 15 J. Solla-Gullón, P. Rodríguez, E. Herrero, A. Aldaz and J. M. Feliu, *Phys. Chem. Chem. Phys.*, 2008, **10**, 1359–1373.
- 16 J. Hernandez, J. Solla-Gullon and E. Herrero, *J. Electroanal. Chem.*, 2004, **574**, 185–196.

- 
- 17 Y. Zhou, N. V. Rees, J. Pillay, R. Tshikhudo, S. Vilakazi and R. G. Compton, *Chem. Commun.*, 2012, **48**, 224–226.
- 18 M. Oyama, *Anal. Sci.*, 2010, **26**, 1–12.
- 19 C. J. Murphy and N. R. Japa, *Adv. Mater.*, 2002, **14**, 80–82.
- 20 Y. Cui, C. Yang, W. Zeng, M. Oyama, W. Pu and J. Zhang, *Anal. Sci.*, 2007, **23**, 1421–1425.
- 21 H. Angerstein-Kozłowska and B. E. Conway, *J. Electroanal. Chem.*, 1987, **228**, 429–453.
- 22 L. D. Burke and P. F. Nugent, *Gold Bull.*, 1997, **30**, 43–53.
- 23 G. Tremiliosi-Filho, L. H. Dall'Antonia and G. Jerkiewicz, *J. Electroanal. Chem.*, 2005, **578**, 1–8.
- 24 E. Herrero, L. J. Buller and H. D. Abruña, *Chem. Rev.*, 2001, **101**, 1897–1930.
- 25 M. O. Finot, G. D. Braybrook and M. T. McDermott, *J. Electroanal. Chem.*, 1999, **466**, 234–241.
- 26 A. Kolics, A. E. Thomas and A. Wieckowski, *J. Chem. Soc., Faraday Trans.*, 1996, **92**, 3727–3736.
- 27 M. A. Diaz, G. H. Kelsall and N. J. Welham, *J. Electroanal. Chem.*, 1993, **361**, 25–38.