

Voltammetric behaviour of hydrogen peroxide at a silver electrode fabricated from a rewritable digital versatile disc (DVD) and its determination in water samples

Mai Shafei and Kevin C. Honeychurch*

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In this study we investigated the possibility of applying Ag electrodes manufactured from recordable rewritable digital versatile discs (DVD-RW) for the voltammetric determination of hydrogen peroxide. The calibration plot was linear from 0.087 mM to 3.41 mM hydrogen peroxide with a sensitivity of 58.7 $\mu\text{A mM}^{-1}$ over this range. A corresponding detection limit of 78.35 μM , based on a signal-to-noise-ratio of 3 was recorded. No interferences were observed by 500 mg L^{-1} chloride, 50 mg L^{-1} nitrate, 700 mg L^{-1} sulphate or 700 mg L^{-1} carbonate which are found in swimming pool water at these concentrations. Using the multiple standard addition method a percentage recovery of 90.67% with a coefficient of variation of 4.69% ($n = 5$) was found for a representative swimming pool water concentration of 1.2 mM hydrogen peroxide. Therefore, the performance data suggests that the method is reliable at the concentrations examined in this study and that a rapid, simple, economical and precise method of monitoring hydrogen peroxide in swimming pool and aquaculture applications is possible.

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1. Introduction

The detection of hydrogen peroxide at low levels is important in several different applications. One example is monitoring the levels of hydrogen peroxide present in swimming pools due to its increasing use as a disinfectant particularly in private swimming pools.¹ The use of hydrogen peroxide as a disinfectant has become more popular as it has benefits over the use of chlorine based chemicals such as its lack of odour and irritation to the eyes associated with swimming pools. Similarly, there is a great deal of interest regarding its use as a disinfectant in food production^{2–4} particularly in aquaculture.^{5,6} It allows for the successful control of a number of pathogens and unlike other control measures it offers the advantages of leaving no harmful residues as only oxygen and water are formed. However, elevated levels of hydrogen peroxide can result in severe toxicity to tissues in the body whilst low levels will result in increased risk of pathogens remaining unchecked. Therefore, there is a pressing need for a simple economic method to ensure the desired concentration of hydrogen peroxide is maintained. Presently, there are several different methods for the determination of hydrogen peroxide which include titration⁷ and colorimetric assays.^{8–10} However, such techniques can be time consuming and require a degree of training. Notably,

electrochemical techniques offer a number of advantages including cost, possibility of miniaturisation and high sensitivity. However, the direct electrochemical determination of hydrogen peroxide is hampered by the high potentials required for its direct oxidation or reduction.^{11–14} This can lead to problems such as high background currents resulting in poor signal-to-noise ratios and interferences from more easily reduced or oxidised compounds. A large volume of research has been centred on overcoming these problems and a number of different mediators and catalysts¹⁵ such as nanoparticles,^{16,17} cobalt phthalocyanine,¹⁸ Prussian blue^{19,20} and ferrocene²¹ have been successfully employed to lower the potentials required. A number of studies have shown the possibility of utilising electrodes manufactured from metals such as Ag^{17,22–27} for electrocatalytic determination of hydrogen peroxide. Table 1 gives an overview of a number of more recent reports of these and their relative performance characteristics. However, electrodes manufactured from noble metals can be quite expensive. Compact discs (CDs) and digital versatile discs (DVDs) have a thin layer of Au or Ag which can be used as an alternative cheap source to prepare such working electrodes.²⁸ Studies have explored the possibility of determining a number of analytes at electrodes prepared from CDs and DVDs,²⁹ however, these have been predominantly Au based.^{29–35} Recently, we have investigated utilising Ag electrodes manufactured from recordable compact discs for the trace determination of Pb by anodic stripping voltammetry.²⁸ In this present study we have investigated the possibility of using DVDs to manufacture Ag electrodes without

Centre for Research in Biosciences, Department of Biological, Biomedical and Analytical Sciences, University of the West of England, Frenchay Campus, Coldharbour Lane, Bristol, BS16 1QY, UK. E-mail: kevin.honeychurch@uwe.ac.uk

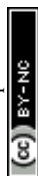


Table 1 Summary of various recently reported Ag based electrodes used for the determination of hydrogen peroxide

Electrode	Technique	Linear range	Detection limit, μM	Sample	Reference
Horseradish peroxidase directly adsorbed at polycrystalline Ag and Au electrodes	Amperometry	0.1 to 1.0 μM	0.01	—	38
Dendritic Ag nanostructures electrochemically deposited at a glassy carbon electrode	Amperometry	4 μM to 36 μM	0.9	Laboratory waste water	39
Ag nanoparticle-decorated graphene on indium-tin-oxide electrode	Amperometry	0.1 mM to 100 mM	5	—	40
Ag nanoparticle-modified glassy carbon electrode	Cyclic voltammetry	5 to 40 μM	2	—	41
Glassy carbon electrode modified with Ag nanograins incorporated poly[3,4-ethylenedioxythiophene] (PEDOT)	Amperometry	Up to <i>ca.</i> 1 mM	7	—	42
Electrochemically pre-treated Ag electrode manufactured from a compact disc	Amperometry	10.0 μM to 22.5 mM	6	—	37
Electrochemically pre-treated Ag electrode manufactured from a DVD	Amperometry	0.588 μM to 67.3 μM	0.2	Peroxide based disinfectant	36
Dodecyl benzenesulphonic acid and KCl modified Ag screen-printed electrodes	Amperometry	1.25 μM to 225 μM	5.8	—	22
HRP biosensor based on Ag@C nano-composite	Amperometry	0.5 μM to 140 μM	0.2	—	43
Ag nanoparticles/multiwalled carbon nanotube-modified glassy carbon electrode	Amperometry	0.1 mM to 10 mM	2	—	44
Ag nanoparticle coated glassy carbon electrode	Amperometry	Up to 75 μM	1.3	—	45
Indium-tin-oxide electrode modified with Ag nanoparticles stabilized by amine grafted mesoporous SBA-15	Amperometry	0.3 mM to 2.5 mM	300	—	46
Silver nanowire (50 nm) array sensor	Amperometry	0.1 mM to 3.1 mM	29	—	47
Unmodified Ag electrode manufactured from a DVD-RW	Cyclic voltammetry	0.087 mM to 3.41 mM	78.4	Artificial swimming pool water	This report

further pre-treatment for the determination of hydrogen peroxide in potable water. To our knowledge, there have only been a small number of reports utilising this approach for the determination of hydrogen peroxide. These have been focused on electrochemical pre-treatment^{36,37} *via* repeated voltammetric scanning, forming a roughened surface characterised by dendritic structures; a process which does not lend itself to possible mass production and commercialisation. Ag electrodes made directly from recycled material have the potential to be a sustainable and economical technique for the measurement of hydrogen peroxide. Initial investigations were undertaken to explore the electrochemical behaviour of hydrogen peroxide at these electrodes. The conditions were then optimised for the determination of hydrogen peroxide in water at levels generally utilised in swimming pools, spas and in fish farming. A number of possible interferences were investigated and a water sample was then examined using the optimised voltammetric assay.

2. Materials and methods

2.1. Apparatus

Cyclic voltammetry was performed with an Autolab potentiostat interfaced to a PC for data acquisition *via* the General Purpose Electrochemical System Software Package (GPES) version 3.4

(Autolab, Windsor Scientific Limited, Slough Berkshire UK). The voltammetric cell contained a graphite rod counter electrode, a saturated calomel electrode (SCE) (Russell, Fife, UK) and a 5 mm diameter Ag electrode manufactured from a rewritable digital versatile disc (DVD-RW) as the working electrode. The electrode was connected to the potentiostat using a crocodile clip attached to coaxial cable inserted into the appropriate sockets. The cell used for the voltammetric measurements was obtained from Metrohm (Switzerland).

2.2. Chemical and reagents

All chemicals were of Primar grade and supplied from Fisher (Loughborough, UK), unless stated otherwise. 174 mM hydrogen peroxide stock solutions were prepared by dissolving the appropriate volume in deionised water. Working standards, for optimisation of studies, were then prepared by dilution of the primary stock solution with deionised water. Deionised water was obtained from a Purite RO200-Stillplus HP System, (Purite Oxon, UK). Solutions of disodium, trisodium, sodium *o*-phosphate and *o*-phosphoric acid were made at a concentration of 0.2 M by dissolving the appropriate mass in deionised water. These were then titrated together to give the desired pH. An appropriate volume was then added directly to the voltammetric



cell and diluted with sufficient deionised water to give an overall phosphate concentration of 0.1 M.

2.3. Construction of compact disc electrode

The DVD-RW used in this study was constructed of several layers;⁴⁸ a lower polycarbonate substrate, a dye data storage layer, a Ag reflective layer and a printable layer for the labelling or incorporation of a design. Fig. 1 gives a diagrammatic explanation of the construction of the silver working electrode from the rewritable digital versatile disk (Imation, DVD-RW). The DVD-RW was mechanically delaminated by cutting with a suitable pair of scissors and applying slight bending pressure by hand until the upper layer can be peeled away. 10 mm × 60 mm sections of the DVD-RW were then cut out and the upper Ag layer cover with dielectric adhesive tape modified with a 5 mm diameter hole to define the working electrode area. A strip of exposed Ag was retained at the opposite end to be used as an electrical contact to the potentiostat. The resulting working Ag electrode was then used without further treatment as part of a three electrode system.

2.4. Voltammetric procedures

Cyclic voltammograms were initially recorded in plain solutions 0.1 M of phosphate buffer, and then in the same solution containing 1.74 mM of hydrogen peroxide. The voltammetric conditions were as follows: initial and final potential, 0.0 V; scan rate 50 mV s⁻¹ and switching potential, -1.0 V.

2.5. Scanning electron microscopy

Scanning electron microscopy was undertaken using a Philips XL30 ESEM. Energy dispersive X-ray microanalysis (EDX) was

undertaken using an Oxford Instruments Link ISIS 3.2 EDX system.

3. Results and discussion

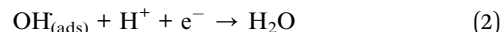
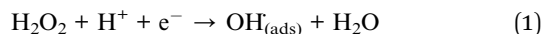
3.1. Scanning electron microscopy

Fig. 2 shows a representative scanning electron micrograph of the Ag metal layer obtained from the DVD-RW. Tracks can be seen across the surface a DVD reader/writer laser to follow. These appear as a series of *ca.* 1 μm spaced parallel stripes. Further EDX analysis showed this layer to be composed of Ag with little evidence of other elements.

3.2. Cyclic voltammetry

Fig. 3d shows the cyclic voltammogram of 1.74 mM hydrogen peroxide in a 0.1 M phosphate buffer pH 7 at our Ag DVD-RW. Similarly to that previously reported at conventional Ag electrodes,^{15,16} a single reduction peak was seen on the negative going scan. Consequently, we believe that this reduction peak results from the same 2e⁻, 2H⁺ reduction processes (eqn (1) and (2)).

The shoulder seen on this main peak ($E_p = -0.35$ V) was concluded to result from the previous reported mechanism,⁴⁹ whereby hydrogen peroxide undergoes a one proton, one electron reduction to give an adsorbed hydroxyl radical and water (eqn (1)). This adsorbed species then undergoes a further one proton, one electron reduction (eqn (2)) resulting in the two waves.



3.3. Effect of pH

The relationship of pH with the peak potential (E_p) of this peak was investigated over the pH range 2 to 10. Fig. 3 shows representative cyclic voltammograms undertaken using a scan rate of 50 mV s⁻¹. A near theoretical relationship between E_p and pH was obtained between pH 4 and pH 10. A marked difference in the voltammetric behaviour was seen at pH 10, presumed to

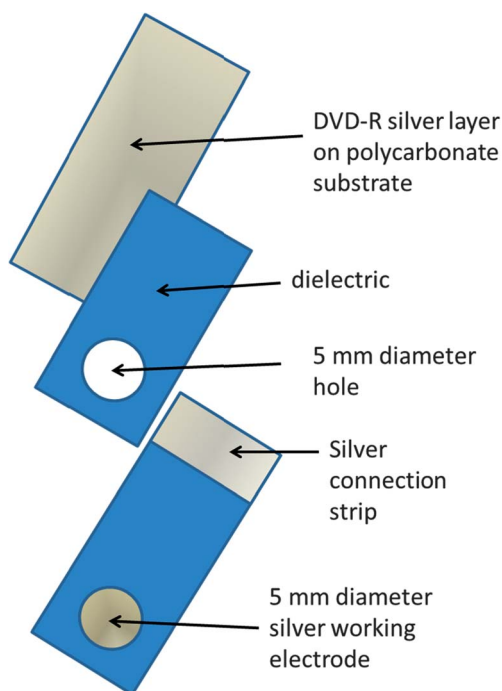


Fig. 1 Schematic of electrode construction.

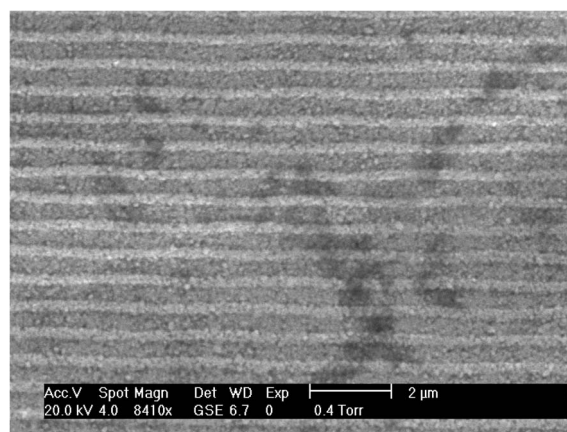


Fig. 2 SEM image of the surface of the DVD-RW Ag working electrode.



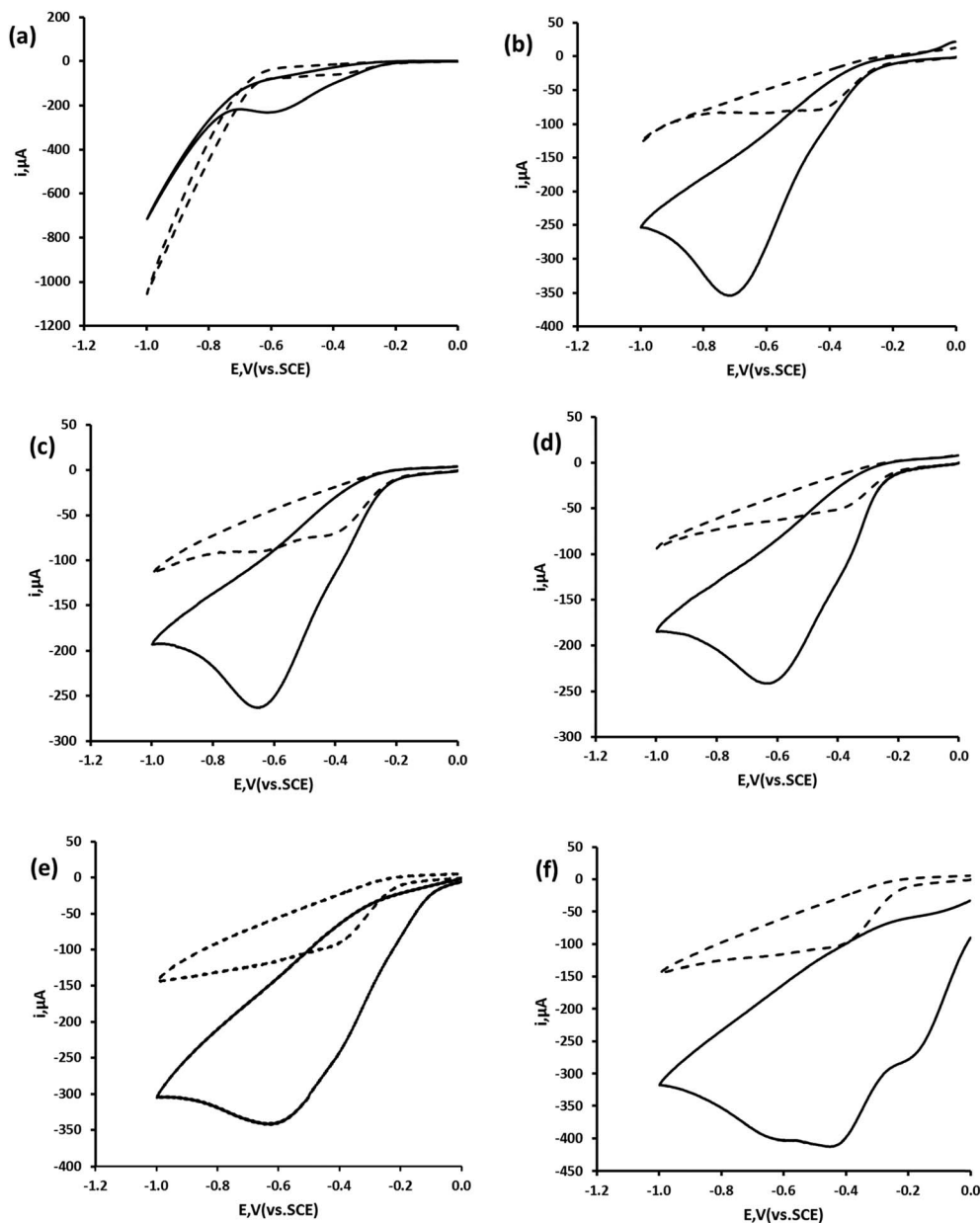


Fig. 3 Cyclic voltammetric behaviour of hydrogen peroxide at Ag DVD-RW electrode in the absence (dashed line) and in the presence of 1.74 mM hydrogen peroxide (solid line) in 0.1 M pH phosphate buffer. (a) pH 2; (b) pH 4; (c) pH 6; (d) pH 7; (e) pH 8 and (f) pH 10. Voltammetric conditions: start and end potential 0.0 V; switching potential -1.0 V; scan rate 50 mV s^{-1} .

result from the ionisation of the hydrogen peroxide molecule ($\text{p}K_{\text{a}} = 11.75$). As we wished to determine hydrogen peroxide concentrations in swimming and potable water samples further investigations were made at pH 7 (Fig. 4).

3.4. Calibration and limit of detection

The calibration plot was found to be linear over the range 0.087 mM to 3.41 mM hydrogen peroxide with a slope of 58.7 $\mu\text{A mM}^{-1}$, with an associated R^2 value of 0.996 . The coefficient of variation was determined on four replicate measurements at 0.174 mM and 0.690 mM was calculated to be 2.2% and 1.67% respectively. The limit of detection was calculated by

making replicate current measurements of a blank solution; the detection limits based on three times the standard deviation of these measurements gave a value of 78.35 μM .

3.5. Interference study

A number of compounds have been reported to be present in relatively high concentrations in swimming pool and potable water supplies,¹ such as, chloride, nitrate, sulphate and carbonate. Smaller concentrations of other electrochemically active species such as Cu^{2+} and Fe^{3+} are also suspected. No interferences were seen for 500 mg L^{-1} chloride, 50 mg L^{-1} nitrate, 700 mg L^{-1} sulphate or 700 mg L^{-1} carbonate. A small



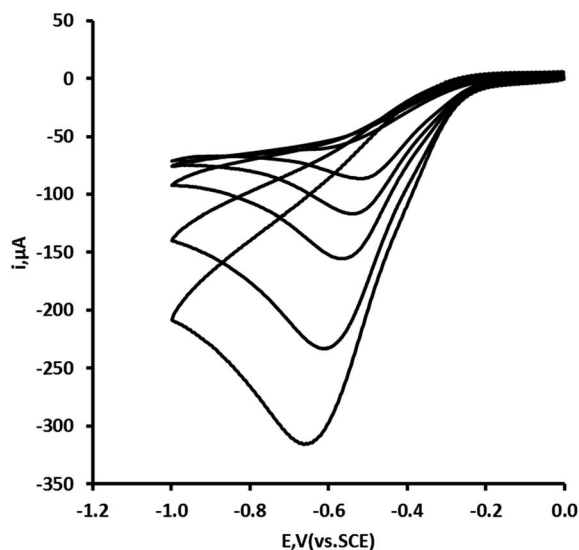


Fig. 4 Effect of scan rate on the cyclic voltammetric behaviour of a 1.74 mM in 0.1 M pH 7 phosphate buffer. Scan rate varied between 5, 10, 20, 50 and 100 mV s^{-1} ; all other voltammetric conditions as Fig. 1.

oxidation peak at 0 V was seen in the presence of Cu^{2+} (3 mg L^{-1}) and for Fe^{3+} (3 mg L^{-1}). However, this did not interfere with the reduction of hydrogen peroxide or with its quantification.

3.6. Analytical application

A 5 mL water sample aliquot was diluted with 5 mL of 0.2 M pH 7 phosphate buffer and the concentration of hydrogen peroxide was determined using a method of multiple standard additions. Fig. 5 shows representative cyclic voltammograms for this sample and the subsequent standard additions of hydrogen peroxide. The resulting standard addition plot is shown alongside. The recovery and precision data obtained for five replicate samples is shown in Table 2. The method can be seen to give reliable data at the concentrations investigated here. The

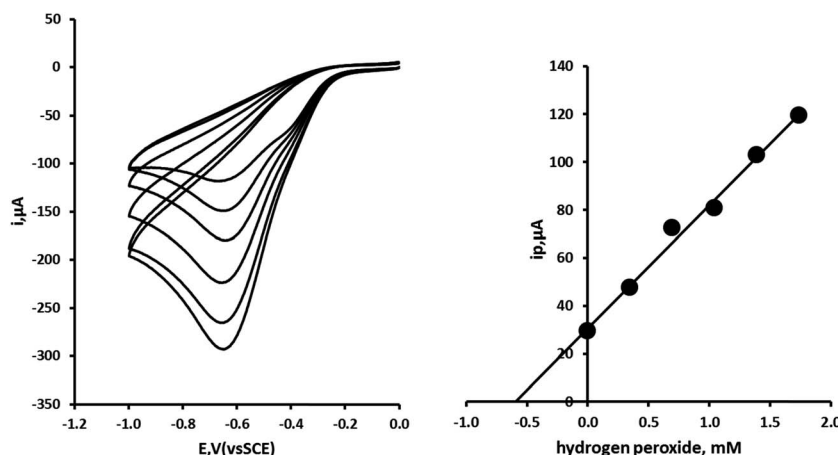


Fig. 5 Multiple standard additions of hydrogen peroxide made to water sample fortified with 1.2 mM (40.8 mg L^{-1}) hydrogen peroxide. Each addition the equivalent of 348 μM (11.8 mg L^{-1}) hydrogen peroxide.

Table 2 Recovery and precision data for hydrogen peroxide obtained on water sample^a

Sample	Native, mM	Added, mM	Found, mM	% Recovery
1	n/d	1.218	1.178	96.71
2	n/d	1.218	1.060	87.03
3	n/d	1.218	1.090	89.49
4	n/d	1.218	1.058	86.86
5	n/d	1.218	1.136	93.27

^a Mean recovery = 90.67%; coefficient of variation = 4.69%; n/d = not detected.

percentage recovery for a typical swimming pool water concentration of 1.2 mM (40.8 mg L^{-1}) of hydrogen peroxide was found to be 90.67% with an associated coefficient of variation of 4.69% ($n = 5$).

4. Conclusions

Quantification of hydrogen peroxide has been shown to be possible at Ag electrodes manufactured from an unmodified DVD-RW. A limit of detection of 78.35 μM (based on three times the standard deviation of the noise) was recorded with a linear range from 0.087 mM to 3.41 mM ($R^2 = 0.996$) hydrogen peroxide. This paper demonstrates that hydrogen peroxide produces a well-defined electrocatalytic signal at our DVD-RW electrodes. A simple and convenient assay for hydrogen peroxide was developed, based on this device in conjunction with cyclic voltammetry. The results indicate that a method based on multiple standard additions is both highly accurate and precise, obtaining a coefficient of variation of 4.69% for a water sample fortified with 40.8 mg L^{-1} (1.2 mM) levels commonly reported in aquaculture and swimming pools applications. In further studies we plan to investigate improving the sensitivity of the assay by the use of more advanced voltammetric waveforms such as differential pulse voltammetry and techniques such as amperometry.



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References

- 1 A. Schwake, B. Ross and K. Cammann, *Sens. Actuators, B*, 1998, **46**, 242–248.
- 2 B. W. Sheldon and J. Brake, *Poult. Sci.*, 1991, **5**, 1092–1099.
- 3 N. Y. Mostafa, *Global Vet.*, 2010, **4**, 362–365.
- 4 D. O. Ukuku, M. L. Bari, S. Kawamoto and K. Isshiki, *Int. J. Food Microbiol.*, 2005, **104**, 225–233.
- 5 L.-F. Pedersen and P. B. Pedersen, *Aquacultural Engineering*, 2012, **46**, 40–46.
- 6 L. J. Schmidt, M. P. Gaikowski and W. H. Gingerich, Environmental Assessment for the Use of Hydrogen Peroxide in Aquaculture for Treating External Fungal and Bacterial Diseases of Cultured Fish and Fish Eggs, U.S. Geological Survey, Biological Resources Division, 2006, <http://www.fda.gov/ucm/groups/fdagov-public/@fdagov-avgen/documents/document/ucm072399.pdf>, accessed 5/8/13.
- 7 E. C. Hurdis and H. Romeyn, *Anal. Chem.*, 1954, **26**, 320–325.
- 8 R. M. Sellers, *Analyst*, 1980, **105**, 950–954.
- 9 P. A. Tanner and A. Y. S. Wong, *Anal. Chim. Acta*, 1998, **370**, 279–287.
- 10 E. Pick and Y. Keisari, *J. Immunol. Methods*, 1980, **38**, 161–170.
- 11 X. Li, D. Heryadi and A. A. Gewirth, *Langmuir*, 2005, **21**, 9251–9259.
- 12 D. Vasudevan, *Bull. Electrochem.*, 2000, **16**, 277–279.
- 13 J. Wang and T. Golden, *Anal. Chem.*, 1989, **61**, 1397–1400.
- 14 K. Schachl, H. Alemu, K. Kalcher, J. Jeřzkova, I. Svancara and K. Vytřoras, *Analyst*, 1997, **122**, 985–989.
- 15 W. Chen, S. Cai, Q.-Q. Ren, W. Wen and Y.-D. Zhao, *Analyst*, 2012, **137**, 49–58.
- 16 S. Chen, R. Yuan, Y. Chai and F. Hu, *Microchim. Acta*, 2013, **180**, 15–32.
- 17 C. M. Welch, C. E. Banks, A. O. Simm and R. G. Compton, *Anal. Bioanal. Chem.*, 2005, **382**, 12–21.
- 18 M. A. T. Gilmartin, R. J. Ewen, J. P. Hart and C. L. Honeybourne, *Electroanalysis*, 1995, **7**, 547–555.
- 19 A. A. Karyakin, E. A. Puganova, I. A. Budashov, I. N. Kurochkin, E. E. Karyakina, V. A. Levchenko and V. N. Matveyenko, *Anal. Chem.*, 2004, **76**, 474–478.
- 20 R. C. Cretu, D. M. Gligor, L. Muresan, I. C. Popescu and L. M. Muresan, *J. Appl. Electrochem.*, 2006, **36**, 1327–1332.
- 21 G. C. Zhao, M. Q. Xu and Q. Zhang, *Electrochem. Commun.*, 2008, 1924–1926.
- 22 L. Gonzalez-Macia, M. Smyth and A. Killard, *Electroanalysis*, 2012, **24**, 609–614.
- 23 M. Honda, T. Kodera and H. Kita, *Electrochim. Acta*, 1983, **28**, 727–733.
- 24 N. D. Merkulova, G. V. Zhutaeva, N. A. Shumilova and V. S. Bagotskii, *Electrochim. Acta*, 1973, **18**, 169–174.
- 25 G. Flatgen, S. Wasle, M. Lubke, C. Eickes, G. Radhakrishnan, K. Doblhofer and G. Ertl, *Electrochim. Acta*, 1999, **44**, 4499–4506.
- 26 F. W. Campbell, S. R. Belding, R. Baron, L. Xiao and R. G. Compton, *J. Phys. Chem. C*, 2009, **113**, 9053–9062.
- 27 M. Honda, T. Kodera and H. Kita, *Electrochim. Acta*, 1986, **31**, 377–383.
- 28 K. C. Honeychurch, *Adv. Anal. Chem.*, 2013, **3A**, 28–33.
- 29 H.-Z. Yu, *Chem. Commun.*, 2004, 2633–2636.
- 30 D. Lowinsohn, E. M. Richter, L. Angnes and M. Bertotti, *Electroanalysis*, 2006, **18**, 89–94.
- 31 E. M. Richter, M. A. Augelli, S. Magarotto and L. Angnes, *Electroanalysis*, 2001, **13**, 760–764.
- 32 L. Angnes, E. M. Richter, M. A. Augelli and G. H. Kume, *Anal. Chem.*, 2000, **72**, 5503–5506.
- 33 M.-C. Radulescu and A. F. Danet, *Sensors*, 2008, **8**, 7157–7171.
- 34 D. C. Kirkpatrick, C. Antwi and R. S. Martin, *Anal. Methods*, 2010, **2**, 811–816.
- 35 E. M. Richter, M. A. Augelli, G. H. Kume, R. N. Mioshi and L. Angnes, *Fresenius' J. Anal. Chem.*, 2000, **366**, 444–448.
- 36 Y. Wenn, A.-J. Lin, H.-F. Chen, Y.-Z. Jiao and H.-F. Yang, *Biosens. Bioelectron.*, 2013, **41**, 857–861.
- 37 W. Lian, L. Wang, Y. Song, H. Yuan, S. Zhao, P. Li and L. Chen, *Electrochim. Acta*, 2009, **54**, 4334–4339.
- 38 E. Ferapontova and L. Gorton, *Electroanalysis*, 2003, **15**, 484–491.
- 39 B. Liu and M. Wang, *Int. J. Electrochem. Sci.*, 2013, **8**, 8572–8578.
- 40 A. M. Golsheikh, N. M. Huang, H. N. Lim, R. Zakaria and C.-Y. Yin, *Carbon*, 2013, **62**, 405–412.
- 41 C. M. Welch, C. E. Banks, A. O. Simm and R. G. Compton, *Anal. Bioanal. Chem.*, 2005, **382**, 12–21.
- 42 A. Balamurugan and S.-M. Chen, *Electroanalysis*, 2009, **21**, 1419–1423.
- 43 S. Mao, Y. Long, W. Lia, Y. Tu and A. Deng, *Biosens. Bioelectron.*, 2013, **48**, 258–262.
- 44 A. Afraz, A. A. Rafati and A. Hajian, *J. Solid State Electrochem.*, 2013, **17**, 2017–2025.
- 45 K. Liao, P. Mao, Y. Li, Y. Nan, F. Song, G. Wang and M. Han, *Sens. Actuators, B*, 2013, **181**, 125–129.
- 46 M. Vinoba, S. Kwan Jeong, M. Bhagiyalakshmi and M. Alagar, *Bull. Korean Chem. Soc.*, 2010, **31**, 3668–3674.
- 47 E. Kurowska, A. Brzozka, M. Jarosz, G. D. Sulka and M. Jaskula, *Electrochim. Acta*, 2013, **104**, 439–447.
- 48 F. R. Byers, *Care and Handling of CDs and DVDs, A Guide for Librarians and Archivists*, Council on Library and Information Resources, Washington, DC, October 2003, <http://www.clir.org/pubs/reports/pub121/pub121.pdf>, accessed 12/2/13.
- 49 R. G. Compton and C. E. Banks, *Understanding Voltammetry*, Imperial College Press, 2nd edn, 2011, p. 400.

