View Online

Thallium underpotential deposition on silver nanoparticles: size-dependent adsorption behaviour

Fallyn W. Campbell, Yi-Ge Zhou and Richard G. Compton*

Received (in Victoria, Australia) 13th November 2009, Accepted 12th December 2009
First published as an Advance Article on the web 11th January 2010
DOI: 10.1039/b9nj00669a

Downloaded by Universidade do Porto (UP) on 20 October 2010
Published on 11 January 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00669A

We report the size-dependent adsorption of thallium on silver nanoparticles (AgNPs) in the region of underpotential deposition; the phenomenon is observed for large nanoparticles, and bulk silver, but absent for nanoparticles below 50 nm diameter.

The use of nanoparticles in electrochemistry provides a number of advantages over their corresponding bulk materials. Probably the most subtle difference is enhanced mass transport due to the convergent rather than linear nature of diffusion.[1] This in turn can facilitate the study of faster electrode processes. More obviously, nanoparticles provide higher active surface area leading to improved selectivity and signal-to-noise ratio which can be highly advantageous in some electro-analytical applications,[2] whilst the reduction in size can lead to changed surface and electronic properties. Crystal faces exposed at the nanoscale, and not seen at the macroscale, may lead to improved current responses and catalytic properties; the converse might also be true. Nanoparticles have therefore found extensive use in catalytic[3] and sensing[4] applications. However, to date little is known on the adsorption behaviour of nanoparticles in the electrochemical environment although the adsorption on macro- and nano-gold supported on carbon nanotubes has been shown to change qualitatively with no adsorption seen on small nanoparticles.[5]

Underpotential deposition (UPD) is the deposition of a monolayer, or sub-monolayer, of a metal onto a different substrate metal electrode at potentials more positive than the equilibrium (Nernst) potential for bulk deposition of this metal. It is possible to deposit a wide variety of metals onto an electrode substrate by UPD. Most relevant to this study is UPD of thallium on macro-sized silver electrodes,[6] which has been extensively reported in the literature. However, the UPD of metals such as lead, bismuth, cadmium, copper, nickel and zinc[7] has also been reported in the literature on silver substrates. Studies have also examined the UPD behaviour of two co-depositing species such as Tl and Pb.[8] Thallium UPD has also been reported on gold, platinum and copper electrodes.[1c] The potential difference between UPD and bulk deposition can be related to the different work functions associated with substrate material and deposit. This can in turn result in partial charging of the adatoms. Since the work function of nanoparticles may be size related this offers a further mechanism by which changed electrochemical behaviour may arise at the nanoscale.[9]

A number of thallium deposition studies have been performed on macro-sized silver single crystal electrodes, each of which displays its own distinct features. The reduction of Tl^+ to an adsorbed layer of Tl metal is represented in eqn (1).

$$Tl^+(aq) + e^- \rightleftarrows Tl(metal) \qquad (1)$$

The structure of a surface is seen to control the ease with which thallium can be deposited: Ag(111) > Ag(100) > Ag(110) > polycrystalline Ag.[10] This evidence clearly indicates that the adsorption of Tl is highly sensitive to the detailed surface structure of a silver electrode.

Little detailed research can be found in the literature relating to the UPD adsorption of metal atoms such as thallium, on nanoparticulate materials,[5,11] or indeed of the adsorption of molecules in general on nanoparticles. This letter will compare the deposition of thallium on silver macrodisk electrodes and silver nanoparticles (AgNPs), examining the influence of both nanoparticle size and electrode coverage on the bulk and underpotential deposition of thallium on AgNPs.

The study of UPD is important as it commonly results in the deposition of a monolayer or sub-monolayer of material. Such layers can be highly significant in the mechanisms of electrocatalytic processes. Accordingly the investigation of adsorption effects on nanoparticulate matter is important for the development of these materials for both synthetic and analytical applications.

We have chosen to examine the underpotential and bulk deposition of thallium on AgNPs of varying sizes.[12] AgNPs were synthesized by a well documented[12,13] seed mediated citrate reduction process. This method allows us to synthesise AgNPs with the following diameters: 20–40 nm, 50–70 nm and 80–120 nm.[13] The as-synthesized colloidal AgNPs suspension was subsequently evaporated on the surface of a basal plane pyrolytic graphite (BPPG) electrode.

Thallium deposition was carried out in a solution of KNO_3 (1.5 M) + $TlNO_3$ (10 mM) at 50 mV s^{-1}. Fig. 1 displays the underpotential deposition [E_p = −0.545 V (*vs.* SCE)] and stripping [E_p = −0.440 V (*vs.* SCE)] of Tl on a silver macrodisk (diameter = 0.7 mm) under the same conditions described above. Tl deposition was also examined on a bare BPPG (diameter = 5 mm) electrode and showed no UPD and a bulk deposition taking place at E_p = −0.822 V and corresponding stripping peak at E_p = −0.637 V.

Department of Chemistry, Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, UK OX1 3QZ. E-mail: richard.compton@chem.ox.ac.uk; Fax: +44 (0)1865 275 41; Tel: +44 (0)1865 275 413

View Online

Downloaded by Universidade do Porto (UP) on 20 October 2010
Published on 11 January 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00669A

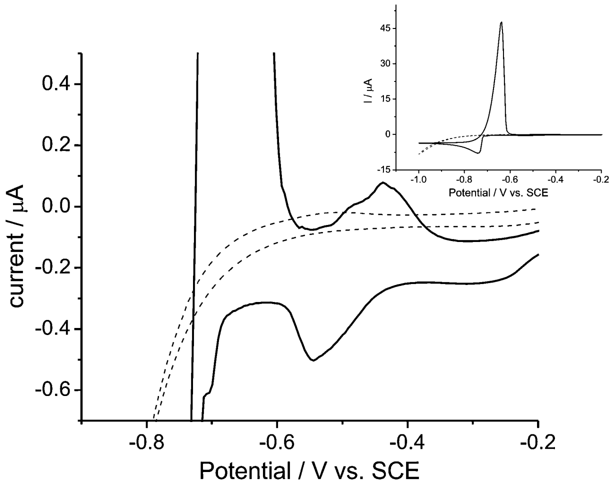

Fig. 1 Thallium deposition on a silver macrodisk electrode. Experimental conditions: KNO_3 (1.5 M) + $TlNO_3$ *vs.* SCE. Scan rate: 50 mV s^{-1}. (Solid line: 10 mM $TlNO_3$; dashed line: 0 mM $TlNO_3$.)

When we compare this with a BPPG electrode modified with AgNPs (20–40 nm) we can see that the bulk deposition peak shifts positively from that of a BPPG bulk deposition to that of silver bulk deposition, as shown in Fig. 2 (inset). Furthermore, when we closely examine the region of UPD it is clear that on the small AgNPs (20–40 nm), no appreciable UPD or stripping of thallium takes place, while we still observe a bulk deposition wave at $E_p = -0.777$ V (*vs.* SCE) and the corresponding dissolution at $E_p = -0.633$ V (*vs.* SCE) as shown in Fig. 2. The same effect is recorded for a range of surface coverages of AgNPs on the BPPG electrode, between 0.5 and 3%. Surface coverage was altered by varying the volume of colloidal suspension dried on the electrode surface *i.e.* by increasing the volume the NP density is increased. Following the deposition and stripping of Tl, the amount of silver on the surface was quantified by linear sweep stripping voltammetry (LSV) in $NaClO_4$ (0.1 M) as shown in Fig. 3.

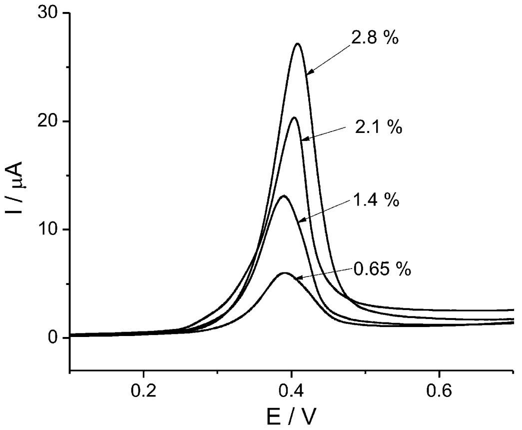

Fig. 3 Stripping voltammetry recorded for increasing surface coverage of AgNPs (20–40 nm, 0.5 and 3.0%). Experimental conditions: $NaClO_4$ (0.1 M) *vs.* SCE. Scan rate: 20 mV s^{-1}.

When the same experiment was repeated using larger AgNPs (80–120 nm) (Fig. 4) a similar effect was observed with respect to the shift in position of the bulk deposition peak. However, unlike the small AgNPs (20–40 nm), the larger AgNPs (80–120 nm) exhibited distinct deposition and stripping peaks in the thallium UPD region, corresponding to those reported on bulk silver. As no UPD is observed for bare BPPG we can attribute this to the presence of AgNPs (80–120 nm). In this case increased AgNP density on the electrode surface corresponds to an increase in the thallium deposition and stripping peak heights (Fig. 4), due to the greater surface area available for thallium adsorption.

The results reported here indicate clearly that silver nanoparticles show qualitatively different adsorption behaviour from below a size threshold of *ca.* 50 nm with Tl adsorption absent below, but observed above this value. It is evident that metal nanoparticles can show qualitatively different adsorption behaviour from bulk materials and that this may cause marked changes in electrochemical reactivity such as size-dependent

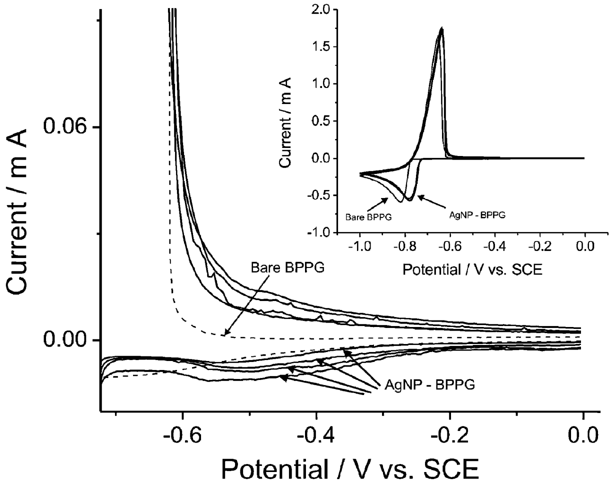

Fig. 2 Thallium deposition on AgNP–BPPG (20–40 nm) electrode. Experimental conditions: KNO_3 (1.5 M) + $TlNO_3$ *vs.* SCE. Scan rate: 50 mV s^{-1}. (Solid line: AgNP–BPPG (20–40 nm) electrode; dashed line: bare BPPG.)

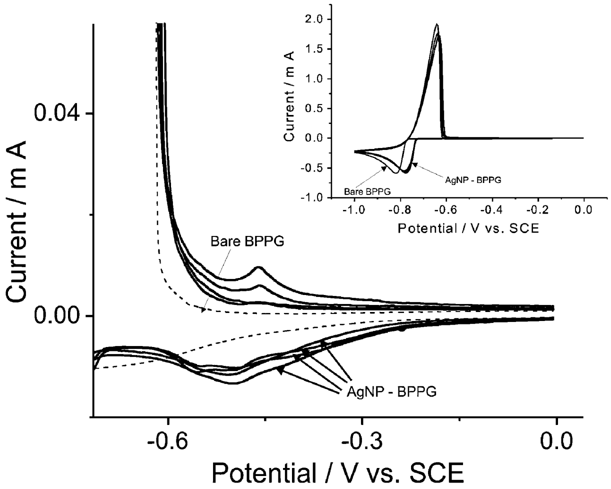

Fig. 4 Thallium deposition on AgNP–BPPG (80–120 nm) electrode. Experimental conditions: KNO_3 (1.5 M) + $TlNO_3$ *vs.* SCE. Scan rate: 50 mV s^{-1}. (Solid line: AgNP–BPPG (80–120 nm) electrode; dashed line: bare BPPG.)

This journal is © The Royal Society of Chemistry and the Centre National de la Recherche Scientifique 2010

Published on 11 January 2010 on http://pubs.rsc.org | doi:10.1039/B9NJ00669A
Downloaded by Universidade do Porto (UP) on 20 October 2010

changes in electrode mechanism: with clear implication for the investigation of electrocatalysis. The observed behaviour likely arises from size-dependent morphology or electronic (work function) properties.[9]

Experimental section

$TlNO_3$ (99.999%, Sigma-Aldrich), KNO_3 (99%, Aldrich) and $NaClO_4$ (98–102%, Johnson Matthey) were used as received without further purification. All solutions were prepared using Millipore pure water with resistivity not less than 18.2 MΩ cm^{-1} at 25 °C (Vivendi Water Systems, UK).

All electrochemical experiments were performed using a μAutolab type III potentiostat and desktop PC. A three-electrode set up was used consisting of a working electrode, carbon rod counter electrode and saturated calomel (SCE) reference electrode (Radiometer Analytical). Carbon rods and BPPG were supplied by Le Carbone, Sussex, UK.

The AgNPs were synthesized by a seed mediated citrate reduction of $AgNO_3$ adapted from a procedure by Pyatenko *et al.*,[12] and detailed in our previous publications.[13] Thallium deposition was performed in KNO_3 (1.5 M) + $TlNO_3$ (10 mM) at 50 mV s^{-1} by scanning negatively from -0.2 V to -1.0 V and reversing the scan direction.

AgNPs were stripped from the BPPG electrode by LSV in $NaClO_4$ (0.1 M), scanning from 0 V to 0.9 V at 20 mV s^{-1}.

Acknowledgements

F. W. C. thanks Abington Partners, Bath, for partial funding. Y-G. Z. thanks St. John's College, Oxford, for funding.

References

1 (*a*) T. J. Davies, S. Ward-Jones, C. E. Banks, J. del Campo, R. Mas, F. Xavier Muñoz and R. G. Compton, *J. Electroanal. Chem.*, 2005, **585**, 51–62; (*b*) T. J. Davies and R. G. Compton, *J. Electroanal. Chem.*, 2005, **585**, 63–82; (*c*) T. J. Davies, C. E. Banks and R. G. Compton, *J. Solid State Electrochem.*, 2005, **9**, 797–808.

2 (*a*) F. W. Campbell and R. G. Compton, *Anal. Bioanal. Chem.*, 2010, **396**, 241–259; (*b*) C. M. Welch and R. G. Compton, *Anal. Bioanal. Chem.*, 2005, **382**, 12–21; (*c*) C. Batchelor-McAuley, Y. Du, G. G. Wildgoose and R. G. Compton, *Sens. Actuators, B*, 2008, **135**, 230–235; (*d*) L. Xiao, G. G. Wildgoose and R. G. Compton, *Anal. Chim. Acta*, 2008, **620**, 44–49; (*e*) X. Dai, G. G. Wildgoose, C. Salter, A. Crossley and R. G. Compton, *Anal. Chem.*, 2006, **78**, 6102–6108.

3 (*a*) J. Manso, L. Agüí, P. Yánez-Sedeño and J. M. Pingarrón, *Anal. Lett.*, 2005, **37**, 887–902; (*b*) H. B. Yildiz, R. Freeman, R. Gill and I. Willner, *Anal. Chem.*, 2008, **80**, 2811–2816; (*c*) S. W. Wu, H. Zhao, H. Ju, C. Shi and J. Zhao, *Electrochem. Commun.*, 2006, **8**, 1197–1203.

4 (*a*) O. Domínguez-Renedo, L. Ruiz-Espelt, N. García-Astorgano and M. J. Acros-Martinez, *Talanta*, 2008, **76**, 854–858; (*b*) K. E. Toghill, L. Xiao, G. G. Wildgoose and R. G. Compton, *Electroanalysis*, 2009, **21**, 1113–1118; (*c*) M. Gao, H. Qi, Q. Gao and C. Zhang, *Electroanalysis*, 2008, **20**, 123–130.

5 C. Batchelor-McAuley, G. G. Wildgoose and R. G. Compton, *New J. Chem.*, 2008, **32**, 941–946.

6 (*a*) T. C. Girija and M. V. Sangaranarayanan, *J. Appl. Electrochem.*, 2006, **36**, 531–538; (*b*) V. Daujotis and E. Gaidamauskas, *J. Electroanal. Chem.*, 1998, **446**, 151–157; (*c*) E. Herrero, L. J. Buller and H. D. Abruña, *Chem. Rev.*, 2001, **101**, 1897–1930.

7 (*a*) Y. V. Bokshits, N. P. Osipovich, E. A. Strel'tsov and G. P. Shevchenko, *Colloids Surf., A*, 2004, **242**, 79–83; (*b*) Y. Bonfil, M. Brand and E. Kirowa-Eisner, *Anal. Chim. Acta*, 2002, **464**, 99–114; (*c*) K.-O. Thiel, M. Hintze, A. Vollmer and C. Donner, *J. Electroanal. Chem.*, 2008, **621**, 7–12; (*d*) S. Morin, A. Lachenwitzer, F. A. Moller, O. M. Magnussen and R. J. Behm, *J. Electrochem. Soc.*, 1999, **146**, 1013–1018; (*e*) J. Miragliotta and T. E. Furtak, *Surf. Interface Anal.*, 1989, **14**, 53–58.

8 (*a*) S. Bharathi, V. Yegnaraman and G. Prabhakara Rao, *J. Appl. Electrochem.*, 1994, **24**, 981–988; (*b*) A. M. El-Halim, K. Jüttner and W. J. Lorenz, *J. Electroanal. Chem.*, 1980, **106**, 193–207.

9 (*a*) D. M. Kolb, M. Przasnyski and H. Gerischer, *J. Electroanal. Chem.*, 1974, **54**, 25–38; (*b*) D. M. Kolb and H. Gerischer, *Surf. Sci.*, 1975, **51**, 323–327; (*c*) H. Gerischer, D. M. Kolb and M. Przasnyski, *Surf. Sci.*, 1974, **43**, 662–666; (*d*) W. J. Plieth, *J. Phys. Chem.*, 1982, **86**, 3166–3170.

10 (*a*) B. W. Mao, Z. Q. Tian and M. Fleishmann, *Electrochim. Acta*, 1992, **37**, 1767–1770; (*b*) J. X. Wang, R. R. Adžić, O. M. Magnussen and B. M. Ocko, *Surf. Sci.*, 1995, **344**, 111–121.

11 K. E. Toghill, G. G. Wildgoose, A. Moshar, C. Mulcahy and R. G. Compton, *Electroanalysis*, 2008, **20**, 1731–1737.

12 (*a*) A. Pyatenko, M. Yamaguchi and M. Suzuki, *J. Phys. Chem. C*, 2007, **111**, 7910–7917; (*b*) A. Pyatenko, M. Yamaguchi and M. Suzuki, *J. Phys. Chem. B*, 2005, **109**, 21608–21611.

13 (*a*) F. W. Campbell, S. R. Belding, R. Baron, L. Xiao and R. G. Compton, *J. Phys. Chem. C*, 2009, **113**, 14852–14857; (*b*) F. W. Campbell, S. R. Belding, R. Baron, L. Xiao and R. G. Compton, *J. Phys. Chem. C*, 2009, **113**, 9053–9062.