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Controlled deposition of nanoparticles at the liquid–liquid interface

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We report a novel method for the preparation of well-defined metallic nanoparticles, which is illustrated with the technologically important example of palladium nanoparticles dispersed in γ-alumina.

We present a novel method for the stable and controlled electrochemical deposition of metallic palladium within a porous γ-alumina substrate, a system of relevance in catalysis and gas separation.[1,2] The method exploits electrodeposition at the template-modified interface between immiscible liquids, where the γ-alumina acts as the template, to control palladium formation.

Electrochemical deposition at organic/water interfaces in the absence of templates has been reported previously.[3–5] This process is of intrinsic interest due to the lack of solid substrate, and associated defect sites, where the energetic barrier to nucleation is assumed to be lowest.[6] However, understanding of the mechanism of electrochemical deposition at the organic/water interface has been hampered by the tendency of the deposited nanoparticles to aggregate.[5] The method described here replaces the metallic substrate previously employed for template-controlled electrochemical deposition[7,8] with an immiscible organic solvent. The γ-alumina membranes were used to separate the aqueous and organic phases of the electrochemical cell, with the aqueous phase forming the lower half of the cell. The organic/water interface is localized at the mouth of the template because of the membrane's hydrophilic properties.† Application of a potential difference across the resultant array of pore-sized organic/water interfaces caused controlled deposition of Pd at the mouth of the alumina pore. An interfacial reduction of aqueous phase tetrachloropalladinate to metallic palladium is induced by the potential difference,[5] with organic phase butylferrocene employed as the electron donor.‡ Pd is thus controllably dispersed within the pores of the alumina template. By contrast with previous template approaches,[7,8] the dispersed nanoparticles are not formed on an underlying metallic substrate, thereby avoiding the requirement for substrate removal.

Both voltammetry and chronoamperometry of the electrified alumina-templated liquid–liquid interface displayed responses characteristic of nucleation (Fig. 1),[5] with an irreversible process at +0.7 V, which corresponds to the deposition of Pd. The nucleation loops are no longer observed after approximately six successive cyclic voltammetric scans, indicating that the current on consecutive scans contains a progressively decreasing contribution from nucleation. Fig. 2(a) shows a high resolution scanning electron microscope (SEM) image of an alumina membrane, following an initial (5 min) electrochemical deposition of Pd particles at the templated 1,2-dichloroethane (DCE)/water interface. The nominal diameter of the alumina pores was 100 nm, the cell was configured with the organic phase above the alumina membrane, with the aqueous phase on the underside. Following this initial deposition, the SEM indicates that around 5% of the pores contain detectable amounts of Pd. Prolonged electrolysis of the DCE/water interface leads to deposition within an increasingly large fraction of the available pores (Fig. 2(b) and (c)). The presence of Pd was confirmed by energy dispersive X-ray analysis (EDX, see Table 1). The structure of the alumina template is generally apparent, indicating that Pd deposits are growing as discrete nanoparticles.

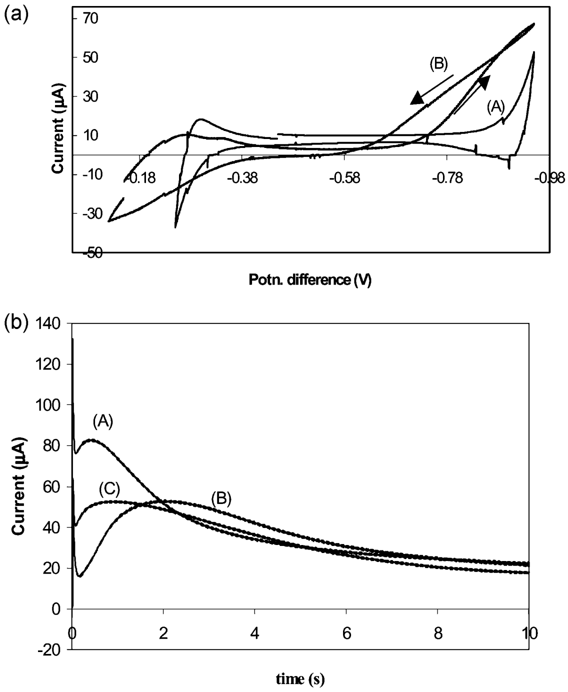

Fig. 1 (a) Cyclic voltammetry of Pd deposition cell at a scan rate of 0.1 V s^{-1}, aqueous phase [$PdCl_4{}^{2-}$] of 1×10^{-3} M, (A) shows the response in the absence of butylferrocene, (B) is the response with organic phase [butylferrocene] of 5×10^{-4} M. The arrows indicate the nucleation loop observed. (b) Successive potential steps from −0.45 V to (A) −0.9 V, (B) −0.8 V and (C) −0.75 V, where the cell contains aqueous phase [$PdCl_4{}^{2-}$] (1×10^{-3} M) and organic phase butylferrocene (5×10^{-4} M). The organic phase was placed above the aqueous phase in these cases.

The dark patches observed in Fig. 2(a)–(c), represent the increasingly large growths of Pd nanoparticles. The particles do not coalesce, even at high Pd coverage, indicating that the alumina membrane serves as an effective template to control deposition at the organic/water interface. The white patches visible in Fig. 2(a)–(c) are due to localised sample charging caused by the presence of precipitates of aluminium oxide.[9] The Pd nanoparticles thus formed are flush with the alumina surround and have a high surface area with a maximum dimension determined by the pore diameter employed (in this case, 100 nm). To confirm the templated-growth mechanism of the membrane-supported Pd, the alumina surround was removed by dissolution over 72 h in 1 M HCl. The liberated Pd particles were washed and filtered, with SEM analysis performed subsequently (Fig. 2(d)). The images show that some particle aggregation has occurred following template dissolution,[10] however the particle morphology retains some spherical structure, with an approximate diameter of 100 nm, indicative

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of the constraint over growth imparted by the template.

Electrochemical deposition at the organic/water interface offers a unique way to observe the relationship between the driving force for particle growth (here, the applied potential) and the form of the resultant particles. By contrast, the initial stages of electrodeposition on solid substrates are governed by the structure of the substrate, leading to phenomena such as under-potential deposition and epitaxial growth.[11–13] The method pioneered here offers a route to the fabrication of metallic nanostructures that does not require an electrical contact to be made to the nanostructure, since particle growth is at the interface between two electrolyte solutions. The method developed offers simpler control over particle morphology than colloidal growth methods, hence it represents an interesting intermediate case between classical electrochemical and chemical routes to the growth of metallic particles.[6,14,15]

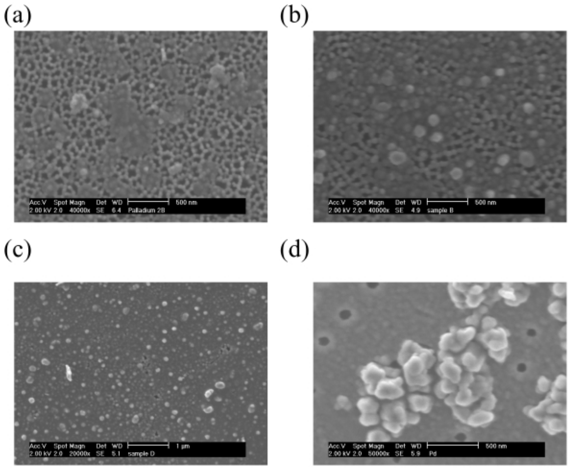

Fig. 2 (a) SEM image of Anopore γ-alumina membrane, after deposition of Pd, at +0.7 V using the cell described‡ for 5 min. (b) SEM image of γ-alumina membrane (nominal pore size 100 nm), after deposition of Pd for 1 h at a potential of 0.95 V. (c) SEM image of alumina membrane following deposition for 1 h at a potential of 0.95 V, as in (a), although the concentration of organic phase butylferrocene was increased (to 1×10^{-3} M). (d) SEM image of Pd particles electro-deposited, following dissolution of the alumina membrane in 1 M HCl. The liberated Pd particles were retained by filtration with a polyester filter (Poretics, Livermore, CA, USA), with a mean pore diameter of 100 nm. The scale bars in the SEM images correspond to 0.5 µm for (a), (b) and (d), and 1 µm in the case of (c).

Table 1 Composition, by wt% and atom% of the membrane shown in Fig. 2(a), as determined by EDX

Sample	Element	Wt%	Atom%
Blank membrane	O	29.86	42.15
	Al	63.07	52.79
	P	3.04	2.22
	S	4.04	2.84
Palladium membrane	O	18.12	31.67
	Al	55.78	57.79
	P	2.56	2.31
	S	3.37	2.94
	Pd	20.17	5.3

We are currently investigating the generalisation of our method to the production of other nanostructured materials, as well as exploring the detailed influence of applied potential on Pd growth. In due course, we envisage important applications, for example in hydrogenation catalysis and separations,[1,2] for the nanoparticle ensembles generated *via* this technique.

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Notes and references

† Membranes of γ-alumina, with nominal pore diameters of 100 nm and thicknesses of 60 µm (Whatman International Ltd, Maidstone, UK) were sealed to a 5 mm i.d. glass tube with silicone sealant.

‡ Electrochemical experiments were performed using an EG&G Model 273 potentiostat (Princeton Applied Research Corp., Princeton NJ, USA) operating in four-electrode mode. The aqueous phase comprised of 1×10^{-3} M ammonium tetrachloropalladate (Fluka, Gillingham, UK), 5×10^{-2} M lithium chloride and 5×10^{-2} M lithium sulfate dissolved in water obtained from a Milli-Q purification system. The organic solvent, 1,2-dichloroethane (HPLC grade, Lancaster Synthesis, Lancaster, UK) was used with an organic electrolyte, bis(triphenylphosphoranylidene)ammonium tetrakis(pentafluoro)phenylborate, prepared in house, at a concentration of 5×10^{-3} M. During deposition experiments butylferrocene (Lancaster, 98%) was added to the DCE solution in concentrations of either 5×10^{-4} or 1×10^{-3} M. Ag/AgCl reference electrodes were employed: potentials are quoted with respect to these electrodes.

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