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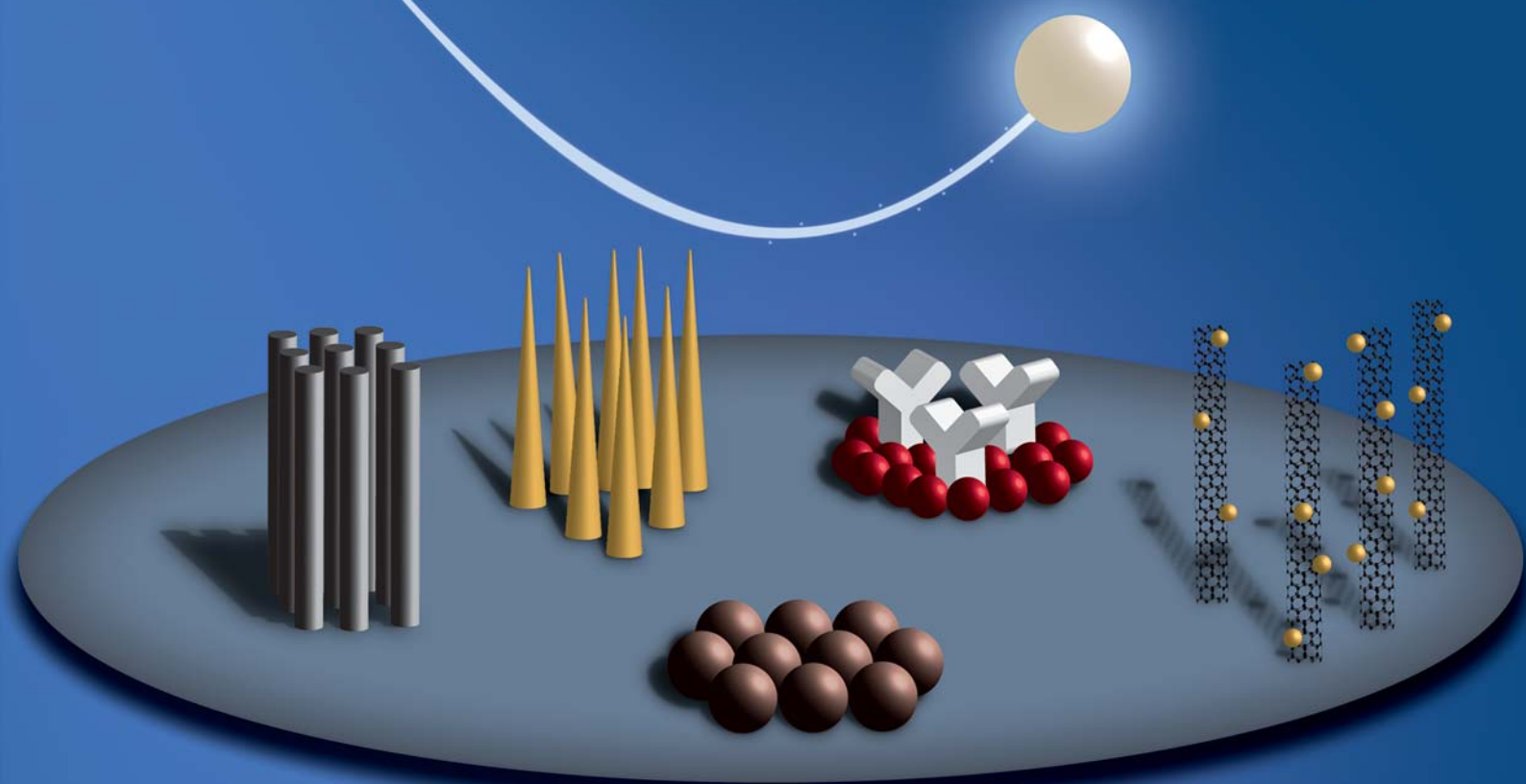
Electrodeposited Metallic Nanostructures

MINIREVIEW
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MINIREVIEW

Electrochemical fabrication of metallic nanostructured electrodes for electroanalytical applications

Blake J. Plowman, Suresh K. Bhargava* and Anthony P. O'Mullane*

The use of electrodeposited metal-based nanostructures for electroanalytical applications has recently received widespread attention. There are several approaches to creating nanostructured materials through electrochemical routes that include facile electrodeposition at either untreated or modified electrodes, or through the use of physical or chemical templating methods. This allows the shape, size and composition of the nanomaterial to be readily tuned for the application of interest. The use of such materials is particularly suited to electroanalytical applications. In this mini-review an overview of recently developed nanostructured materials developed through electrochemical routes is presented as well as their electroanalytical applications in areas of biological and environmental importance.

Introduction

The fabrication of nanostructured materials has recently received much attention due to their interesting optical, electronic,

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chemical and electrochemical properties.[1,2] One of the more popular methods of creating such materials is through electrochemical approaches. The use of electrochemical methods has resulted in a plethora of interesting shaped metals such as spheres, cubes, prisms, dendrites, stars, spikes, rods and flowers to name just a few. This offers a significant advantage as it is known that shape plays a critical role in electrocatalytic processes[3,4] upon which many electroanalytical applications are

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alisation of gold and platinum for use in electrocatalytic and sensing applications, along with a fundamental investigation of the electrochemical behaviour of these metal films.

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based. Therefore, it is important to tune this property as well as identifying the correct composition of the sensing layer for a particular application. The latter can be readily achieved by varying the precursors in the electrochemical plating bath to fabricate either metallic, bimetallic, metal oxide or alloyed nanostructures. Another advantage is the ability to create deposits with high surface areas that are rigidly attached to a substrate or underlying support. This is often problematic using chemically synthesised nanomaterials due to poor attachment and agglomeration effects. It also alleviates any influence of capping agents which may adversely affect the surface chemistry of the material for specific applications and in particular sensing of trace analytes. Other advantages include the ease of fabrication, low cost, sample homogeneity and precise control over the amount of material electrodeposited. Electrochemical methods are also compatible with other manufacturing techniques including sputtering and evaporation processes or photolithography, which is particularly useful for the design of lab-on-a-chip assemblies for use in portable sensing.

The applicability of nanostructured materials created through electrochemical methods is quite extensive and includes electrocatalysts for fuel cells,[5] heterogeneous catalysts,[6] substrates for surface enhanced Raman spectroscopy (SERS),[7] electrodes for batteries,[8] superhydrophobic surfaces[9] and as sensing layers for electroanalytical applications.[10] In particular the latter area has received significant attention due to the enhanced electrocatalytic activity of materials in the nanostructured form. In general electroanalysis is based on the electrochemical detection of redox-active species at an electrode surface, and offers advantages over other methods of sensing as many analytes may be studied in a straightforward manner without the need for extensive sample preparation. Indeed a vast array of important analytes can be detected which are of biological and environmental importance. Electrochemical detection methods are also well suited to practical applications as they are capable of rapidly sensing environmental and biological samples in the range of concentrations of interest, and can also be readily miniaturised for portable applications.

The first aim of this mini-review is to outline the main electrochemical strategies used in the recent literature for the creation of nanostructured metal-based materials that have electroanalytical applications. Secondly, an overview of the type of analytes that are important from an environmental and biological perspective which are detected through use of these novel sensing layers is presented.

Common electrodeposition protocols

The electrodeposition of nanostructured metals is an intense area of research interest, which is largely driven by two factors; the desire to attain an improved fundamental understanding of often complex electrodeposition processes and the wide-spread applicability of these materials in important analytical applications. A major advantage is that electrochemical methods are often quite straightforward to perform. In short the electrodeposition process basically involves applying a potential to a conducting substrate with respect to a reference electrode such that a metal salt may be reduced from an oxidised form in solution to a metallic state at the surface. This process can be controlled by a number of means, one of which is the choice of electrodeposition technique, such as cyclic voltammetry (CV), step methods such as chronoamperometry (CA), chronopotentiometry (CP) and chronocoulometry (CC), pulsed plating at a fixed or varying potential or using AC methods. However it should be noted that there have been many excellent articles and reviews dedicated to the techniques and mechanisms of electrodeposition,[11,12] and such a detailed discussion is outside the scope of this review.

Electrodeposition of nanomaterials at untreated surfaces

Many researchers have chosen to electrodeposit metals onto untreated substrates in order to maintain an overall clean surface, thereby avoiding possible complications in later applications with surface capping organic moieties. In particular, recent research in the sensor field has focussed on the electrodeposition of several of the noble metals as a sensing layer, in particular gold,[13–19] silver[20–24] and platinum.[25–28] An example of hierarchical nanostructured gold is shown in Fig. 1 where Zhang and co-workers[18] demonstrated that the growth of berry-like gold nanostructures could be tuned by altering the pH of the deposition bath without the addition of templates or surfactants.

As mentioned previously, the applied potential employed during the electrodeposition process is a key parameter in controlling the morphology of the deposit. This is clearly visible from Fig. 2, where Chen et al.[29,30] produced Fe nanostructures of different shapes and crystallographic growths by changing the applied growth potential at electrochemically nucleated seeds. Such modifications were found to alter the electrocatalytic behaviour of the materials, with the predominantly {100} faceted cubic nanocrystals showing the highest activity towards nitrite reduction. Other work by these authors on electrochemically faceted nanostructures include the electrodeposition of Pd

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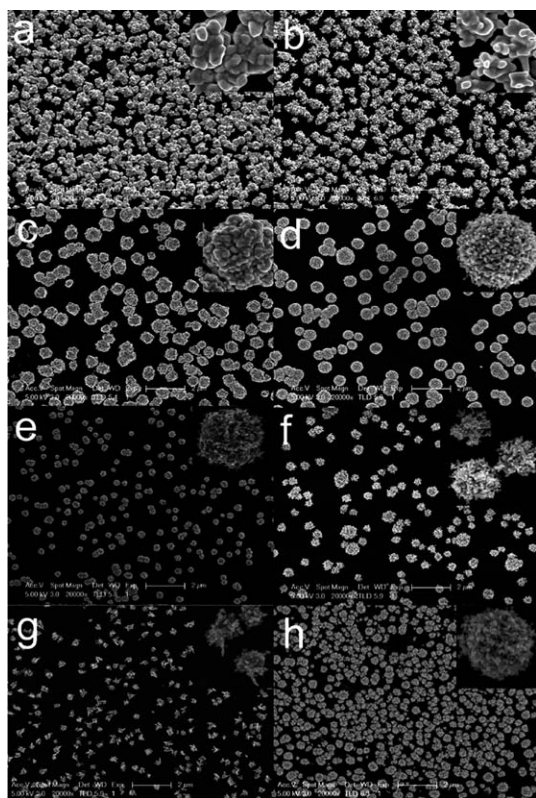
Fig. 1 SEM images of berry-like gold nanostructures (Reprinted with permission from ref. 18. Copyright 2008, American Chemical Society).
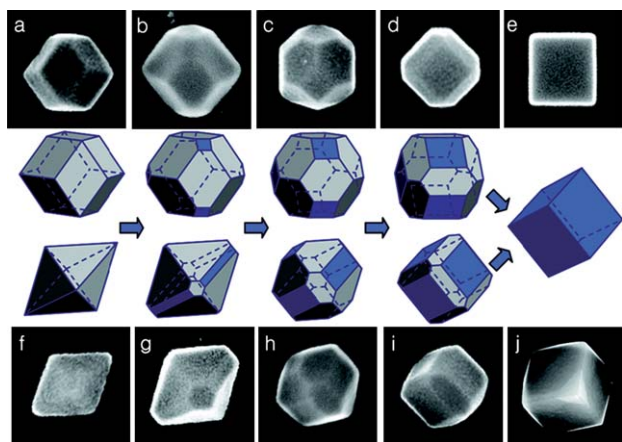

Fig. 2 Schematic and SEM images of Fe nanocrystals (Reprinted with permission from ref. 29. Copyright 2009, American Chemical Society).

nanorods by pulsed square wave deposition[31] and also the formation of highly faceted Pt and Pd nanocrystals by employing a post-electrodeposition square wave treatment on spherical nanoparticles.[30,32] These methods were found to create nanostructures bounded by high-index facets, making them more active, through oxygen place exchange reactions which were capable of re-arranging the exposed lower-index facets on the materials.

The electrodeposition of bimetallic nanostructures is also readily achievable with electrochemical methods. By including an additional metal salt in the deposition bath and ensuring that the deposition potential is sufficiently negative enough to reduce both metals either alloy or bimetallic nanoparticles can be formed. Examples include the formation of NiCu by Jafarian et al.,[33] AuAg by Tsai et al.[34] and also Au-MnO$_2$ by Yang et al.[35]

A further extension of this approach is the formation of a bimetallic surface followed by its de-alloying. Sattayasamitsathit et al.[36] reported the electrodeposition of ZnCu after which dissolution of the sacrificial Zn was accomplished by immersion in 0.5% (w/v) NaOH. This method increased the porosity of the surface, resulting in a material with an increased surface area and higher sensitivity towards glucose detection.

The electrodeposition of nanostructured materials is not just limited to metallic or bimetallic materials but also extends to metal oxides. These can be readily fabricated and include SnO$_2$,[37] ZnO[38] as well as highly oxygen deficient ZnO,[39] ZrO$_2$,[40] MnO$_2$[35] and IrO$_x$.[41] Typically the formation of such films is achieved by the deposition of the metal on the electrode surface followed by its oxidation, either by electrochemical or thermal treatments. It should be noted that the electrodeposition of metal complexes is also receiving attention. Examples include the formation of films of a tetrasulfonated nickel phthalocyanine,[42] Zn/Al layered double hydroxide film,[43] and a nickel(II)-curcumin complex.[44] While these examples may seem somewhat sporadic, the importance of electrodepositing metal complexes can be seen in the emergence and application of metal hexacyanoferrates (HCFs) in electroanalytical applications as detailed later. These films are of the general form M$_i^{m+}$[M$'$(CN)$_6$]$^{n-}$, and one of the most notable metal hexacyanoferrate films is Prussian blue (KFe^{3+}[Fe^{2+}(CN)$_6$]).[45] As will be discussed further, Prussian blue (PB) films have shown excellent promise for its use in sensors.[46,47] Also a variety of Prussian blue analogues have been formed and tested in analytical environments, including nickel,[48,49] copper[50] and ruthenium oxide[51,52] HCFs, and also mixed HCFs of Cu/Pd[53] and Cu/Co.[54] It is expected that this area will continue to be explored as other novel HCFs are synthesised and tested.

Electrodeposition on modified surfaces

In addition to the interest in electrodeposition on untreated electrodes, another major area of research in this field is electrodeposition at modified surfaces. This often involves dropcasting or fabrication of a material on the surface of the electrode by chemical or physical methods to act as a seed and/or blocking layer prior to electrodeposition. Common examples of such modifications include carbon nanotubes, titania nanotubes and self-assembled monolayers (SAMs) of organic molecules. In particular carbon nanotubes are a material that has been the subject of intense research efforts due to their interesting electronic, catalytic and optical properties. However, in order to increase the specific activity of carbon nanotubes for certain applications, the decoration of these nanotubes with noble metal nanoparticles is often required which can be achieved both chemically and electrochemically. While there are advantages and disadvantages for both methods, the electrochemical approach has been shown to be well suited for the task of producing surface-bound decorated carbon nanotubes, as can be seen from the schematic in Fig. 3. In general this is achieved at both single and multi-walled CNTs that have been deposited by
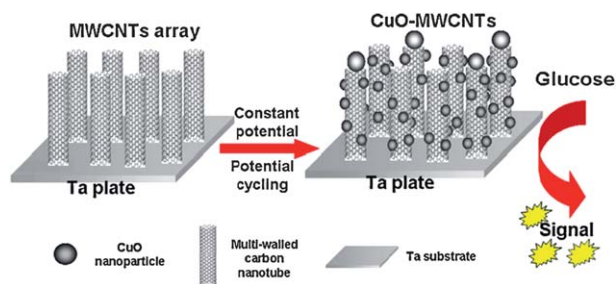
Fig. 3 Schematic of electrodeposition on a MWCNT array (Reprinted with permission from ref. 56. Copyright 2010, Elsevier).

chemical vapour deposition (CVD) on a conductive substrate to afford a well-defined composite substrate. This procedure has been employed by a number of research groups, for instance by decoration with nanoparticles of copper oxide,[55] Ag[56] and TiO$_2$.[57] While the deposits at these modified electrodes tend to be quasi-spherical in nature, variations do exist, including work by Chen et al.[56,58] who formed homogeneous coatings of MnO$_2$ on MWNTs, as well as the deposition of Pt nanoflowers on a SWNT membrane by Su et al.[59] and the electrodeposition of copper nanocubes by Yang et al.[60] In the latter case the shape direction was mainly attributed to chemical templating effects (as will be addressed below), however it was noted that the MWNT array was required for the growth of nanocubes, as such growth was not observed at a planar glassy carbon electrode.

Another common procedure for preparing CNT films is by drop-casting from a suspension of CNTs in liquids such as n-methylpyrrolidone or sodium dodecyl sulphate on the electrode surface and allowing to dry. This approach has been adopted quite extensively, and the sensing performance of these materials is often excellent, although this method does not achieve the same control of the surface morphology as CVD methods. Drop-cast films of CNTs have been decorated with gold,[61,62] platinum,[63] copper,[64] ruthenium oxide,[65] zinc oxide,[66] iron oxide,[67] Prussian blue[68] and nickel HCF.[48] In these instances the metals again generally form quasi-spherical deposits on the nanotubes, however aggregates have been observed[64,69,70] and depending on the conditions used either continuous films[65,71] or nanostructures with a more irregular shape can be formed.[64,72] There have also been several variations of this dropcasting method reported which include dropcasting on electrodes in the presence of chitosan.[73,74] In this case metal electrodeposition is accompanied by the precipitation of a chitosan film, as the local pH is raised sufficiently for its precipitation to occur. Alternatively, Zeng's group have dropcast MWNTs in the presence of ionic liquids prior to the electrodeposition of alloys including PtRu,[75] AuPt[76] and PtRuNi.[77] The presence of an ionic liquid was found to have several effects such as limiting the extent of nanoparticle agglomeration, increasing the density of nanoparticles across the surface, causing the MWNT bundles to cross-link and also behaving as a chemical template.

The use of TiO$_2$ nanotubes as a support material has also gained attention. Generally these are formed by electrochemical oxidation of titanium electrodes in a solution containing fluoride and various additives to generate a surface-confined array of conductive nanotubes which may be decorated electrochemically. For instance, Hosseini et al.[78] and Babu et al.[79] have

investigated their decoration with gold nanoparticles, while Cui et al.[80] investigated platinum, Yang et al.[81] reported cadmium telluride decoration and Benvenuto et al.[82] studied Prussian blue decoration on gold-sputtered TiO$_2$ nanotubes. As with the decoration of carbon nanotube films, the deposits found on TiO$_2$ nanotube films tend to be quasi-spherical nanoparticles, with some clustering observed depending on the electrodeposition parameters. Another interesting report of TiO$_2$ nanotubes being decorated for use as a sensor was reported by Huang et al.,[83] who masked off areas for electrodeposition by firstly applying a SAM to the surface, which increased the hydrophobicity and thereby blocking electrodeposition at the surface. The researchers were then able to selectively pattern the material by exposing the surface to UV light through the use of a photomask, thus locally degrading the SAM and allowing electrodeposition to occur in the defined regions, demonstrating the processability of these materials.

It should be noted that the use of SAMs is not limited to a masking or inhibiting role. Rather, when an appropriate molecule is chosen, whose length is not too great as to significantly impede electron transfer from the underlying surface to the metal salt in solution, SAM-modified electrodes can also be decorated using electrochemical methods. Reports in this area have been focussed on the modification of either gold or glassy carbon electrodes, with SAMs on gold electrodes being based on the well-known affinity of sulphur-containing molecules to the gold surface. In the case of glassy carbon electrodes, there are reports on SAM layers based on 3-aminopropyltriethoxysilane (APTES)[84] and cystamine.[85] In addition to the variety of SAM layers chosen, a number of metals have been electrodeposited, including gold,[84,85] silver,[86] copper,[87] Prussian blue,[88] zirconia[89] and also Pt and AuPt alloys,[84] which generally form quasi-spherical nanoparticles on the solution-exposed section of the SAM. While the decoration of SAM-modified electrodes for sensing has not yet received as much attention as the previously discussed methods, it is worth considering in the context of biosensors where methods to reduce non-specific binding are sought.

Chemically templated electrodeposition

While attention so far has been paid to the electrodeposition of metals on both unmodified and modified surfaces, we now describe the use of templates which may be chemical or physical in nature to direct electrochemical growth. The aim of chemical templating is to include a species in the deposition bath that is capable of directing the growth of the material and therefore its properties such as shape and/or crystallography. One method of chemical templating is the inclusion of a surfactant in the plating solution. While this is a common feature in the chemical formation of nanostructured materials,[90] it remains a method which is comparatively underused in the electrochemical preparation of nanomaterials. The surfactants are often the same as used in chemical syntheses, such as cetyltrimethylammonium bromide (CTAB),[91] cetyltrimethylammonium chloride (CTAC)[7,92] or sodium dodecyl sulphate (SDS),[93] and are able to alter the growth kinetics at particular facets of the electrodeposited material due to their preferential adsorption at these sites.[7,93] Another interesting surfactant is Brij 56, as investigated

by Ling et al. This non-ionic surfactant behaves differently to the other listed surfactants, forming a hexagonal lyotropic liquid crystalline phase solution. The authors have reported electro-depositing mesoporous nickel films in this manner,[94] which they later plated with a thin layer of gold[95] in order to increase the stability of the nickel film. The activity of these materials was demonstrated in sensing ethanol and glucose, respectively.

The inclusion of inorganic anions in the deposition solution is another means of influencing the nature of the electrodeposited material. For example, Feng et al.[96] investigated how the presence of a range of different anions (chloride, bromide, iodide, sulphate and perchlorate anions) altered the electrodeposition of platinum nanoparticles for use as a methanol sensor. It was found that with the inclusion of these anions in the deposition bath that monodispersed, quasi-spherical nanostructures were produced, which contrasted with the polydisperse, irregular shapes found without the addition of these anions. A possible reason given for this templating effect was the altered electro-deposition kinetics based on the electrostatic repulsion of anions adsorbed at the growing electrodeposit and the reactant $PtCl_6^{2-}$ ions, encouraging the growth of spherical nanoparticles. In addition, the size of the Pt nanoparticles could be tuned by the choice of the anion, where the presence of larger anions promoted the formation of smaller Pt nanoparticles, due to both the electrostatic repulsion and the steric hinderance of these larger species. The effect of anion-based growth direction is noteworthy as anions such as those studied by Feng et al. are commonly employed as background electrolytes or are liberated from the metal salt during electrodeposition,[97] in particular in the case of halides. A range of other anions have also been reported to influence the electrodeposition process, and various explana-tions on how these species affect the electrodeposition mecha-nisms have been proposed. For instance, in the electrodeposition of gold the inclusion of cysteine in the deposition bath was found by Sakai et al.[98] to lead to a bumpy surface, rather than the smooth deposits found in its absence. This was explained by the potential-dependent adsorption/desorption characteristics of cysteine to particular crystal facets of the growing electrodeposit through the formation of thiol bonds, which were able to lead to preferential growth along the {111} direction. Meanwhile, Yang et al.[7] reported that the inclusion of nitrate can influence gold electrodeposition, as it was speculated to oxidise less stable gold facets in a similar manner to aqua regia. However, the exact influence of nitrate under the electrochemical conditions employed was not determined, as the deposition solutions also contained CTAC, which has previously been discussed as a shape-directing agent. One further case of anionic templating is the inclusion of citrate, as used by Nunes et al.[99] to control Bi electrodeposition. It was found that citrate lead to the formation of aggregates of Bi nanoparticles (several nanometres in diam-eter), whereas a less homogeneous deposit was formed in its absence.

While the templating effect of anions in certain cases may be related to their adsorption to particular facets on the electrode-posit or to their partial dissolution, in other cases the templating effect may also be related to the speciation of the metal salt. For instance, Yang and co-workers[60] reported the electrodeposition of copper nanocubes on MWNTs, where the directed growth of these nanocubes was attributed to the stabilisation of an intermediate Cu(I) chloride species during the electrodeposition and its interaction with the growing electrodeposit. Similarly, proline was found to influence Cu deposition by Sun et al.,[100] where the synthesis of pillar-like structures were attributed to local enrichment of Cu^{2+} as it complexed with the carboxyl groups of the proline.

Recent work by Plowman and others has demonstrated that the inclusion of a heavy metal salt such as lead acetate in the deposition solution has proved an efficient means of influencing gold electrodeposition, resulting in the formation of gold nano-spikes[101,102] and a range of other nanostructures[103,104] depending on the electrodeposition conditions. The growth of nanospikes is the result of Pb^{2+} and $AuCl_4^-$ showing affinities for different crystallographic facets of the growing gold electrodeposit, where the former is reported to bind more strongly to the Au {110} and {100} facets than the {111} facets, while the reactant $AuCl_4^-$ ions bind most strongly to the {111} facets. The combination of these preferences leads to preferential growth being observed along the {111} facets, resulting in the formation of gold nanospikes, as seen in Fig. 4. Ye et al.[105] have also investigated the effect of lead acetate on the electrodeposition of platinum, reporting the formation of hierarchical nanoflowers.

Another means of chemical templating is through the use of dynamic hydrogen bubble templating. In this method a strong cathodic potential is applied to an electrode from an acidic solution containing the metal salt for deposition. This results in the evolution of hydrogen bubbles and the electrodeposition of the metal around these bubbles. This process introduces a number of interesting features, such as the templating of the deposit into a macroporous structure with a highly dendritic internal wall structure (Fig. 5), which results from the hydrogen bubbles restricting where electrodeposition may occur. This approach has been demonstrated previously for copper by Nikolic and co-workers,[106–109] for silver by Cherevko and co-workers[110,111] and for gold by Plowman et al.[112] This method has also been extended to the creation of bimetallic CuPd by Naj-dovski et al.[113]
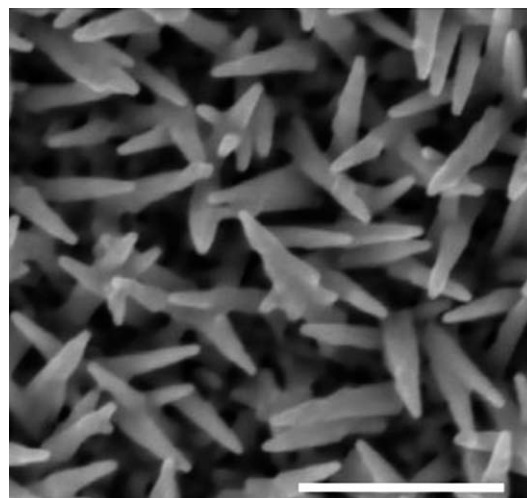

Fig. 4 SEM images of gold nanospikes. Scale bar is 500 nm. (Reprinted with permission from ref. 102. Copyright 2009, The Royal Society of Chemistry).
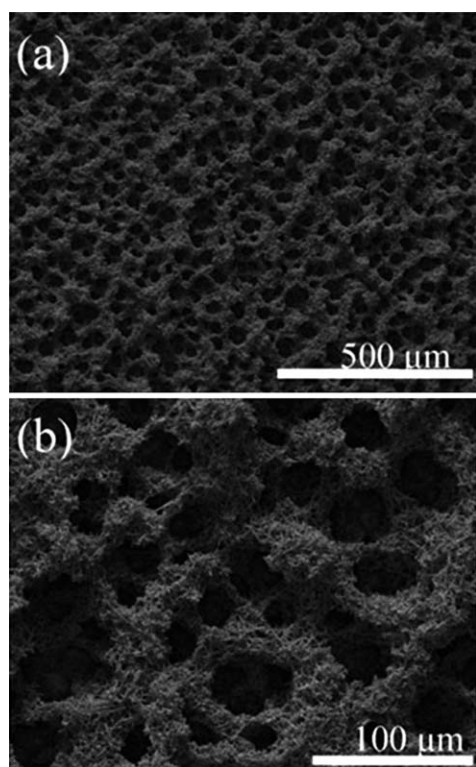
Fig. 5   SEM images of honeycomb gold film. (Reprinted with permission from ref. 107. Copyright 2010, The Royal Society of Chemistry).
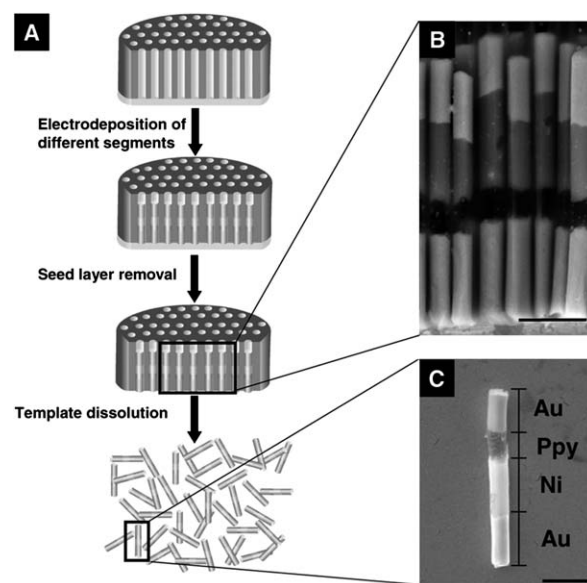

Fig. 6   Schematic showing the use of AAO templates for electrodeposition (A), along with SEMs (B,C) of multi-segmented nanotubes (Reprinted with permission from ref. 123. Copyright 2009, Wiley-VCH Verlag GmbH & Co.).

Physically templated electrodeposition

While chemical templating has been shown to control the shape of the growing nanostructures, another method is to electrodeposit on surfaces that have been altered with physical templates. While this may appear similar to the electrodeposition on modified surfaces as discussed previously, there are a number of points that separate these categories. In this instance the templates are used as a mould, defining where the nucleation and growth can occur and altering the diffusion layer (and therefore the reduction kinetics) for the electrodeposition process, following which the template is removed. One of the most common methods of physical templating is the use of anodised aluminium oxide (AAO) templates. These templates are formed by the electrochemical oxidation of alumina sheets in a solution of hydrofluoric acid, which leads to the formation of a film containing an ordered array of pores. It is these pores that are used to direct electrodeposition, as the growing electrodeposit is confined to growth within this template (Fig. 6). This is generally achieved by sputtering a conductive layer, such as silver, on one side of the AAO membrane, which provides electrical contact for deposition within the pores. This approach has several advantages, as well ordered arrays of nanotubes can be synthesised and the removal of the AAO template can be readily achieved by immersion in alkaline solution. If desired, the conductive layer onto which the nanotubes were deposited may also be dissolved, leaving free nanorods in solution (Fig. 6), however most reports on electrodepositing within AAO templates for sensing do not involve this latter step.

Much attention has been given to the use of AAO templates for the electrochemical growth of oriented nanostructures. For instance, nanowires with diameters below 150 nm have been reported for gold by Anandan et al.,[114] Claussen et al.,[115] Liao et al.[116] and for Prussian blue by Ang et al.[117] and Nguyen et al.[118] Nanoparticle decoration of AAO templates with silver have been published by Gu et al.[119] and Ji et al.[120] and with gold nanoparticle decoration by Takahashi et al.[121] However novel approaches are being used to further extend the limits of general AAO templating. A notable example includes the formation of multi-segmented nanowires (as shown in Fig. 6) by using multiple electrodeposition steps from different plating baths.[122,123] Bai et al. have also used a variation on AAO templating, which was to first coat the AAO template with a thin layer of CdS. The presence of the thin CdS layer in the pores of the AAO encouraged the formation of porous nanorods of either palladium[124] or silver,[125] as the inorganic metal salts showed an affinity to the S^{2-} layer in the pores. As a comparison, when CdS was absent from the template, only solid nanorods were obtained.

Similarly to AAO, polymers can also be used as physical templates. This includes the use of polycarbonate templates, which are used in a very similar manner to AAO templates and have been used to form tungsten oxide nanowires.[126] The reason why AAO is predominantly chosen may lie in the facile modification of the AAO template during the anodisation process, where factors such as the bath contents, the applied potential and the anodisation time can all influence the formation of the pores.[127]

Another method of physical templating is the use of polystyrene beads. Once drop-cast on the electrode surface and allowed to dry, these beads can form an ordered array, for example as a hexagonal crystal lattice.[128] These beads, with typical dimensions on the order of several hundreds of

nanometres, align in a way that small voids exist at the inter-section between several beads, which confines electrodeposition to the available voids.[129] As with the case of AAO, the templates are then removed, in this case by a treatment such as immersion in dimethylformamide (DMF) or by sonication.

Analytical areas of interest

Environmental sensing

One of the most widely investigated analytes in the field of environmental sensing is hydrogen peroxide. This is due to its extensive use in the paper, textile and food industries,[130] while its popularity is also related to its role in glucose sensing, where peroxide is a by-product of the enzymatic oxidation of glucose and can therefore provide an indication of glucose concentra-tions. There are two main approaches to sensing hydrogen peroxide when electrodeposited materials are utilised as the sensing layer, which are enzymatic and non-enzymatic routes. In the enzymatic route, after the desired electrode surface is formed it is then functionalised with the relevant enzyme, typically horseradish peroxidase (HRP). This functionalization is gener-ally achieved by dropcasting HRP onto the surface with or without a framework material, particularly chitosan. In many reports the electrodeposition of metallic nanomaterials is carried out at previously modified surfaces. For instance, Chen et al. conducted a two-step electrodeposition protocol,[131] firstly of polyaniline nanofibres and then decorating them with electro-deposited Pt nanoparticles before functionalising the surface with a solution of chemically synthesised Au nanoparticles, chi-tosan and HRP, while work by Yang et al.[132] and Wang et al.[133] have investigated the electrodeposition of Au or Au/Pt on dropcast chitosan and MWNT/polyaniline nanotube films, respectively, before introducing HRP. Reported detection limits for the above-mentioned sensors range from 0.1 μM to 2.8 μM, which are consistent with other HRP-based peroxide sensors,[134,135] and due to the inherent selectivity shown by HRP towards peroxide and its activity in physiological conditions this is an effective method of sensing peroxide.

The other approach taken to sensing peroxide is the non-enzymatic approach, where the activity of the electrodeposited material is responsible for its direct detection. This approach affords several advantages over the enzymatic approach, for instance the synthesis and storage of the electrodes is simpler as no enzyme attachment/degradation is involved and the sensors may show improved tolerance towards temperature, pH and the presence of toxic chemicals which are known to limit the activity of enzymatic sensors.[57,136] In addition, the absence of a chitosan matrix, as commonly employed in enzymatic sensors, provides an increased number of recognition sites across the surface available for sensing. In several instances lower detection limits have been reported than those found at enzymatic sensors.[46,128,137–139]

Several successful examples of these non-enzymatic peroxide sensors have been demonstrated by Bolshakov et al.[46] and Lupu et al.,[128] who both reported a LOD of 1 nM for their PB films. The former utilised electrodeposited PB on Au microelectrodes, whilst the latter used a polystyrene-based physical templating method to co-deposit polypyrrole and PB. Prussian blue is

a particularly effective material for peroxide detection, to the extent that it is known as an artificial peroxidase,[88] however it is known to be sensitive to the presence of particular species in solution. Specifically, the stability of the film is reduced at high pH levels[47] and also when exposed to cations including Na^+, H^+, Ca^{2+} and Mg^{2+} which slow electrocatalytic reactions due to their inability to enter the PB lattice.[51] Thus, the chemistry of the solution should be considered before utilising PB films in sensing applications. However, a wide variety of other HCF films have also been developed to improve the stability and activity of PB films, including nickel,[48,49] copper,[50] copper-palladium,[53] copper-cobalt[54] and ruthenium oxide[51,52] hexacyanoferrate films.

Copper and copper oxides have also been studied for their ability to sense peroxide. Lin et al.[139] electrodeposited Cu on a glassy carbon electrode, followed by an electrochemical oxidation procedure in 10 mM NaOH. This produced a CuO film which was found to possess a LOD towards peroxide of 25 nM. Selvaraju et al.[138] also electrodeposited Cu on GC electrodes, and in spite of not employing a post-electrodeposition oxidation procedure, X-ray photoelectron spectroscopy (XPS) data revealed the presence of copper oxides. This nanostructured film also provided a low limit of detection towards peroxide, with a LOD of 10 nM from studies in phosphate buffer at pH 7.2.

One of the other well-researched areas of environmental sensing is the detection of metal species in solution, particularly the heavy metals due to their highly toxic nature and detrimental effect to the environment. Among these heavy metals much attention is paid to the detection of lead,[99,140,141] cadmium,[140,141] mercury,[142] arsenic[143,144] and chromium.[24,144,145] The most common strategy for sensing these metals is by anodic stripping voltammetry at electrodeposited bismuth films (as shown in Fig. 7), as bismuth is known to form fused alloys with heavy metals in a similar way to mercury amalgamation,[146] but unlike mercury it is insensitive to dissolved oxygen[147] and does not possess the same level of toxicity. Bismuth coatings for heavy metal detection are commonly formed using constant potential electrodeposition, either by ex situ[148,149] (i.e. where Bi electrode-position occurs prior to the immersion of the working electrode into the sample solution) or by in situ electrodeposition[140,150,151] (where the sample solution is doped with a bismuth salt and the deposition occurs during a preconcentration step). In these studies the electrodeposits are evaluated for their stability and their sensing performance while unfortunately little attention was given to the effect of morphology or crystallography. Other approaches to heavy metal detection at bismuth electrodes are also employed, such as the formation of bunch-like three-dimensional Bi electrodeposits[152] (Fig. 7) which were shown to effectively detect Cd^{2+}, Pb^{2+}, Cu^{2+} and Hg^{2+}. Screen printed bismuth oxide films followed by electrochemical reduction to their metallic form, as reported by Kadara et al.[153] for the simultaneous detection of Cd^{2+}, Pb^{2+} and Zn^{2+} have also been demonstrated. Work reported by Compton's group found that the electrodeposition of either bismuth[154] or antimony[155] at boron doped diamond (BDD) electrodes allowed the simulta-neous detection of Pb^{2+} and Cd^{2+}, which could not be achieved at unmodified BDD electrodes. In both cases the electrodeposition was performed in situ with the analytes present, which was advantageous in the case of bismuth in particular as it limited the formation of a native bismuth oxide that could interfere with
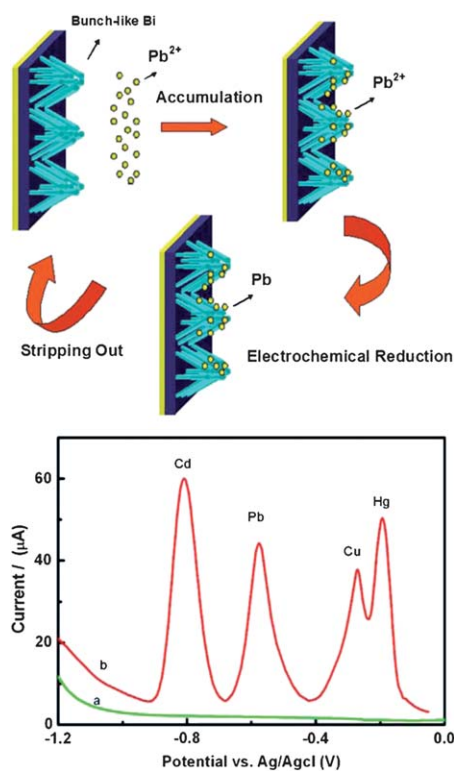
Fig. 7 Schematic and results for anodic stripping voltammetry of metals at a bunch-like Bi electrode. (Reprinted with permission from ref. 153. Copyright 2010, Springer).

sensing. Improvements were also observed at nanoparticle films over bulk bismuth or antimony films, attributed to factors such as improved mass transport and increased surface area.

Besides bismuth electrodes, there are also a variety of other metallic or metal oxide surfaces that have been produced for heavy metal sensing. For instance, Martínez-Paredes and co-workers[17] employed a gold film to detect Pb^{2+} to concentrations of 0.8 ng mL^{-1}, while Xu and coworkers[24] sensed Cr^{6+} to 0.65 ppb at an electrodeposited silver film. In the case of metal oxides, Salimi et al.[143] employed an electrodeposited cobalt oxide film to detect As^{3+} to a LOD of 11 nM, while iridium oxide[140] has been used to simultaneously sense Pb^{2+} and Cd^{2+} to 0.7 nM and 8 nM, respectively, in the presence of Cu^{2+}. Electrodeposition of gold on organic nanofibres doped with Pt^{2+} has also been reported,[142] which was capable of sensing Hg^{2+} to 8 ppt. Another interesting report on heavy metal detection was published by Choudhry et al.[156] who electrodeposited either palladium, platinum or gold on a screen printed carbon electrode as disordered semi-continuous films. The surface was then further modified with a polymeric matrix by spraying it with a commercially available deodorant. This had the effect of changing the current responses into that of a random array of gold quasi micro-electrodes, and in the case of electrodeposited gold this method achieved a LOD for As^{3+} of 0.48 μM.

Insecticides and pesticides are other commonly targeted analytes due to their significant environmental impacts. These are generally in the form of organophosphates, and many reports use methyl parathion as a model system. The development of such sensors has been reported for electrodeposited zirconia

nanoparticles, as it is known to adsorb phosphoric groups, with depositions performed on both screen printed electrodes[40] as well as SAM-modified electrodes.[89] In the latter case it was found that the SAM chosen lead to the formation of smaller, more uniform zirconia nanoparticles upon electrodeposition and also that their stability was increased. Other means of sensing organophosphates include the electrodeposition of Cu on dropcast MWNTs[64] and the dropcasting of a suspension of chitosan, acetylcholine and free gold nanorods on a glassy carbon electrode, in which the gold nanorods were formed by AAO templated electrodeposition and the subsequent dissolution of their template and backing materials.[157]

Another environmental analyte of interest are nitrites, which are of particular interest in wastewater management and the agricultural sector as they are known to convert to carcinogenic nitrosamines in the presence of amines.[66,87,158] While a variety of approaches have been adopted, several of the more successful nitrite sensors involve the use of electrodeposited copper as the sensing layer. This has been performed at a variety of surfaces including a dropcast suspension of Nafion and MWNTs,[159] on DNA-SWNT hybrids[158] and on a SAM-covered Au electrode.[87] In the latter case Ko et al. reported a LOD for nitrite as low as 0.1 nM, showing the efficiency of sensors developed in this manner. Chen et al.[29] have also described the electrocatalytic activity of Fe nanocrystals (as shown in Fig. 2) towards nitrite reduction, showing the importance of the nanocrystal structure on their electrocatalytic activity, which underlies the sensing performance of the material.

Biological sensing

The detection of glucose is one of the major areas of biological sensing given its importance in the diagnosis and management of diabetes. In this field, as in the case of hydrogen peroxide, both enzymatic and non-enzymatic routes are employed. In the former case an enzyme such as glucose dehydrogenase or more commonly glucose oxidase (GOx) is immobilised on the sensing surface that is often in a nanostructured form created by electrochemical methods. An example of enzymatic sensing is shown in Fig. 8, where SWNTs decorated with either Pt nanospheres or Pd nanocubes through an electrochemical approach[160] were employed as a support for glutamate oxidase, allowing the electroanalysis of glutamate which is an important neurotransmitter. This approach utilises the inherent selectivity of the enzyme towards its target analyte, while the nanostructured surface ensures an increased surface area which is used to detect reaction products from the enzyme. In the case of glucose oxidase, this reaction is the oxidation of glucose to gluconolactone and hydrogen peroxide,[161] and by sensing the concentration of peroxide present at the electrode surface the concentration of glucose in solution can be determined (as schematically shown in Fig. 8a). The use of enzymes also brings about another advantage, which is their inherent stability under biological conditions. In fact, as reported by Liang et al.[47] their activity is maximised at around physiological pH levels. A consequence of this is that any underlying supports must also be stable in these conditions, for example in the latter work it was necessary to optimise the solution pH for sensing glucose at a GOx on PB film, as GOx activity decreases in acidic conditions
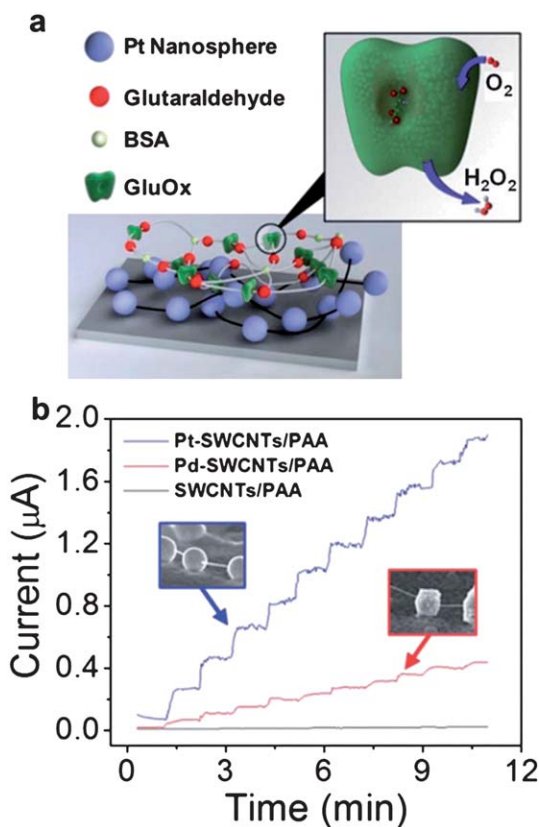
Fig. 8 Schematic showing glutamate sensing at an enzyme-modified decorated nanotube electrode (a), with a chronoamperogram showing activity towards peroxide along with SEM images of the modified surfaces (b) (Reprinted with permission from ref. 161. Copyright 2011, The Royal Society of Chemistry).

while the stability of PB is decreased in alkaline conditions. Recent reports of electrodeposited materials for enzymatic glucose sensing are largely focused on nanostructured gold,[115,162,163] platinum[63,164,165] and PB[47,68,74,82,166] films, owing to their electrocatalytic activity towards hydrogen peroxide. In addition, there are reports on the employment of hybrid materials such as PB/Au from Wang et al.[45] and Du et al.[91] and also Au/Pt by Zhang et al.[76]

While the limits of detection of numerous enzymatic electrodeposited glucose sensors are reported to be in the sub millimolar range[47,165,167] and thus meet the requirements of typical analytical levels (3–8 mM),[18] other reported sensors show LODs at or above these levels, highlighting that in some cases the selectivity and activity of the enzymatic sensors can come at the expense of their sensitivity.

As with the previously discussed hydrogen peroxide sensors, there is a significant research effort to develop non-enzymatic sensors for glucose detection. Several of the more popular metals being investigated include copper, nickel and gold. Copper has received much attention as it is a particularly active electrocatalyst towards glucose in alkaline solutions, with copper-based sensors reporting LODs in the sub-micromolar range,[55,100,168,169] even down to as little as 50 nM.[161] Other examples include the use of porous copper films,[36] and the activity of copper oxide for sensing glucose has also been reported.[55]

Nickel based electrodeposits have also been used in glucose sensing with LODs reported in the sub-micromolar range.[95,168,170,171] although recent reports on nickel show a larger variety of electrodeposition methods than those found for copper. For example, there are reports on the electrodeposition of Ni(II)-curcumin[171] and NiHCF[49] films alongside work on the electrodeposition of nickel hydroxide nanoparticles.[170] One of the reasons for the variety of surfaces reported is the need for stability, as the electrocatalytic activity of mesoporous nickel films towards the oxidation of glucose[95] and ethanol[94] has been reported to rapidly decrease upon exposure to air. Attempts to increase the stability of nickel films include the electrodeposition of CuNi alloy films,[33] which also reported synergistic effects towards glucose oxidation,[168] and the electrodeposition of mesoporous nickel films from a liquid crystal solution followed by the electrodeposition of a thin layer of gold, in order to limit the oxidation of the Ni surface and thus increase the stability of the sensor.[95] Whilst copper and nickel electrodes show promising glucose sensing results in alkaline solutions,[92] their application in physiological pH environments is not widely reported. While sampling strategies such as diluting real samples with a NaOH solution can be employed for this purpose,[36,60] this can in turn lead to poorer LODs and introduce other possible sources of error, whilst the additional sample preparation requirements are also not ideal.

An alternative material that overcomes such issues is gold. Although it is significantly more expensive than either copper or nickel and it was long thought of as an inert material, gold has been found to possess both catalytic and electrocatalytic activity when in the nanostructured form.[101,112,172,173] Reports of glucose sensing in alkaline solution with electrodeposited gold materials include gold nanospikes (Fig. 4) and honeycomb porous gold (Fig. 5), as well as the decoration of gold on TiO$_2$ nanotubes,[78] mesoporous nickel electrodes[95] and the co-electrodeposition of MnO$_2$ with gold.[35] One of the more unique approaches using electrodeposited gold for glucose sensing was done by Rassaei and Marken,[174] who electrodeposited gold on two platinum electrodes until a gap of 500 nm existed between the gold electrodeposits. By locally generating OH$^-$ at one gold electrode, glucose detection could be performed at the other gold electrode under the generated quasi-alkaline conditions, thereby increasing its sensitivity.

For glucose sensing at or near physiological pH, electrodeposited noble metal films are commonly employed, for example gold,[18,92,114] nanoporous gold decorated with platinum,[175] platinum-decorated SWNT membranes[59] and also porous palladium nanotubes.[124] While it has been reported that these metals may not be ideal for glucose sensing due to the poisoning of platinum surfaces by carbonaceous species[176] or the co-oxidation of interfering species such as ascorbic acid, uric acid and dopamine at gold electrodes,[35] these issues can be reduced by employing these metals in a nanostructured form. For instance, nanostructured Pt can show altered poisoning behaviour from its bulk counterpart,[177] and in the case of nanostructured gold large shifts in the onset potential of electrocatalytic reactions, such as glucose oxidation, can lead to greater selectivity in oxidising glucose in the presence of common interferents.[92]

Another important group of biomolecules which are being sensed at electrodeposited metal surfaces are neurotransmitters.

Amongst these neurotransmitters, dopamine is one of the more widely studied analytes. The electrochemical detection of dopamine from biological media is complicated by the presence of several species such as uric acid and ascorbic acid, which are known to oxidise at a similar potential to dopamine. This leads to challenges in selectively, and so several research groups have been working on this problem by applying electrodeposited metals to dopamine detection. For example, Atta and coworkers have investigated the electrodeposition of Pd nanoparticles on pre-modified surfaces such as electrodeposited polyfuran[178] and poly(N-methylpyrrole)[179] films for dopamine detection, finding LODs of 48.2 and 12 nM, respectively, whilst resolution was achieved between the dopamine response and the interfering species in solution. Shaidarova et al. investigated various other methods, such as the electrodeposition of a self-organised cystamine layer onto which gold nanoparticles were electrodeposited,[85] and the electrodeposition of an iridium oxide film which was then modified with a layer of Nafion.[180] The purpose of including a Nafion layer is to screen potentially interfering anionic species from the electrode surface by electrostatic repulsion from the negatively charged sulfonate groups on the Nafion. Plowman et al.[102] also investigated Nafion-modification of electrodeposited gold nanospikes (as illustrated in Fig. 4), where dopamine detection in the presence of uric acid and ascorbic acid was achieved which also benefited from increased sensitivity of nanostructured gold over a bulk gold electrode. Other work in this field has been reported by Prabakar and coworkers[181] as well as Adekunle and coworkers,[67] where dopamine LODs were 0.49 μM at NiHCF films and 0.36 μM at Fe_2O_3-coated SWNTs, respectively.

Nitric oxide is another key biological analyte, and is known to function not only as a neurotransmitter but also to influence blood pressure regulation, control of platelet activity and is involved in various immune responses.[182,183] For the detection of nitric oxide, gold has received significant attention. Marken's group have employed the junction method described previously[174] for the detection of nitric oxide across gold electrodes.[184] By oxidising NO to NO^+ at one of the gold electrodes, the byproduct could then be reduced at the other gold electrode and provide data on the lifetime of the nitrosonium phosphate intermediate species, with a LOD towards NO of 10 μM. Other instances of successful NO sensors include nickel oxide electrodeposited on dropcast MWNT/chitosan films,[185] which reported a LOD of 20 nM, and also a gold HCF film,[182] where the LOD was 10 nM in solution or 1 nM for gaseous samples.

Another common theme of biological electroanalysis is the detection of therapeutic drugs. While these drugs are selected for their beneficial properties, it is important to ensure that the correct dosages are given and also to track where these drugs travel in the body (in vivo studies). Recently there have been a number of reports of nanostructured metal electrodes for sensing these drugs. As with other analytical applications, there are a number of different approaches taken, ranging from the untemplated electrodeposition of Pt,[28] Au[15,186] or cobalt hydroxide[187] on planar electrodes to the electrodeposition of a Ni (II)-curcumin film[44] and the decoration of polyfuran films with Pd nanoparticles.[178] These materials have been reported for sensing a number of different classes of drugs, ranging from analgesics such as morphine[15] and aspirin[187] to antibacterial agents[186] and

non-steroidal anti-inflammatory drugs.[44,188] Given the diversity of analytes of this type and the continual improvements in the design and composition of nanostructured materials it is expected many more advances in this area will be achieved.

Conclusions

The electrodeposition of metal-based nanostructures is a burgeoning field in both fundamental and applied research. As highlighted here, nanostructured materials can be created by electrodeposition at either untreated or modified electrodes, or through the use of physical or chemical templating methods. These approaches have been shown to create a variety of different nanostructured materials of various size, shape and composition that can be tuned for specific applications. In particular the area of electroanalysis is well suited for the application of electrodeposited materials where easily fabricated sensing layers at low cost are required, in particular for portable applications. It was shown that a significant number of important analytes from both an environmental and biological perspective have been detected using such a versatile approach. It is expected that as further developments and insights into the electrodeposition of nanostructured metals are realised that continuing improvements will be seen in this field of electroanalytical science.

Acknowledgements

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