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Rapid synthesis of porous honeycomb Cu/Pd through a hydrogen bubble templating method

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Abstract

A rapid electrochemical method based on using a clean hydrogen bubble template to form a bimetallic porous honeycomb Cu/Pd structure has been investigated. The addition of palladium salt to a copper plating bath under conditions of vigorous hydrogen evolution was found to influence the pore size and bulk concentration of copper and palladium in the honeycomb bimetallic structure. The surface was characterised by X-ray photoelectron spectroscopy which revealed that the surface of honeycomb Cu/Pd was found to be rich with a Cu/Pd alloy. The inclusion of palladium in the bimetallic structure not only influenced the pore size but also modified the dendritic nature of the internal wall structure of the parent copper material into small nanometre- sized crystallites. The chemical composition of the bimetallic structure and substantial morphology changes was found to significantly influence the surface enhanced Raman spectroscopic response (SERS) response for immobilised Rhodamine B and the hydrogen evolution reaction. The ability to create free standing films of this honeycomb material may also have many advantages in the areas of gas and liquid phase heterogeneous catalysis.

Introduction

The fabrication of porous metallic structures has wide ranging applications in areas such as sensing,[1, 2] catalysis,[3] electrocatalysis,[4, 5] superhydrophobic surfaces[6] and Li ion batteries.[7] Popular methods to create these type of networked structures include hard template methods in which the metal is deposited in the interstitial spaces,[8, 9] de-alloying of materials such as Ag/Au,[4, 10] electrodeposition in the presence of surfactants[11] and sol-gel methods.[12] However, each of these approaches has limitations in terms of the removal of templates through combustion or chemical treatments, and the use of organic moieties which may alter the surface chemistry of the material and be detrimental to its performance in certain surface sensitive applications. New approaches to the direct formation of porous metals are therefore required for the creation of clean unmodified surfaces; this research is an ongoing challenge from both a fundamental and applied viewpoint. Recently, it has been reported that metal electrodeposition can be undertaken during the course of hydrogen evolution where hydrogen bubbles act as a transitory micron sized template over which metals such as copper,[6, 7, 13-17] silver,[18] tin[17] and most recently gold[19] has been performed.

The most widely studied metal using this approach has been copper.[6, 7, 13-17] However, there has been no report to date using this method for a bimetallic porous honeycomb system based on the important combination of Cu/Pd. Bimetallic materials based on Cu/Pd are of significant interest given their use in a vast array of applications including hydrogen storage,[20] hydrogen transport membranes,[21] CO oxidation,[22] oxygen reduction catalysts,[23] alkaline fuel cells,[24] corrosion resistance[25] and water purification through the catalytic destruction of alkyl halides[26] and nitrates.[27-29] Several synthetic approaches for the formation of Cu/Pd materials have been reported including high energy ball milling[27], galvanic replacement,[30] co-electrodeposition from aqueous[28] and ionic liquid media.[31] However, we have demonstrated recently an added benefit of utilizing the hydrogen bubble templating method for gold. Using this approach it was found that the gold surface is activated through a hydrogen embrittlement process to generate surface active states which mediate electrocatalytic processes.[19] It has also been reported that cathodic polarization in the hydrogen evolution region activates copper electrodes[32-34] and that electrochemical activation of palladium electrodes[35] is also possible to improve catalytic performance. Therefore, it is envisaged that this approach would create a highly active bimetallic Cu/Pd material. In this work, the hydrogen bubble templating method is reported for the rapid and facile fabrication of macroporous honeycomb Cu/Pd with different pore sizes, internal wall structures and bulk and surface compositions.

Results and Discussion

Honeycomb copper can be fabricated under conditions of constant current deposition from a solution containing 0.4 M $CuSO_4$ in 1.5 M H_2SO_4 using copper as the working electrode. Illustrated in Figure 1a is a SEM image of such a structure formed using a current density of 3 A cm^{-2} for 15 s. It can be seen that the regular macroporous structure consists of layers of material as reported elsewhere.[17] The pore size generally increases from the bottom to the top of the film due to coalescence of the hydrogen bubbles. To incorporate palladium into this structure $Pd(NO_3)_2$ at various concentrations from 5 to 50 mM was introduced into the electroplating solution. Illustrated in Figure 1c-d are SEM images of Cu/Pd materials fabricated under the same conditions to produce the copper honeycomb material.

It can be seen that upon introducing 5 mM $Pd(NO_3)_2$ to the solution that the morphology of the Cu/Pd honeycomb material has changed. It should be noted that the presence of palladium was confirmed by X-ray photoelectron spectroscopy (XPS) and atomic absorption spectroscopy (AAS) analysis (as discussed later). In particular the pore size diameter decreased from an average of 63 μm (Figure 1a) to 33 μm (Figure 1b). Upon increasing the concentration of $Pd(NO_3)_2$ in the deposition solution to 10 mM, the pore size decreased further to 19 μm. Increasing the Pd salt concentration to 20 mM only marginally decreased the pore size to 14 μm. This decrease in pore size is likely due to the enhanced rate of hydrogen evolution occurring at the initially formed electrodeposited material, as it is known that palladium is a more effective hydrogen evolution catalyst than copper. The more efficient hydrogen evolution process results in a smaller bubble size and therefore smaller pores, due to an increased driving force of bubble departure from the surface that is related to the agitation and increased convection at the solid solution interface.[6] The addition of a second metal salt not only allows a bimetallic structure to be formed but has the added benefit of tuning the pore size. To date the pore size of single metallic honeycomb structures has mainly been controlled using organic surfactants which may adversely affect the surface chemistry for certain applications. The overall pore structure is maintained at all concentrations of $Pd(NO_3)_2$ employed (5 - 50 mM). The structure is multilayered but to a slightly lesser extent than that observed in the case of pure copper. However, the internal wall structure of the honeycomb material is significantly affected when Pd is incorporated into the structure. For the pure honeycomb copper sample a highly dendritic material is formed (Figure 2a). This dendritic formation is gradually suppressed when Pd is incorporated and the internal structure becomes more block-like, with distinct crystallites of ca. 200 nm diameter formed at the highest palladium concentration (Figure 2d). In the case of honeycomb copper deposition, the growth occurs under non equilibrium conditions which leads to diffusion limited aggregated growth and the formation of dendrites.[36] The hydrogen bubbles formed at the newly deposited copper generate turbulence in the electrolyte at the surface which disrupts continuous growth and results in dendritic formation.

When copper and palladium are being co-deposited not only does the rate of hydrogen evolution increase but the rate of metal deposition must also increase to a significant extent to facilitate the filling of the internal walls with metal. This can be seen from linear sweep voltammograms run in a solution of 1.5 M H_2SO_4 and 0.4 M $CuSO_4$ with and without 20 mM $Pd(NO_3)_2$ (Figure 3). The onset for the hydrogen evolution reaction (HER) is shifted to less negative potentials, indicating a more facile process, while the current magnitude over the potential range of 0.1 to -0.5 V (Figure 3) increases significantly with the addition of $Pd(NO_3)_2$, indicating accelerated metal (Cu and Pd) electrodeposition.

Interestingly, when the concentration of $Pd(NO_3)_2$ is increased to 50 mM the pore structure becomes less well defined with a larger average size of 32 μm (Figure S1a), while the internal wall structure returns to a more branched form (Figure S1b). This suggests that the competition between the metal deposition rate and the hydrogen evolution rate at the bimetallic Cu/Pd surface is unbalanced, in that the latter becomes too dominant due to an increased amount of palladium and results in less structural integrity. Several electrodeposition parameters were changed and it was found that varying the concentration of $CuSO_4$ in the range of 0.1 to 0.4 M with a constant $Pd(NO_3)_2$ concentration did not affect the porous nature of the film formed, which is consistent with previous studies for copper foam deposition.[17] The effect of electrodeposition time was significant in that well defined porous structures were only formed after 5 s of deposition (Figure S2). Similarly, current densities lower than 1.5 A cm^{-2} resulted in random structures with little pore formation due to the low rate of hydrogen evolution (Figure S3). Given the diverse range of applications of this combination of metals in terms of gas and liquid phase catalysis it is important to be able to fabricate free standing films to maximise their surface area. Significantly, these films could be detached from the underlying substrate with mechanical scraping as shown in Figure S4 which could be handled carefully with tweezers.

The bulk concentration of copper and palladium was determined by AAS (Figure 4a and Table 1 in supporting information) and it was found that the concentration of palladium increased in an almost linear fashion with respect to the concentration of $Pd(NO_3)_2$ used in the electrodeposition bath up to a value of 17.4 atomic percent. XPS was employed to determine the surface composition of honeycomb Cu/Pd (Figure 4a), which did not match with the bulk concentration and suggests an uneven distribution of palladium within the host Cu matrix, in particular at the outer layers of the material. Indeed, the surface concentration of palladium did not vary significantly over the entire concentration range which may be related to the fact that palladium nanoparticles are known to be extremely effective catalysts for the electroless deposition of copper thereby facilitating a higher surface concentration of copper. [28, 37]

Significantly, however, there is a shift in the Cu $2p_{3/2}$ peak (Figure 5a) of -0.5 eV at all Cu/Pd compositions compared to honeycomb Cu, which indicates an electronic interaction between the two metals and surface alloy formation.[38] It should be noted that satellite peaks were present at 943 eV in all samples, indicating some copper CuO formation that is most likely due to air oxidation. The Pd $3d_{5/2}$ peak at 335.2 eV (Figure 5b) does not shift and is insensitive to alloy formation as reported previously. [38] This binding energy also indicates that palladium is present as Pd^0 with no evidence of oxide formation[39]. Absence of the N 1s binding energy corresponding to nitrate anions indicates that there is no adsorption of nitrate onto the surface of the Cu/Pd honeycomb material which may influence its surface properties.

Given that the penetration depth of XPS is ~ 5 nm, this suggests that Pd may be incorporated under a very thin layer of copper oxide that prevents its air oxidation. This coverage is most likely the result of catalysed electroless deposition of copper at nanoparticles of palladium on the surface. XRD analysis indicated only a very slight shift in the copper peak positions, even at the highest bulk Pd concentration (Figure S5). This may be due to the high percentage of copper within the sample relative to palladium. In addition the crystallite size, calculated from the width of the Cu {111} peak at $2\theta = 43°$ using the Scherrer equation, was observed to decrease from 32 nm to 23 nm upon the incorporation of palladium into the structure when 5 mM $Pd(NO_3)_2$ was used in the deposition solution. Characteristic peaks at $2\theta = 36.8$, 48.8 and 61.7° indicated again the presence of some CuO in all honeycomb samples. A gradual increase in crystallite size was then observed upon the incorporation of more palladium into the material up to a value of 28 nm (Figure 4c). This is reflected in the SEM images in Figure 2 that show a significant decrease in the sharpness of the nanostructures formed in the internal wall structure upon the incorporation of palladium, which facilitates the formation of block like crystallites which are likely to be agglomerates of smaller particles.

The surface to bulk palladium ratio calculated from the individual AAS and XPS values drops from 2:1 to 1:2 as the palladium salt concentration in the plating bath was increased from 5 to

50 mM. This clearly indicates that palladium goes into the bulk of the material rather than accumulating at the surface over this concentration range. However, it should be noted that the variation in the $Pd(NO_3)_2$ concentration used here is not significant compared to the large excess of $CuSO_4$ (0.4 M) in the solution. As stated earlier palladium is known to catalyse the deposition of copper, therefore small palladium clusters formed initially will act as nucleation centres for the growth of copper and the percentage of seed sites may dictate the morphology of the individual particles that make up the internal wall structure of the honeycomb material. As the palladium salt concentration is increased the number of palladium seed sites increases which seems to promote the formation of block like structures. Since the palladium catalysed deposition process takes place under non equilibrium conditions, copper tends to be deposited around only the palladium seeds.

Surface enhanced Raman spectroscopy (SERS) is an extremely sensitive method for the investigation of surface phenomena. SERS spectra for Rhodamine B immobilised on the honeycomb Cu and Cu/Pd structures are shown in Figure 6. Significantly, there is an intense SERS signal obtained at porous honeycomb copper that is homogeneous across the sample and which has not previously been reported. The use of such a substrate may provide a cheaper alternative to the more commonly used silver and gold substrates. Upon the incorporation of the lowest concentration of palladium the intensity of the signal is maintained (Figure 6 and 3d) with an improvement in resolution. However upon increasing the concentration of palladium further results in an abrupt decay in signal intensity which at the highest Pd concentration is similar to an unmodified flat copper substrate (Figure 6). Interestingly, the surface concentration of palladium at the lowest concentration level is nearly the highest of all the samples and given that the surface plasmon resonance of palladium nanomaterials is in the UV region, which is well removed from the wavelength at which Rhodamine B absorbs light, suggests that it is the sample morphology that dictates the SERS response. It is known that nanostructured metals that exhibit a surface plasmon resonance with sharp tips are good SERS substrates due to the lightning rod effect which enhances the local electromagnetic field.[40] From the SEM images in Figure 2 it can be seen that when palladium is incorporated at the lowest level the dendritic nature of the internal wall structure is maintained but to a lower extent with less branching. Recently, it has been demonstrated that another explanation for significantly enhanced Raman signals and improvement in resolution is from a sandwich type effect where the molecule of interest is trapped between connected nanoparticles. [41] It is believed that localised plasmons created by electromagnetic coupling between touching particles is responsible for these enhancements which can be regarded as hot spots.[42] For the sample with the lowest concentration of palladium the improved resolution may be due to a contribution from the tips of the structure but also the right inter particle spacing to facilitate a sandwich type effect. However, when the concentration of palladium is increased further the morphology of the internal wall structure becomes quite block like which does not compensate for a surface consisting of a high percentage of palladium which does not possess a surface plasmon resonance feature in the visible region.

The hydrogen evolution reaction (HER) under acidic conditions was chosen as an electrocatalytic process given the large difference in activity between copper and palladium for this reaction. Therefore this allows any synergistic effects between the two metals to be more readily observed. Illustrated in Figure 7 are linear sweep voltammograms recorded in 1 M H_2SO_4 for a palladium electrode, honeycomb copper and various honeycomb Cu/Pd films. It should be noted that XPS measurements showed no evidence of adsorbed nitrate ions on the surface and the responses recorded are due to the reduction of protons and not adsorbed nitrate. It can be seen that the incorporation of palladium into the honeycomb structure results in an increase in the magnitude of the response, most likely attributable to increased surface area, but more significantly the shift to less negative potential is clear with increasing palladium content, indicating an electrocatalytic effect. The responses observed at Cu/Pd with the higher loadings of palladium (11 and 17.4 atomic %) were also shown to be more effective than a pure polished palladium electrode. This is most likely due to the internal wall structure of the honeycomb material having a nanostructure which is known to promote electrocatalytic activity.[19] Interestingly, the gradual improvement in the response for the Cu/Pd samples correlates more with the bulk concentration of palladium rather than the surface composition determined by XPS. It has been demonstrated by density functional theory (DFT) calculations that the HER on Pd films with underlayers of noble metals was influenced up to 5 monolayers of Pd on a Au {110} surface.[43] Therefore, the electronic nature of the surface, which affects the metal hydrogen bond strength and dictates the rate of reaction,[44] may still be significantly influenced by the underlying Cu/Pd and account for the positive shift in onset potential for the reaction.

Conclusion

In summary, a rapid method to form a bimetallic porous honeycomb Cu/Pd structure is reported. It was found that the pore size decreases and bulk concentration of palladium increases with an increased concentration of palladium salt used in the deposition solution. The surface concentration was almost constant at 9 atomic percent and XPS analysis indicates the formation of a surface rich with a Cu/Pd alloy. SERS spectra were particularly sensitive to both the surface composition and morphology whereby the latter dominated the response. The Cu/Pd material was also shown to be sensitive to the hydrogen evolution reaction whereby an increased electrocatalytic effect was observed with an increase in the bulk concentration of palladium. The facile fabrication of this type of honeycomb bimetallic material, which could also be fabricated as a free standing film, may open up many applications in the area of gas and liquid phase catalysis, water purification, electrocatalysis and sensing.

Experimental Section

Solutions containing $CuSO_4$, $PdNO_3$ and H_2SO_4 (Ajax Finechem), or Rhodamine B (Merck) were used as received and were made up with deionized water (resistivity of 18.2 MΩ cm) purified by use of a Milli-Q reagent deioniser (Millipore). Electrochemical experiments were conducted at (20 ± 2)°C with a CH Instruments (CHI 760C) electrochemical analyser. A copper foil (99.999 % purity purchased from Goodfellow) (0.158 cm^2 area) was used as the working electrode, which was first immersed in diluted HNO_3 (10 % v/v) to remove any surface oxides and then washed in acetone and methanol followed by drying in a stream of nitrogen gas prior to use. The reference electrode was Ag/AgCl (aqueous 3 M KCl). For electrodeposition of honeycomb Cu and Cu/Pd an inert graphite rod (3 mm diameter, Johnson Matthey Ultra “F’ purity grade) was used as the counter electrode to avoid any possible contaminants from electrodissolution.[45] The Pd electrode (3 mm diameter) (BAS) was polished prior to use with a 0.3 µm alumina slurry on a Microcloth, rinsed with Milli-Q water and dried with a flow of nitrogen. All electrochemical measurements were commenced after degassing the electrolyte solutions with nitrogen for at least 10 min prior to any measurement. All electrocatalytic data is normalized to the geometric area of the electrode. SEM measurements were performed on a FEI Nova SEM instrument. Prior to imaging, samples were thoroughly rinsed with Milli-Q water and dried under a flow of nitrogen. XRD measurements were carried out on a Bruker AXS X-ray diffraction system operated at a voltage of 40 kV and current of 40 mA with Cu Kα radiation. X-ray photoelectron spectroscopy measurements were obtained with a Thermo K-Alpha XPS instrument at a pressure better than 1×10^{-9} Torr with core levels aligned with C 1s binding energy of 285 eV. Atomic absorption spectroscopy (AAS) analysis was done with a Varian AAS spectrophotometer. SERS activity was measured using a PerkinElmer RamanStation 400 at an excitation wavelength of 785 nm after immersing the samples in an aqueous 1 mM solution of Rhodamine B (Merck) for one hour before the unbound Rhodamine B was washed off with water.

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Figure captions

Figure 1. SEM images of Cu/Pd electrodeposited at a current density of 3 A cm^{-2} for 15 s from a solution of 0.4 M $CuSO_4$ and 1.5 M H_2SO_4 containing (a) 0 (b) 5 mM (c) 10 mM and (d) 20 mM $Pd(NO_3)_2$.

Figure 2. Higher magnification SEM images of Cu/Pd samples as shown in Figure 1.

Figure 3. Linear sweep voltammograms recorded at a copper foil electrode at a sweep rate of 50 mV s^{-1} in a 1.5 M H_2SO_4 solution containing 0.4 M $CuSO_4$ (grey) and 0.4 M $CuSO_4$ containing 20 mM $Pd(NO_3)_2$ (black).

Figure 4. Plots of (a) bulk composition (■) and surface composition (●) (b) pore size (c) particle size and (d) SERS signal intensity of Rhodamine B at 1503 cm^{-1} for honeycomb Cu and Cu/Pd as a function of $Pd(NO_3)_2$ used in the electrodeposition solution.

Figure 5. XPS spectra for Cu/Pd deposited from 0.4 M $CuSO_4$ and 1.5 M H_2SO_4 containing (1) 0 (2) 5 (3) 10 (4) 20 and (5) 50 mM $Pd(NO_3)_2$ (a) Cu $2p_{3/2}$ and (b) Pd $3d_{5/2}$.

Figure 6. SERS spectra for Rhodamine B immobilised on Cu/Pd electrodeposited at a current density of 3 A cm^{-2} for 15 s from a solution of 0.4 M $CuSO_4$ and 1.5 M H_2SO_4 containing (1) 0 (2) 5 mM (3) 10 mM (4) 20 mM and (5) 50 mM $Pd(NO_3)_2$.

Figure 7. Linear sweep voltammograms recorded at 10 mV s^{-1} in 1 M H_2SO_4 at a Pd electrode (grey) and Cu/Pd deposited from 0.4 M $CuSO_4$ and 1.5 M H_2SO_4 containing (1) 0 (2) 5 (3) 10 (4) 20 and (5) 50 mM $Pd(NO_3)_2$.

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Catch phrase: Bimetallic honeycombs

A rapid method based on a hydrogen bubble template to form a bimetallic porous honeycomb Cu/Pd structure has been investigated. The addition of palladium salt to a copper plating bath under conditions of vigorous hydrogen evolution was found to influence the pore size and bulk concentration of Cu and Pd in the honeycomb bimetallic structure. The surface of honeycomb Cu/Pd was found to be rich with a Cu/Pd alloy which significantly influenced both the SERS response for immobilised Rhodamine B and the hydrogen evolution reaction.

Keywords: honeycomb Cu/Pd • electrodeposition • bimetallic • porous • bubble templating