Size-controlled Gold-catalyzed Growth of Prussian Blue Nanopillars

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Size-dependent nanopillars of Prussian blue were obtained by chemical deposition technique and porous alumina membranes coated with a bottom gold layer.

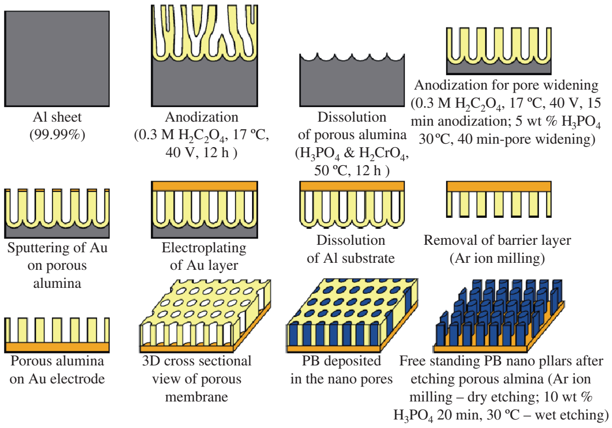
While many coordination compounds exhibit one or two significant properties confining to a single chemical formula, Prussian blue (PB), the prototype of all mixed-valent hexacyanometalates, $A^{I}_{x}B_{y}[C(CN)_6]^{z-}$ (A^{I} = alkali metal ion; B and C = transition-metal ions) exhibits multifunctionalities like dye pigments, molecular magnetic,[1] electrocatalytic,[2] electrochromic,[3] ion-exchange,[4] ion-sensing,[5,6] and photomagnetic[7] properties. Hence, even after 300 years of its discovery, PB is being continuously explored for its properties in its various physical and chemical forms. The studies on PB mainly involved surfaces electrochemically modified by PB films. Though chemical deposition of PB has been reported previously,[8,9] it is not practiced as a common method. There is a recent report on the magnetic properties of PB nanowires which have been grown electrochemically in a porous alumina template.[1]

There are several established methodologies towards generation of size- and shape-dependent nanostructures of interest, of which anodically oxidized porous alumina template is well accepted.[10,11] Efforts to achieve high aspect ratios still continues, as properties of nanostructures are highly dependent on the fine features of the size and shape of the structure generated. In this communication we report for the first time, the growth of PB nanorods chemically, in a home made high aspect ratio gold-coated porous alumina template. Our efforts demonstrate that nanostructures can be generated chemically by proper modification of the porous alumina membranes.

The highly ordered gold-coated porous alumina template was fabricated by a two-step anodizing process as shown in Scheme 1.

Anodization of a clean Al sheet “in 0.3 M oxalic acid at 40 V for a long period” results in a regular pore arrangement at the bottom side of the oxide film, which was removed by treating with a mixture of phosphoric and chromic acid mixture. This surface was once again anodized as before for uniform pore development and treated with phosphoric acid to widen the formed pores. After second anodization, gold was sputtered to provide electrical contact for further electroplating of gold layer onto the porous alumina surface. After electroplating of gold layer, removal of “bottom alumina layer (barrier layer)” results in a porous alumina membrane “with opened pores” on a gold electrode. This electrode is used for PB deposition, as detailed below.

Prior to deposition within the membrane the spontaneous growth conditions were optimized by control experiments. A gold–mica sheet is immersed in 0.01 M HCl solution containing equimolar mixture of $K_3Fe(CN)_6$ and $FeCl_3 \cdot 6H_2O$, on which spontaneous growth of PB film was observed. From these experiments, we found that the presence of gold surface and a solution pH of 2 were necessary criteria for the spontaneous self deposition of PB without any external stimuli as current or potential because the total charge consumed in the reduction of PB estimated from the cyclic voltammograms was proportional to the immersion time (see Supporting Information, Figure S1). In the absence of gold surface, PB film formation could not be observed. Also, when the pH exceeded 3, chemical deposition did not take place even if the gold–mica sheet was left overnight.



Scheme 1. Schematic illustration of the fabrication of gold-coated porous alumina membrane and PB deposition within the membrane following a two-step anodization process.

Following above findings, PB was deposited in the porous alumina membrane as described. Initially, when a **type 1** membrane was used without any pretreatment for deposition for 30 min, nanopillars limited to certain area are obtained. To obtain more wide spread nanopillars, later a **type 2** membrane was used with pretreatment. Prior to deposition for 5 and 15 min, respectively, the template was immersed in water under vacuum for 1.5 h, immersed in 5 wt % H_3PO_4 (aq) for 1 min, then immersed in water under vacuum for 1.5 h, to make the pores free of any remaining alumina and air gaps. Such pretreated membrane gave nanopillars spread over all the membrane area.

The nanorods of PB have been grown by chemical deposition from equimolar solutions of $FeCl_3 \cdot 6H_2O$ and $K_3Fe(CN)_6$ in the porous alumina template. The addition of $K_3Fe(CN)_6$ solution to $FeCl_3 \cdot 6H_2O$ solution in equal amounts resulted in the formation of wine red colored solution, from which the nanopillars are deposited. The formation of wine red color upon mixing of both solutions indicates the formation of a charge-transfer

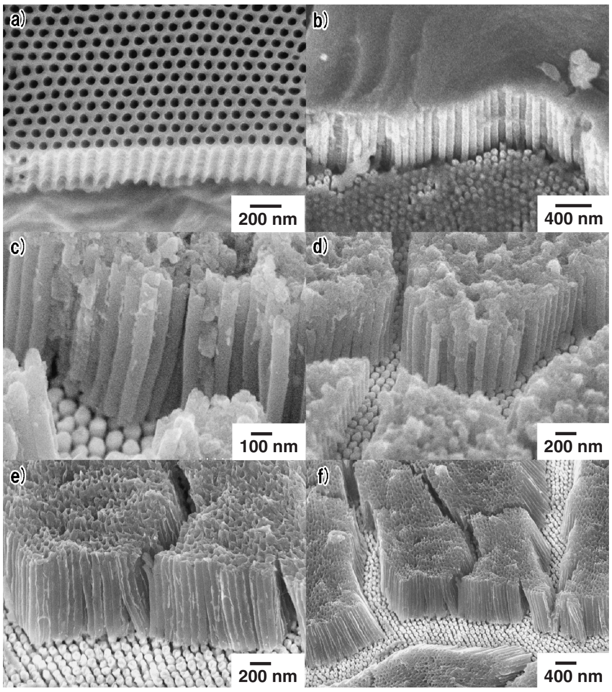


Figure 1. SEM images of (a) free template, (b) free standing nanopillars deposited for 30 min, (c) and (d) free standing nanopillars deposited for 5 min, and (e) and (f) free standing nanopillars deposited for 15 min of Prussian blue after removal of porous alumina membrane. The gold rods (≈200 nm long) can be seen at the bottom as small protrusions.

complex.

A neutral complex formation from equimolar solutions containing ferric ion and ferricyanide ion was previously reported by Neff et al.,[8] with the formation of BG precipitate slowly, which contains indefinite amounts of hexacyano ferrate (II) and (III) ions. Possible mechanism for the formation of PB from such solutions prior to the precipitation of BG involves the reactions as in eqs 1 and 2.

$$\mathrm{Fe^{3+} + 1/2H_2O \rightarrow 1/4O_2 + H^+ + Fe^{2+}}, \qquad (1)$$

$$\mathrm{K^+ + Fe^{2+} + [Fe(CN)_6]^{3-} \rightarrow KFeFe(CN)_6} \qquad (2)$$

It has been suggested that reaction (1) is catalysed by gold or platinum substrates where the free iron (II) ion or iron (II) ion in the associated complex is reduced to give iron (II) ion, with eq 2 providing the necessary driving force for step (1) to proceed. Following the same argument, we believe that the gold layer at the bottom of the alumina template nanopores, catalyzes the reaction (1), leading to the formation of iron (II) ion, which further complexes with hexacyanoferrate (III) ion resulting in PB formation.

The SEM images (Figure 1) show that the nanopillars are highly ordered and dense. After removal of the bulk PB layer covering the template surface by Ar ion milling, followed by wet etching to remove the porous alumina template walls, the free standing nanorods on gold surface remained. Figure 1a shows a typical membrane in top and cross-sectional views, before deposition. From this figure, it can be understood that the holes are highly ordered and uniformly spaced with hexagonal arrangement. Figure 1b shows the cross-sectional view of free standing nanopillars in **type 1** membrane after removal of template walls. The bulk PB layer covering the membrane surface can be seen as a thick layer above the pillars. Figures 1c and 1d correspond to nanopillars deposited in **type 2** membrane for 5 min, after removal of the template. Figures 1e and 1f correspond to that of 15 min deposition in **type 2** membrane after removal of the template. In all these cases, we can see the highly ordered, dense and uniformly spaced nanopillars, standing over the gold protrusions. Depending on the deposition time, these nanorods vary in length from ≈600–1000 nm, with a diameter of ≈70 nm.

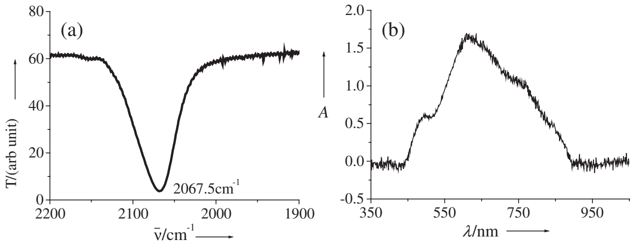


Figure 2. (a) IR spectrum and (b) UV–vis spectrum of PB nanopillars deposited in gold-coated porous alumina membrane.

The nature of the formed nanorods is further confirmed by XPS, micro IR, and micro UV experiments (Figure 2). The value of $\mathrm{Fe2p_{3/2}}$ from XPS spectra is 709.2 eV, which is similar to that of bulk PB (see Supporting Inoformation, Figure S2 and Table S1). The IR spectrum of the nanorods also shows the characteristic, –C≡N stretch at 2067 $\mathrm{cm^{-1}}$, which is in accordance with the reported value of –C≡N stretch in the IR region, 2068 $\mathrm{cm^{-1}}$.[12] While, the UV–vis spectrum shows the CT band centered about 615 nm, with shoulders at 494 and 765 nm probably due to interference bands both consistent with the formation of PB, which is shifted to about 80 nm from the value of bulk PB, 700 nm. The size effect as a reason of the blue shift is currently under investigation.

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