Gold nanowire synthesis by semi-immersed nanoporous anodic aluminium oxide templates in potassium dicyanoaurate-hexacyanoferrate electrolyte

Margarita Baitimirova[1], Anita Pastare[1], Juris Katkevics[1,2], Arturs Viksna[1,2], Juris Prikulis[1], Donats Erts[1]

[1]*Institute of Chemical Physics, University of Latvia, Riga, 19 Raina Blvd., LV-1586, Latvia*
[2]*Department of Chemistry, University of Latvia, Riga, 48 Kr. Valdemara Str., LV-1013, Latvia*
E-mail: donats.erts@lu.lv

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The synthesis reaction of potassium dicyanoaurate-hexacyanoferrate electrolyte and the pertinence of this electrolyte for gold nanowire synthesis are reported. Gold nanowires were synthesised in anodic aluminium oxide (AAO) nanopores using an improved design of the electrochemical cell. AAO templates with thick gold layers were placed on the surface of the electrolyte, thus the ends of the nanopores were opened, allowing the electrolyte to freely diffuse into the nanopores, extruding gases. The presented procedure simplifies the preparation before nanowire synthesis: AAO templates before synthesis do not need to degas and isolate themselves from contact with the electrolyte by a parafilm or a non-conductive adhesive. A considerably faster nanowire growth in the given conditions in the case of a semi-immersed AAO template when compared with the complete immersion method is reported. For comparison with literature data, gold nanowires were synthesised by the classical electrochemical cell using potassium dicyanoaurate-citrate electrolyte. Long, smooth and high purity nanowires were obtained using semi-immersed templates.

1. Introduction: Gold nanowires are of interest to diverse communities of nanoscience research and nanosensor development. They have good electrical conductivity and are chemically inert. Application examples include biosensors [1, 2], nanoelectronics [3] or plasmonic devices [4]. Several nanowire synthesis methods exist, for example, lithography, photochemical synthesis, chemical reduction and electrochemical deposition [5–9].

Until recently, gold nanowires were successfully fabricated from electrolytes which contain cyanides [10, 11], sulphites [12] and other corrosive or health-endangering gas-releasing chemicals [13]. In some cases, nanowires were fabricated from electrolytes which also consist of heavy metals, for example, Co, Ni and Cu [10, 11, 13]. Some studies [14–18] show that Au can be deposited from cyanide-free electrolytes. However, such studies are relatively few. Gold(I) sulphate and gold(I) thiosulphate electrolytes are more difficult to use because of insufficient compound stability. Auro-organic complexes are more stable; however, quality problems regarding the appearance and thickness of coating have been reported [15]. Another electrolyte used for gold nanowire fabrication is potassium dicyanoaurate-hexacyanoferrate electrolyte, which is known as a gold-plating electrolyte [19, 20]. In contradistinction to other cyanide-containing electrolytes, this electrolyte is safer for use because harmful gases are not produced during the nanowire deposition process. Components of this electrolyte are stable in weak acid and neutral solution, which allows the use of sodium carbonate as a neutralising agent for freed cyanide ions.

Typical electrochemical methods for gold or other metal nanowire fabrication include complete immersion of electrodes in the electrolyte solution [9–14]. To control the direction of metal-ion flow, the back side of the nanoporous material, for example, anodic aluminium oxide (AAO), is protected from interaction with the electrolyte solution by a non-conductive material [21–24]. Such pores are often filled with air or other gases, produced in the process of water electrolysis or the electrolysis of indifferent electrolyte components, which may prevent metal-ion diffusion into pores. To remove the gases, electrochemical cells can be connected to a vacuum [24, 25]. Gas removal is particularly important during the initial stage of nanowire growth.

In this Letter, we demonstrate the successful use of potassium dicyanoaurate-hexacyanoferrate electrolyte for gold nanowire production. We studied reactions of electrolyte synthesis and adapted the method for nanowire deposition. A further change to the process was the placement of the porous AAO template onto the surface of the electrolyte, instead of complete immersion in the electrolyte solution. Thus, the back side of aluminium oxide with a thin layer of noble metal was protected from interaction with the electrolyte without the use of seals, plasters or non-conducting adhesives which may contaminate the electrolyte and nanowire. We refer to this as 'semi-immersed template' in this Letter.

2. Experimental

2.1. Preparation of potassium dicyanoaurate-hexacyanoferrate electrolyte: Adjustments of the component ratio, pH value and mixing sequence were introduced to the methods reported in the literature [19, 20]. A 0.2 M chloroauric acid solution was added to a 0.2 M potassium hexacyanoferrate(II) solution until blue precipitates of iron(III) hexacyanoferrate(II) stopped forming (1), (2). Thereafter the solution was heated to 80°C to decrease the hydrogen cyanide concentration in the electrolyte and then left to cool to room temperature. The solution was neutralised by potassium carbonate to pH 5–7. After stratification, the pale greenish-yellow solution of potassium dicyanoaurate-hexacyanoferrate was separated for experiments. The prepared solution contained 1–4 g Au/l. Ultraviolet (UV) spectra of reactants and products were obtained by UV/Vis spectrophotometer Perkin Elmer Lambda 25.

$$4H[AuCl_4](III) + 9K_4[Fe(CN)_6](II) \rightarrow 4K[Au(CN)_2](I) + Fe_4[Fe(CN)_6]_3\downarrow (III) + 2K_3[Fe(CN)_6](III) + 16KCl + 10KCN + 4HCN \uparrow \quad (1)$$

$$6H[AuCl_4] + 7K_4[Fe(CN)_6] \rightarrow 6K[Au(CN)_4] + Fe_4[Fe(CN)_6]_3 \downarrow + 22KCl + 2HCl + 2H_2 \uparrow \quad (2)$$

The quality of the prepared electrolyte was verified using two methods: by depositing the mass of gold on the plate electrode and by cyclic voltammetry. For the first method, gold was deposited a constant voltage of 2 V. The observed current density was 11–14 mA/cm^2. An Autolab PGSTAT30 potentiostat was

used for the cyclic voltammograms obtaining a potential scan from −1.3 V to +1.3 V. The scan step was 0.0024 V and the speed was 0.09 V/s. A calomel reference electrode was used during the above measurement.

2.2. Gold nanowire synthesis: In the experiments, 45–60 μm-thick AAO templates (ANOPORE, SPI Supplies) with 100 nm pore diameter were used. The AAO templates were treated with 0.5 M orthophosphoric acid for 70 min at 20–25°C to remove the barrier layer and to expand the pores. As a result, the pore diameter was enlarged from 100 to ∼150 nm. The back side of the AAO template was then coated with a 50–100 nm-thick gold layer by using the etching and coating system Gatan 682. The thickness of the gold layer was kept 5–50% less than the diameter of nanopores, which leaves the ends of nanopores open to allow gas to diffuse. The prepared AAO-gold structure was used as a cathode. A platinum electrode was used as an anode and an Ag-AgCl electrode was used as the reference electrode.

Gold nanowires were produced with porous material placed on the electrolyte surface. Fig. 1 shows the design of the electrochemical cell. A platinum wire spring was attached to the gold layer using conductive glue. The diameter and number of platinum spiral turns depend on the AAO template size. AAO was placed on the electrolyte for a few seconds and then was lifted (a fraction of a millimetre at a time) until a concave meniscus was formed. The meniscus indicates that the electrolyte is wetting the foil and has entered into the nanopores of the AAO template by capillary forces. The spring force was kept in balance with the surface tension of the electrolyte to allow the formation of a concave meniscus between the electrolyte and the nanoporous material. The experimentally determined optimal tension of the platinum spring was 5.4–5.6 mN/cm².

For the purposes of comparison, gold nanowires were also produced by complete immersion of the porous material into the electrolyte in a classical electrochemical cell [9–14] from potassium dicyanoaurate-citrate electrolyte, which was prepared as described in [5] from 25 mg potassium dicyanoaurate(I), 730 mg diammonium citrate, 236 mg succinic acid, 45 mg oxalic acid dihydrate and 384 mg citric acid. Each component was dissolved in 1 ml distilled water and the solutions were subsequently mixed. Before nanowire synthesis, the metal parts of the AAO template were isolated from contact with the electrolyte by a parafilm or a non-conductive adhesive. To remove any air from the AAO pores, the prepared template was immersed in the electrolyte solution and evacuated by a vacuum pump. The concentration of gases in the electrolyte was decreased in the pumping process, so all of the bubbles from AAO nanopores were dissoloved.

The nanowire deposition process was controlled by a potentiostat (Autolab PGSTAT 30). The parameters of gold deposition were as follows: for the first 5–7 s the potential was −0.9 V, the current was −1 to −2 mA, the work potential −1.2 V, the current flow was −4 to −5 mA/cm², and the electrolysis time was 3 h. The electrolyte was stirred and heated at 40–50°C.

To analyse the resulting filling quality and determine the nanowire density, the AAO was dissolved in 0.5 M orthophosphoric acid for 10–15 min [26, 27] from the template front side. To clear the nanowires from deposited Au on the AAO surface and membrane residues, the surface was subsequently etched by Ar ions at an energy of 9.5 keV and at a current of 600–614 μA for 4–6 min at an etching angle from 22.5° to 45°, with sample rotation using a Gatan precision etching coating system. The resulting gold nanowires were characterised by field emission scanning electron microscope (SEM) Hitachi S-4800 with EDX analyser B-QANTAX, Energy Dispersive Spectrometer Quanta (detector type XFlash 5010).

3. Results and discussion

3.1. Analysis of potassium dicyanoaurate-hexacyanoferrate electrolyte: Fig. 2*a* shows the UV spectra obtained for the reactants and products of the chemical reaction of potassium dicyanoaurate-hexacyanoferrate synthesis. The reactants absorb UV-light: $H[AuCl_4]$ reaches absorbance maximum at 287 nm and $K_4[Fe(CN)_6]$ – at 325 nm. During the synthesis reactions (1) and (2), by mixing these components, gold(III) in the $H[AuCl_4]$ molecule reduces to gold(I) and forms the $K[Au(CN)_2]$ molecule, which has an absorbance maximum plateau from 200 to 250 nm. At the same time, iron(II) in $K_4[Fe(CN)_6]$ oxidises to iron(III) and forms the $K_3[Fe(CN)_6]$ molecule with absorbance maximums at 260 and 306 nm. The obtained absorbance spectra of the compounds used in electrolyte preparation were in agreement with the UV-spectra from the literature [28–31] and confirm that electrolyte synthesis followed according to reactions (1) and (2).

Fig. 2*b* shows the changes in UV-light absorbance of the potassium dicyanoaurate-hexacyanoferrate electrolyte during gold nanowire synthesis. Initially, the absorbance maximum at 306 nm and absorbance maximum plateau from 200 to 250 nm were observed, which correspond to the absorbance of $K_3[Fe(CN)_6]$ and $K[Au(CN)_2]$, respectively. After nanowire synthesis, the absorbance maximum plateau changed from 200–250 to 200–260 nm and absorbance maximum was observed at 325 nm, which coincides with the UV-spectrum of $K_4[Fe(CN)_6]$. This means that $K_3[Fe(CN)_6]$ (Fe – III) was changed into $K_4[Fe(CN)_6]$ (Fe – II) during the gold deposition process.

Figs. 3*a* and *b* show cyclic voltammograms of potassium dicyanoaurate-hexacyanoferrate electrolyte. Gold was deposited on the cathode at potential $\varepsilon = -0.61$ V as (3) [19, 32]

$$\left[Au(CN)_2\right]^- + e^- \rightarrow Au^0 + 2\ CN^- \qquad (3)$$

The decomposition potential was $-U_0 = -1.75$ V and the overpotential of oxygen discharging on the anode was only $\eta_{an,0} = 0.09$ V. Both maximums at −0.37 and +0.37 V were related to the

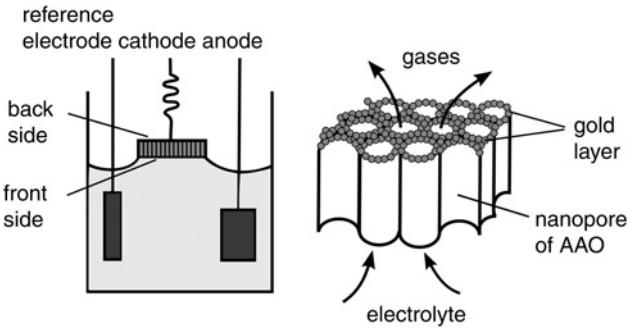

Figure 1 *Electrochemical cell for AAO template placement on the electrolyte surface (semi-immersed template)*

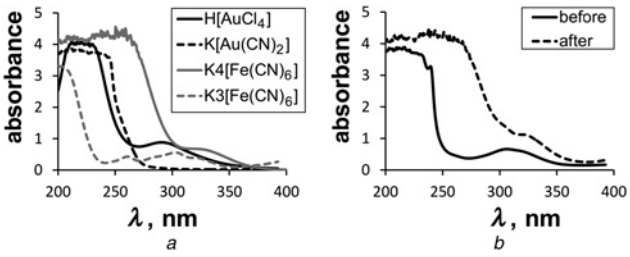

Figure 2 *UV-spectra of potassium dicyanoaurate-hexacyanoferrate electrolyte*
a Components of synthesis reaction
b Electrolyte before and after gold nanowires synthesis

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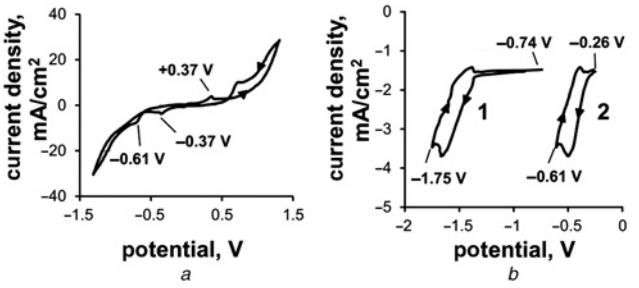

Figure 3 *Cyclic voltammograms of potassium dicyanoaurate-hexacyanoferrate electrolyte for gold deposition*
a Full electrochemical window
b Electrochemical window for negative part of potentials, 1 shows cyclogram of potential of cathode, 2 shows cyclogram of decomposition potential

change of oxidation state of iron in the hexacyanoferrate molecule as shown by (4) [19, 33]

$$\left[\mathrm{Fe(CN)_6}\right]^{3-} + \mathrm{e}^- \rightarrow \left[\mathrm{Fe(CN)_6}\right]^{4-} \quad (4)$$

3.2. Comparison of gold nanowires obtained by different filling methods: For the purpose of comparison of the classical electrochemical cell and the cell for the semi-immersed template, gold nanowires were synthesised from potassium dicyanoaurate-citrate electrolyte. The cross-section of the AAO template with gold nanowires obtained by the semi-immersed AAO template is shown in Figs. 4*a* and *b*. In the semi-immersed template case, gold nanowires grew up to 60 µm long, extending through the whole template thickness in less than 3 h. In contrast, after 3 h the deposition length of the gold nanowire obtained by complete AAO immersion in the electrolyte solution was limited to approximately 3 µm (Figs. 4*c* and *d*). The experiment conditions for synthesis of the above samples were the same, except for the immersion of the template. In both cases, the obtained gold nanowires were 100–150 nm in diameter as governed by the template geometry. The shorter length of the nanowires obtained by immersion in the electrolyte can be explained by the sealing the back side of the membrane. As a result, accumulated gases partly block the pores and hamper the gold ion flow into the membrane.

The observed current density of gold deposition in a semi-immersed AAO template was higher than the current density of

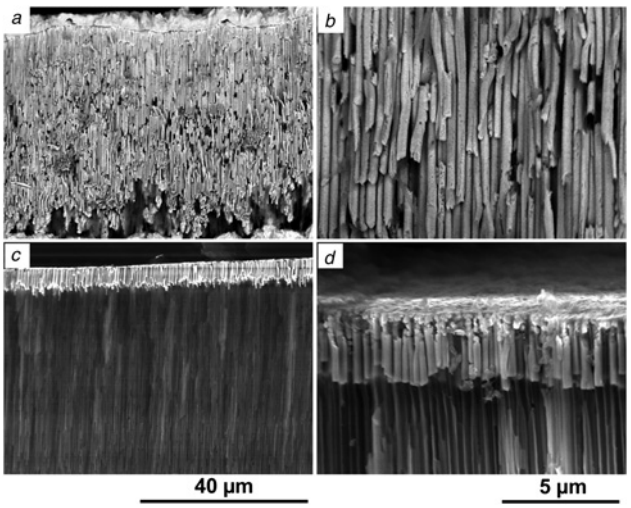

Figure 4 *SEM images of gold nanowires produced from dicyanoaurate-citrate electrolyte*
a and *b* By semi-immersed AAO template
c and *d* By complete immersion of AAO template in electrolyte

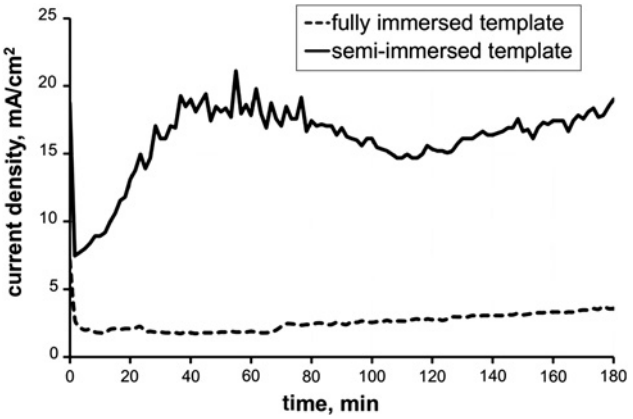

Figure 5 *Change in current density during potentiostatic electrodeposition of gold nanowires at −1.2 V*

gold deposition using a classical electrochemical cell (Fig. 5). The initial current during the first few seconds of electrolysis is higher than the observed steady current during optimal nanowire growth, because a higher charge is accumulated on transitional surfaces of the system. For the process with the semi-immersed template, it was important not to block the ends of the nanopores with the gold layer. In this case, the electrolyte wets the surface of the AAO and quickly soaks through the nanopores into the gold cover, extruding gas from the nanopores. Thus, the contact between the electrolyte, the gold layer and the metal wire is established. In the case of blocked pore ends, the above processes hamper metal-ion diffusion into the nanopores and local regions with a high field gradient arise in the system. As a result, the process of electrolysis may change the preferred direction. If the ends of the nanopores are not blocked by gold or another sealing material, gases diffuse freely into the atmosphere, and nanopore blocking is less probable. In this case, metal ion deposition stabilises faster and anion diffusion from the nanopores to the outside bulk solution remains steady.

Fig. 6 shows the SEM image of gold nanowires produced by the semi-immersed template after AAO dissolution. The nanowire arrangement is dense and all pores are filled. Although the nanowire ends appear to have irregular shapes (triangles or polygons), the wires are cylindrical, with little diameter variation throughout the sample. The same arrangement was observed for gold nanowires fabricated by immersion of the sample in the electrolyte.

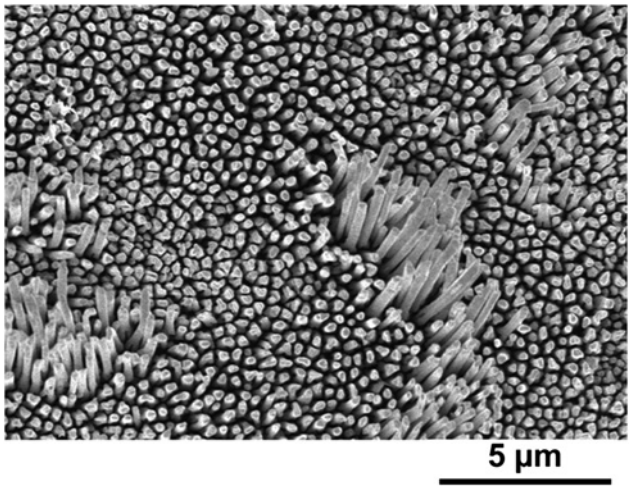

Figure 6 *SEM image of gold nanowires produced by semi-immersed template after AAO removal*

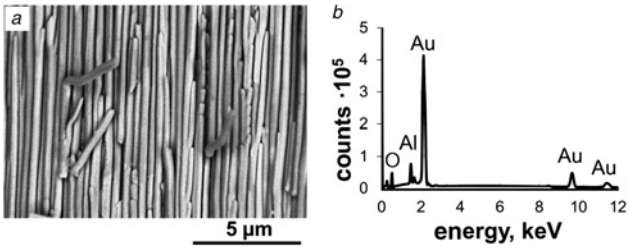

Figure 7 *Gold nanowires produced from dicyanoaurate-hexacyanoferrate electrolyte by semi-immersed AAO template*
a SEM image
b EDX spectrum

Fig. 7*a* shows a cross-section of the AAO template with gold nanowires produced from potassium dicyanoaurate-hexacyanoferrate electrolyte by the semi-immersed AAO template. The produced nanowires were 60 μm long and 100–150 nm in diameter as compared to the size of used AAO nanopores. Gold nanowires formed from dicyanoaurate-hexacyanoferrate electrolyte were smoother and more uniform in comparison to nanowires from dicyanoaurate-citrate electrolyte.

Chemical elemental analysis by EDX showed that gold (Au) nanowires, deposited in the pores of a semi-immersed AAO template, were of high purity (Fig. 7*b*). Aluminium and oxygen were detected, the presence of which is to be expected from the remains of the AAO template. No other elements (for example, iron and potassium) from the electrolyte or silver residues from the conductive glue could be detected.

4. Conclusion: We have demonstrated an improved electrochemical cell, in which AAO was placed on the electrolyte surface. The key feature of the new design is the free flow of residual gases through the top opening of the pores. The average achieved nanowire length is 30 to 60 μm, which is 10–20 times longer than the gold nanowires produced by immersion of the sample in the electrolyte with the same conditions of electrolysis. Using this method, the isolation of the back side of the AAO template from interaction with the electrolyte was not needed. This reduces the risk of electrolyte and nanowire contamination from isolation material. Gold nanowires produced from prepared potassium dicyanoaurate-hexacyanoferrate electrolyte are of high purity and are smoother and more uniform in comparison to nanowires produced from dicyanoaurate-citrate electrolyte. The obtained nanowires can be used in various applications, for example, as electrodes for three-dimensional nanoelectronic devices or as miniature electric contacts for studies of biological samples, where processes involving vacuum (e.g. electron lithography) are not permitted.

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6 References

[1] Grieshaber D., MacKenzie R., Voros J., Reimhult E.: 'Electrochemical biosensors – sensor principles and architectures', *Sensors*, 2008, **8**, pp. 1400–1458
[2] Andreu A., Merkert J.W., Lecaros L.A., Broglin B.L., Brazell J.T., El-Kouedi M.: 'Detection of DNA oligonucleotides on nanowire array electrodes using chronocouolmetry', *Sens. Actuators B*, 2006, **114**, (2), pp. 1116–1120
[3] So H.-M., Kim J., Yun W.S., *ET AL.*: 'Molecule-based single electron transistor', *Phys. E*, 2003, **18**, (1–3), pp. 243–244
[4] Lal S., Link S., Halas N.J.: 'Nano-optics from sensing to waveguiding', *Nat. Photonics*, 2007, **1**, pp. 641–648
[5] Xiang C., Yang Y., Penner R.M.: 'Cheating the diffraction limit: electrodeposited nanowires patterned by photolithography', *Chem. Commun.*, 2009, **2009**, (8), pp. 859–873
[6] Pei L., Mori K., Adachi M.: 'Formation process of two-dimensional networked gold nanowires by citrate reduction of $AuCl_4^-$ and the shape stabilization', *J. Am. Chem. Soc.*, 2004, **20**, (18), pp. 7837–7843
[7] Kim F., Song J.H., Yang P.: 'Photochemical synthesis of gold nanorods', *J. Am. Chem. Soc.*, 2002, **124**, pp. 14316–14317
[8] Kim F., Sohn K., Wu J., Huang J.: 'Chemical synthesis of gold nanowires in acidic solutions', *J. Am. Chem. Soc.*, 2008, **130**, pp. 14442–14443
[9] Wang Z., Su Y.K., Li H.L.: 'AFM study of gold nanowire array electrodeposited within anodic aluminum oxide template', *Appl. Phys. A*, 2002, **74**, pp. 563–565
[10] Bozzini B., Cavalloti P.L.: 'Effects of cathodic hydrogen evolution on electrodeposited Au-Cu-Cd alloys', *J. Electrochem. Soc.*, 2001, **148**, (3), pp. C231–C235
[11] Bozzini B., Giovannelli G., Natali S., Brevaglieri B., Cavallotti P.L., Signorelli G.: 'Hydrogen incorporation and embrittlement of electroformed Au, Cu and Au – Cu', *Eng. Failure Anal.*, 1998, **6**, pp. 83–92
[12] Zhang J., Shi G., Liu C., Qu L., Fu M., Chen F.: 'Electrochemical fabrication of polythiophene film coated metallic nanowire arrays', *J. Mater. Sci.*, 2003, **38**, pp. 2423–2427
[13] Dolati A., Ghorbani M., Ahmadi M.R.: 'An electrochemical study of Au–Ni alloy electrodeposition from cyanide – citrate electrolytes', *J. Electroanal. Chem.*, 2005, **577**, pp. 1–8
[14] Guan M., Podlaha E.J.: 'Electrodeposition and electrochemical etching of Au/CoAu multilayered nanowires'. 205th Meeting of the Electrochemical Society, San Antonio, TX, May 2004
[15] Dimitrijevic S., Rajcic-Vujasinovis M., Trujic V.: 'Non-cyanide electrolytes for gold plating – a review', *Int. J. Electrochem. Sci.*, 2013, **8**, pp. 6620–6646
[16] Lucatero S., Fowle W.H., Podlaha E.J.: 'Electrodeposited Au/FeAu nanowires with controled porosity', *Electrochem. Solid-State Lett.*, 2009, **12**, (12), pp. D96–D100
[17] Lonjon A., Laffont L., Demont P., Dantras E., Lacabanne C.: 'Structural and electrical properties of gold nanowires/p(VDF-TrFe) nanocomposites', *J. Phys. D, Appl. Phys.*, 2010, **43**, (34), p. 345401
[18] Moghimian N., Sam M., Coelho J.D., Warwick S.D.W., Bhiladvala R.B.: 'Suppressing electroless growth allows cyanide-free electrodeposition of straight separable gold nanowires', *Electrochem. Acta*, 2013, **114**, pp. 643–648
[19] Bersirova O.L., Gerasimenko V.A., Kublanovsky V.S.: 'Electrochemical formation of the structure of functional gold deposits from ferrocyanide electrolyte', *Chem. Series*, 2009, **17**, (40), pp. 265–269
[20] Burkat G.K.: 'Silver Plating, gold plating, palladium plating and rhodium plating (Serebrenie, zolochenie, palladirovanie i rodirovanie)' (Mashinostroenie, Moscow, 1984), p. 85
[21] Leopold S., Schuchert I.U., Lu J., Toimil Molares M.E., Herranen M., Carlsson J.-O.: 'Electrochemical deposition of cylindrical Cu/Cu2O mocrostructures', *Electrochem. Acta*, 2002, **47**, pp. 4393–4397
[22] Li J., Cassell A.M., Han J.: 'Catalyst patterning for nanowire device'. US Patent, No. 6,831,017 B1, class Int. Cl. H01 L 21/311; H011 21/20; H01 L 21/36, 14 December 2004
[23] Den T., Iwasaki T.: 'Structure having pores, device using the same, and manufacturing methods therefor'. US Patent, No 7,319,069 B2, 29 January 2006
[24] Kadota H.: 'Electrolytic gold plating method and apparatus therefor'. US Patent, No 6,746,579 B2, 8 June 2004
[25] Bhansali S., Aravamudhan S., Luongo K., Kedla S.: 'Method for the assembly of nanowire interconnects'. US Patent, No 7,112,525 B1, 26 September 2006
[26] Erts D., Polyakov B., Daly B., *ET AL.*: 'High density germanium nanowire assemblies: contact challenges and electrical characterisation', *J. Phys. Chem. B*, 2006, **110**, pp. 820–826
[27] Birjukovs P., Petkov N., Xu J., *ET AL.*: 'Electrical characterisation of bismuth sulfide nanowire arrays by conductive atomic force microscopy', *J. Phys. Chem. C*, 2008, **112**, pp. 19680–19685
[28] Shaw G.F. III, Schraa S., Gleichmann E., Grover Y.P., Dunenann L., Jagarlamudi A.: 'Redox chemistry and $[Au(CN)_2]^-$ in the formation of gold metabolites', *Metal Based Drugs*, 1994, **1**, (5–6), pp. 351–362
[29] Jiang G., Wang L., Chen W.: 'Studies on the preparation and characterization of gold nanoparticles protected by dendrons', *Mater. Lett.*, 2007, **61**, pp. 278–283
[30] Chakrabarti M.H., Roberts E.P.L.: 'Analysis of mixtures of ferrocyanide and ferricyanide using UV-visible spectroscopy for

characterisation of a novel redox flow battery', *J. Chem. Sos. Pak.*, 2008, **30**, (6), pp. 817–823
[31] Liang Z., Wang Z.-j., Liu C.-j.: 'Size – controlled synthesis of colloidal gold nanoparticles at room temperature under the influence of glow discharge', *Nanoscale Res. Lett.*, 2010, **5**, (1), pp. 124–129
[32] Schlesinger M., Paunovic M.: 'Modern electroplating' (Windsor Ontario, Canada Milan Paunovic IBM T.J. Watson Research Center, Yorktown Heights, NY, 2010, 5th edn.)
[33] Haynes W.M.: 'CRC handbook of chemistry and physics' (CRC Press, 2012, 93rd edn.), p. 2664