Revisiting metal electrodeposition in porous anodic alumina: toward tailored preparation of metal nanotube arrays

Zhang, Aiqin; Zhou, Jiajing; Das, Paramita; Xiao, Yuanhua; Gong, Feilong; Li, Feng; Wang, Lizhen; Zhang, Linsen; Wang, Lixia; Cao, Yang; Duan, Hongwei

2018

Zhang, A., Zhou, J., Das, P., Xiao, Y., Gong, F., Li, F., et al. (2018). Revisiting Metal Electrodeposition in Porous Anodic Alumina: Toward Tailored Preparation of Metal Nanotube Arrays. *Journal of The Electrochemical Society*, 165(3), D129-D134.

<https://hdl.handle.net/10356/87050>

<https://doi.org/10.1149/2.0651803jes>

© 2018 The Electrochemical Society (ECS). This is the author created version of a work that has been peer reviewed and accepted for publication by Journal of the Electrochemical Society, The Electrochemical Society (ECS). It incorporates referee' s comments but changes resulting from the publishing process, such as copyediting, structural formatting, may not be reflected in this document. The published version is available at: [<http://dx.doi.org/10.1149/2.0651803jes>].

Downloaded on 26 Apr 2023 17:02:54 SGT

Revisiting metal electrodeposition in porous anodic alumina: toward tailored preparation of metal nanotube arrays

Aiqin Zhang,^{a, z} Jiajing Zhou,^b Paramita Das,^b Yuanhua Xiao,^a Feilong Gong,^a Feng Li,^a Lizhen Wang,^a Linsen Zhang,^a Lixia Wang,^a Yang Cao^a and Hongwei Duan^{b, z}

^aState Laboratory of Surface and Interface Science and Technology, Henan Collaborative Innovation Center of Environmental Pollution Control and Ecological Restoration, Zhengzhou University of Light Industry, Zhengzhou, 450002, PR China

^bSchool of Chemical and Biomedical Engineering, Nanyang Technological University, 70 Nanyang Drive, Singapore 637457

ABSTRACT: Metal electrodeposition in porous anodic aluminum oxide (AAO) is a complicated and multi-step process, consisting of diffusion of metal ions in the pores, reduction of metal ions and crystallization of metal atoms. The growth mechanism is also complex and changing with electrodeposition conditions. In this paper, we present new insights into the growth of metal nanostructures in AAO via electrodeposition. Two different growth modes for metal electrodeposition in porous AAO, namely centre growth mode and lateral growth mode, are revealed, opening a new approach to preparing metal nanotube arrays with tailored structures. This strategy is broadly applicable to varieties of metals, such as Ni, Cu, and Ag. The resultant metal nanotube arrays give rise to improved electro-catalytic activity to small molecule oxidation (such as ethanol and urea) due to the larger surface areas. These findings help to deeply understand the metal electrodeposition in AAO, extend the application of template-

assisted electrodeposition and provide innovative ideas to prepare novel metal nanomaterials.

KEYWORDS: Metal nanotube; Growth mechanism; Metal electrodeposition; Anodic aluminum oxide

One dimensional metal nanostructures have attracted great attention in fundamental research and technical applications in nanoelectrics devices,¹⁻³ magnetic memories,⁴⁻⁶ biosensor,⁷⁻⁹ catalysts¹⁰⁻¹² and energy storage materials.¹³⁻¹⁵ A wide spectrum of methods were reported to prepare metal nanowires,¹⁶⁻¹⁸ nanotubes,¹⁹⁻²¹ nanorods,^{22, 23} nanocables²⁴ and other nanostructures.²⁵ In particular, template-assisted electrodeposition is considered as a simple and effective way to prepare one dimensional metal nanostructures.²⁶⁻²⁸ In this strategy, porous anodic aluminium oxide (AAO) membranes are typically used as sacrificial templates due to their controllable channel length, diameter and pore density.^{29, 30} Metal nanowires, including Au, Ag, Pt, Pd, Ni, Cu, Fe, Co and alloys of them, have been electrochemically synthesized in the pores of AAO under specific electrochemical conditions.^{24, 31-35}

In comparison with metal nanowires, the development of metal nanotubes, especially arrayed nanotubes, is slow because of the difficulties in fabricating metal nanotubes with well-controlled dimensions. Several techniques have been developed for the synthesis of nanotubes besides template-assisted electrodeposition.³⁶⁻³⁹ Although it is more difficult than the preparation of metal

nanowires, metal nanotubes can also be fabricated by electrodeposition with the assistance of AAO template.^{38, 40-42} Usually, surface modification of AAO before electrodeposition is necessary to increase the metal ion concentration along the inner wall surface.^{43, 44} It still remains challenging to produce metal nanotubes arrays directly by metal electrodeposition in AAO, creating a technical barrier for the development of nanotubes as well as its applications.

The growth behaviour of metal electrodeposition in AAO membrane has been extensively examined previously.^{43, 45, 46} It is widely accepted that electric field or applied current is the major controlling factor based on the fact that nanowire can be easily formed at low current density ($\leq 1\text{mA/cm}^2$) and almost no metal grows in the pores at higher current density ($20 \sim 300\text{mA/cm}^2$)⁴⁵. Usually, to avoid a so called “puddling effect”, which might cause nail-head shape at one end of nanowire, a thin layer of sacrificial membrane (Ag or Ni) is electrodeposited into AAO at initial stage.⁴⁷ Hence, the actual growth details in the pores are often ignored and a comprehensive understanding of metal electrodeposition in the pores of AAO is still lacking.

Innovation and aim of the work.— In this paper, we present new insights into the growth mode of metal electroplating in AAO membrane according to the growth of Ni nanostructures, namely, nanowires and nanotubes. Centre growth mode and lateral growth mode are proposed, respectively. Of note is that the growth mechanism is applicable for electrodeposition of diverse metallic species, such as Ni, Cu, and Ag. Take advantage of this mechanism, a facile method to

prepare metal nanotube directly in AAO is also developed. The metal nanotube array has been proved to exhibit superior electro-catalytic performance to small molecule oxidation (such as ethanol and urea) owing to larger surface areas. We envisage that our convenient strategy offer insight into the development of metal nanotubes in AAO, paving the road for the future applications of metal nanostructures.

Experimental

Materials and chemicals.— The anodic aluminium oxide (AAO) membranes with porous diameter of 200 nm were purchased from Whatman. All chemical reagents were purchased from Shanghai Chemical Industrial Co. Ltd. (Shanghai, China), which were analytical grade and used in the experiments without additional purification. Double distilled ultrapure water ($\geq 18 \text{ M}\Omega\cdot\text{cm}$) was used for all solution preparation.

Electrodeposition of metal nanowires and nanotubes.— All electrodeposition were performed in a three-electrode cell with an electrochemical workstation (Reference 3000, Gamry). The electrochemical cell consisted of a saturated calomel reference electrode (SCE) and a platinum wire counter electrode. An AAO membrane ($1\text{cm} \times 1\text{cm}$) were connected with a copper wire and sputtered a thin gold layer to be used as working electrode. The gold sputtering was performed with a vacuum coating equipment (ETD-2000, JEOL) for 15 mins. The electrolytes were mixed solution of 30 g/L NiSO_4 , 20 g/L NiCl_2 and 30 g/L H_3BO_3 for nickel electrodeposition, mixed solution of 12 g/L CuSO_4 and 80 g/L

H₂SO₄ for copper electrodeposition, and mixed solution of 40 g/L AgNO₃, 120 g/L KCN and 8 g/L K₂CO₃ for silver electrodeposition respectively. All electrolytes were deoxygenated by bubbling high-purity nitrogen for 20 min before use.

Galvanostatic electrodeposition was carried out at different cathodic current density (1, 5 and 10 mA/cm²) to investigate the growth of Ni nanostructures. Ni, Cu and Ag nanowire arrays were all synthesized at constant cathodic current density of 1 mA/cm². Galvanostatic and pulse galvanostatic deposition were combined to prepare metal nanotube arrays. The preparation process consists of two segments: constant cathodic current (1~5 mA/cm², 10~30 min) and subsequent cathodic pulse deposition (pulse current: 10~20 mA/cm²; t_{on}: 0.1~1 ms; t_{off}: 1~10 ms). Finally, all the samples were immersed in 1 M NaOH for 8 hours to remove the AAO template.

Characterization.— The microstructure of metal nanomaterials was characterized by field emission scanning electron microscopy (FESEM, JSM7001F, JEOL), transmission electron microscope (TEM, JEOL-2100) and X-ray diffraction (XRD, PW3040/60, PANalytical).

Electrochemical tests.—The electro-catalytic performances of Ni nanotube and nanowire arrays for the oxidation of ethanol and urea were investigated by cyclic voltammogram and chronoamperometry. The electrochemical cell consisted of a saturated calomel reference electrode (SCE), a platinum wire counter electrode, and Ni (nanotube array, nanowire array and plate) working electrode.

Electrochemical tests were carried out in the solution of 1 mol/L KOH with 1 mol/L $\text{CH}_3\text{CH}_2\text{OH}$ (or 0.2 mol/L $\text{CO}(\text{NH}_2)_2$), which were deoxygenated by bubbling high-purity nitrogen for 20 min and maintained under nitrogen atmosphere during the measurements. The scan rate of CV tests was 50 mV/s, and the chronoamperometry curves of ethanol and urea electro-oxidation were performed at constant potential of -0.38 V and 0.31 V (the peak potential of the corresponding CV curves) respectively.

Results and Discussion

The growth of Ni nanomaterials in AAO.— To investigate the growth of metal nanomaterials in the pores of AAO, we first performed nickel electrodeposition at different cathodic current density. The morphology of Ni nanostructures produced at 1, 5, and 10 mA/cm² after different deposition time are shown in Figure 1. At low current density (1 mA/cm²) well-distributed Ni nanotubes can be obtained after 30 min (Figure 1a), however, these short (~400 nm) and thin-walled (~25 nm) nanotubes are quite fragile, therefore inhibiting its potentials for further application, as shown in Figure 2a. It is interesting that the inner diameter of these nanotubes became smaller after longer deposition time (Figure 1b), and the hollow nanotubes were filled eventually by reduced Ni atoms to form uniform nanowire array after 2 hours (Figure 1c). In other words, nanowires are formed finally with the time prolonging at low current density.

Similarly, Ni nanostructures synthesized at 5 mA/cm² also formed nanotubes at initial stage, see Figure 1d, which is the same as the results at low current

density. By contrast, the nanotubes produced at 5 mA/cm² possessed extended length (~750 nm) and thicker wall (~55 nm) (Figure 2b) compared to the ones synthesized at 1 mA/cm². After 1 hour, an array of randomly mixed nanowires and nanotubes was obtained (Figure 1e) and the difference with respect to Figure 1b can be ascribed to higher deposition rate. If the deposition was extended to 2 hours, all the nanotubes also transformed into nanowires, see Figure 1f. As expected, further increasing the applied current density, for example 10 mA/cm², would result in unregular nanostructures (Figure 1g-i) with some Ni atoms deposited on the other side of AAO (Figure 2c), which is consistent with the previous report and could be ascribed to the fast reaction rate at high current density.⁴⁵

Two aspects can be concluded from the growth of Ni nanomaterials in the nanopores of AAO at different current density. First, at the beginning Ni atoms grow along the inner wall of AAO to form nanotubular structures, the structural parameters of which largely depend on the applied current density. In addition, high current is beneficial to the growth of nanotubes due to “tip effect”.⁴⁵ For example, the nanotubes produced at 5 mA/cm² are more thick-walled and longer than the ones synthesized at 1 mA/cm²; Second, no matter how high the applied current is, continuous Ni deposition at constant current would fill the pre-formed nanotubes after longer deposition time, leading to the formation of nanowires

eventually. This is the reason why metal nanotubes produced by direct electrodeposition (no surface modification of AAO) in AAO exhibit limited dimensions, at least limited length.

In other word, at constant applied current the growth of Ni nanomaterials in the nanopores of AAO consists of two stages. Nanotubes produced at initial stage will be filled by nanowires with the time prolonging. Nanowires synthesized at low current density can clearly illustrate the filling process. As exhibited in Figure 3a and 3b, a small piece of hollow structure with a cone can be observed at the bottom of nanowires. This unique cone-like structure further implies that nanotube was formed at the beginning of deposition, followed by filling the cavity of the nanotube. As the geometry of the pre-formed nanotubes is highly dependent on the applied current, nanotubes produced at low current density are thin-walled and fragile. Hence, the nanotubular part is easily destroyed during the membrane removing process and the bottom of the nanowires are cone-shaped (Figure 3c). In previous reports about metal nanowires, to avoid this cone-shaped or nail-head structure another metal (Ag or Ni) is electrodeposited in the bottom of AAO to be used as sacrificial membrane.⁴⁷

Notably, longer nickel nanotube arrays (≥ 800 nm) prepared at constant current cannot obtained when the porous diameter of AAO is 200 nm. However, if the growth is intervened after the formation of nanotubes, for example, the electrodeposited Ni atoms are guided to grow along the inner surface, the pre-

formed nanotubes can be lengthened. To obtain nanotubes of controllable length, cathodic pulse galvanostatic was applied on the Ni nanotubes pre-synthesized at 5 mA/cm² for half an hour, which are more thick-walled than that produced at lower current density. When the applied current density and total charge amount of pulsed deposition are 10 mA/cm² and 1.2 C/cm², the length of the nanotubes significantly increased to 3 μm without thickening obviously the wall, as illustrated in Figure 4a and 4b. If the total charge amount is 2.4 C/cm², the length of nanotubes further increases to about 5 μm (Figure 4d and 4e). Compared with Figure 3c, the TEM image of Ni nanotubes shows obviously hollow structure (Figure 4c) and the lattice fringes with d-spacing of 0.203 nm on the surface of the nanotube correspond to the [111] plane of Ni. Moreover, the XRD pattern (Figure 4f) of the as-prepared nanotubes consists of diffraction peaks attributed to [111], [200] and [220] planes of nickel (JCPDS no. 04-0850) and no peaks due to by-product are observed in the pattern, which is almost the same as that of Ni nanowires.

Growth modes of metal electrodeposition in AAO.— According to the growth of Ni nanomaterials, two different growth modes, aiming to nanowires and nanotubes, respectively, can be proposed for comprehensive understanding of metal deposition in AAO. An illustration about the formation of nanowires and nanotubes during electrodeposition is presented in Figure 5. Firstly, Au nanoparticles are formed at the vent of the pore by sputtering, as shown in Figure

6. The sputtering time is very important because continuous film will be formed after long time and nanotube cannot be fabricated. Then reduced metal atoms will be deposited on the inner wall of the pore to form nanotubular structure at initial stage. When a constant current density was further applied, nanowire fills in the centre of the nanotube subsequently and the growth follows centre growth mode.

To enhance the length of metal nanotubes formed at initial stage, the reduced atoms are expected to grow along the inner surface of the pore (lateral growth mode). Based on above discussion of Ni nanostructure, brief time and high reaction rate are favourable for the formation of nanotubes. So, pulse deposition can be performed on the pre-formed nanotubes, which can provide high current instantaneously and keeps the lateral growth mode of metal atoms. By this way metal nanotubes with adjustable length can be prepared facilely. Figure 7 shows FESME images of Ni nanowires and nanotubes at low magnification, the length of which are $5.8\mu\text{m}$ and $5.0\mu\text{m}$. It can prove that large scale metal nanowire and nanotube arrays can also be prepared conveniently based on our strategy by changing current density or corresponding reaction rate.

Electro-catalytic performance of Ni nanomaterials.— Theoretically, metal nanotubes have larger specific surface area than nanowires owing to their special

nanostructure, and therefore better catalytic performance of them has been expected. To test this hypothesis, we performed electro-oxidation of ethanol and urea on the various electrodes, including nickel nanotube arrays, nanowire arrays and Ni plate, respectively. The results of electrochemical tests, of which the current densities have been normalized by the weight of corresponding electrodes, show that nickel nanotube array electrode exhibits better electro-catalytic performance than the other two. From the CV curves (Figure 7a and 7b), the value of the peak current on Ni nanotube electrode is 1.4 times for ethanol oxidization and 1.6 times for urea oxidization as high as those on Ni nanowire electrode. Figure 7c and 7d show the chronoamperometric curves of these Ni electrodes in electrolytes containing ethanol or urea. The select potential is the peak potential of the above corresponding CV curves. Ni nanotube array electrode produced a higher steady state current density than that of the other two, which was consistent with the results of CV tests. Moreover, according to the method reported previously⁴⁸, the electrochemically active surface areas (EASAs) of Ni nanowire and nanotube-based electrodes were also estimated by measuring their double layer capacitance. The values are 9.32 cm²/mg and 13.80 cm²/mg. Larger active area and superior catalytic property of Ni nanotube array makes it to be a promising choice of electro-catalyst for small molecule.

Electrodeposition of metal nanomaterials.— Of particular interest, this strategy is also confirmed applicable to other metal electrodeposition in the

nanopores of AAO, such as Cu and Ag. No nanotube arrays of Cu or Ag have been reported so far by direct electrodeposition in AAO.⁴⁶ The FESEM images of Cu nanowire and nanotube arrays are shown in Figure 8a and 8b, which indicate that both Cu nanowire and nanotube arrays can also be obtained by using our method. It is notable that as-prepared Cu nanowires and nanotubes are actually Cu₂O@Cu nanostructures based on corresponding XRD patterns (Figure 8c) due to its easy oxidization performance. The surface of Cu nanostructure might have been oxidized to Cu₂O in the process of membrane removing.²⁴ On the other hand, although they are not as regular and longer as other metals, both Ag nanowire arrays and nanotubes have been successfully prepared, as shown in Figure 8d-f. The versatility of our strategy provides new opportunities to design metal nanotube arrays of various metal precursors. It can also prove that the growth modes of metal electrodeposition and method to prepare metal nanotube arrays which we proposed is correct and universal.

Conclusions

In summary, we have presented novel insights into the growth mode of metal electrodeposition in AAO according to the growth of Ni nanostructures at different current density, which is proved to be applicable to other metal electroplating in AAO, such as Cu and Ag. Based on our result, two different electrodeposition modes are proposed, namely, centre growth mode and lateral growth mode. Taking advantage of this mechanism, a facile method has been

developed to prepare high-quality metal nanotube arrays successfully and the resultant metal nanotube arrays give rise to improved electro-catalytic activity to small molecule oxidation due to the larger surface areas. This research will extend the application of metal template-assisted electrodeposition and suggest a new way to prepare novel metal nanomaterials.

Acknowledgements

All authors gratefully acknowledge the support from the National Natural Science Foundation of China (Grant 21501152), the Key Program of Henan Province for Science and Technology (Grant 172102210067) and the Doctoral Research Foundation of Zhengzhou University of Light Industry (Grant 2014BSJJ057).

References

1. L. Yu, C. Shearer, and J. Shapter, *Chem. Rev.*, **116** (22), 13413-13453 (2016).
2. R. Chen, K. L. Jungjohann, W. M. Mook, J. Nogan, and S. A. Dayeh, *Nano Lett.*, **17** (4), 2189-2196 (2017).
3. L. Lian, D. Dong, S. Yang, B. Wei, and G. He, *ACS Appl. Mater. Interfaces*, **9** (13), 11811-11818 (2017).
4. S. Heedt, A. Manolescu, G. A. Nemnes, W. Prost, J. Schubert, D. Grützmacher, and T. Schäpers, *Nano Lett.*, **16** (7), 4569-4575 (2016).
5. W. Liu, Y. Bao, M. L. Lam, T. Xu, K. Xie, H. S. Man, E. Y. Chan, N. Zhu, R. H. W. Lam, and T.-H. Chen, *ACS Nano*, **10** (8), 7409-7417 (2016).
6. C.-S. Tan, Y.-J. Lu, C.-C. Chen, P.-H. Liu, S. Gwo, G.-Y. Guo, and L.-J. Chen, *J. Phys. Chem. C*, **120** (40), 23055-23060 (2016).
7. S. Kurbanoglu, S. A. Ozkan, and A. Merkoçi, *Biosens Bioelectron*, **89**, Part 2 886-898 (2017).
8. X. Cao, X. Cao, H. Guo, T. Li, Y. Jie, N. Wang, and Z. L. Wang, *ACS Nano*, **10** (8), 8038-8044 (2016).
9. J. W. Park, S. J. Park, O. S. Kwon, C. Lee, and J. Jang, *Anal. Chem*, **86** (3), 1822-1828 (2014).
10. K. Lee, A. Mazare, and P. Schmuki, *Chem. Rev.*, **114** (19), 9385-9454 (2014).
11. D. S. Choi, Y. Ni, E. Fernández-Fueyo, M. Lee, F. Hollmann, and C. B. Park, *ACS Catal.*, **7** (3), 1563-1567 (2017).

12. T. Guo, G. Yu, Y. Zhang, H. Xiang, F. Chang, and C.-J. Zhong, *J. Phys. Chem. C*, **121** (5), 3108-3116 (2017).
13. N. M. Ali and N. H. Rafat, *Renew Sust Energ Rev*, **68**, Part 1 212-220 (2017).
14. G. Otnes and M. T. Borgström, *Nano Today*, **12** 31-45 (2017).
15. Q. Zhang, X. Wang, Z. Pan, J. Sun, J. Zhao, J. Zhang, C. Zhang, L. Tang, J. Luo, B. Song, Z. Zhang, W. Lu, Q. Li, Y. Zhang, and Y. Yao, *Nano Lett.*, **17** (4), 2719-2726 (2017).
16. H. Y. Hui, M. de la Mata, J. Arbiol, and M. A. Filler, *Chem. Mater.*, **29** (8), 3397-3402 (2017).
17. S. J. Percival and B. Zhang, *J. Phys. Chem. C*, **117** (27), 13928-13935 (2013).
18. J. Li, Z. Guo, J.-H. Liu, and X.-J. Huang, *J. Phys. Chem. C*, **115** (34), 16934-16940 (2011).
19. A. Zhang, F. Gong, Y. Xiao, X. Guo, F. Li, L. Wang, Y. Zhang, and L. Zhang, *J. Electrochem. Soc*, **164** (2), H91-H96 (2017).
20. A. M. Schwartzberg, T. Y. Olson, C. E. Talley, and J. Z. Zhang, *J. Phys. Chem. C*, **111** (44), 16080-16082 (2007).
21. M. A. Lim, D. H. Kim, C.-O. Park, Y. W. Lee, S. W. Han, Z. Li, R. S. Williams, and I. Park, *ACS Nano*, **6** (1), 598-608 (2012).
22. A. Kumar, A. Sanger, A. Kumar, Y. Kumar, and R. Chandra, *Electrochim Acta*, **222** 1761-1769 (2016).
23. S. Zaster, E. R. Bittner, and A. Piryatinski, *J. Phys. Chem. A*, **120** (19), 3109-3116 (2016).
24. A. Zhang, Y. Tian, M. Liu, Y. Xiao, D. Jia, and F. Li, *RSC Adv.*, **4** (83), 43973-43976 (2014).
25. J. Li, L. Hu, C. Li, and X. Gao, *ACS Appl. Mater. Interfaces*, **5** (20), 10376-10380 (2013).
26. C. Hou, G. Meng, Z. Huang, B. Chen, C. Zhu, and Z. Li, *Electrochem Commun*, **60** 104-108 (2015).
27. A. P. Leontiev, O. A. Brylev, and K. S. Napolskii, *Electrochim Acta*, **155** 466-473 (2015).
28. Y. Su, M. Feng, C. Zhang, Z. Yan, H. Liu, J. Tang, and H. Du, *Electrochim Acta*, **164** 182-186 (2015).
29. A. M. Md Jani, D. Losic, and N. H. Voelcker, *Prog Mater Sci*, **58** (5), 636-704 (2013).
30. S. Zhao, H. Roberge, A. Yelon, and T. Veres, *J. Am. Chem. Soc.*, **128** (38), 12352-12353 (2006).
31. A. Brzózka, A. Jeleń, A. M. Brudzisz, M. M. Marzec, and G. D. Sulka, *Electrochim Acta*, **225** 574-583 (2017).
32. P. Y. Loh, K. K. Lee, Y. Ng, C. H. Sow, and W. S. Chin, *Electrochem Commun*, **43** 9-12 (2014).
33. X. Tian, J. Li, and D. Xu, *Electrochem Commun*, **12** (8), 1081-1083 (2010).
34. Y. Feng, K.-D. Kim, C. A. Nemitz, P. Kim, T. Pfadler, M. Gerigk, S. Polarz, J. A. Dorman, J. Weickert, and L. Schmidt-Mende, *J. Electrochem. Soc*, **163** (8), D447-D452 (2016).

35. L. Liu, E. Pippel, R. Scholz, and U. Gösele, *Nano Lett.*, **9** (12), 4352-4358 (2009).
36. A. Yourdkhani and G. Caruntu, *J. Mater. Chem.*, **21** (20), 7145-7153 (2011).
37. G.-F. Chen, X.-X. Li, L.-Y. Zhang, N. Li, T. Y. Ma, and Z.-Q. Liu, *Adv. Mater.*, **28** (35), 7680-7687 (2016).
38. X.-F. Han, S. Shamaila, R. Sharif, J.-Y. Chen, H.-R. Liu, and D.-P. Liu, *Adv. Mater.*, **21** (45), 4619-4624 (2009).
39. S. A. Needham, G. X. Wang, and H. K. Liu, *J Power Sources*, **159** (1), 254-257 (2006).
40. C. J. Brumlik and C. R. Martin, *J. Am. Chem. Soc.*, **113** (8), 3174-3175 (1991).
41. C. J. Brumlik, V. P. Menon, and C. R. Martin, *J. Mater. Res.*, **9** (5), 1174-1183 (1994).
42. C. R. Martin, *Science*, **266** 1961-1966 (1994).
43. L. M. Graham, S. Cho, S. K. Kim, M. Noked, and S. B. Lee, *Chem. Commun.*, **50** (5), 527-529 (2014).
44. M. Steinhart, Z. Jia, A. K. Schaper, R. B. Wehrspohn, U. Gösele, and J. H. Wendorff, *Adv. Mater.*, **15** (9), 706-709 (2003).
45. W. C. Yoo and J. K. Lee, *Adv. Mater.*, **16** (13), 1097-1101 (2004).
46. W. Lee and S.-J. Park, *Chem. Rev.*, **114** (15), 7487-7556 (2014).
47. S. J. Hurst, E. K. Payne, L. Qin, and C. A. Mirkin, *Angew Chem Int Edit*, **45** (17), 2672-2692 (2006).
48. C. C. L. McCrory, S. Jung, J. C. Peters, and T. F. Jaramillo, *J. Am. Chem. Soc.*, **135** (45), 16977-16987 (2013).

Captions

Figure 1. FESEM images (top view) of Ni nanostructures produced at constant current density of 1 mA/cm² (a-c), 5 mA/cm² (d-f) and 10 mA/cm² (g-i) for 30 min (a, d and g), 1 h (b, e and h) and 2 h (c, f and i).

Figure 2. FESEM images (side view) of Ni nanostructures produced at constant current density 1 mA/cm² for 30 min (a), 5 mA/cm² for 30 min (b) and 10 mA/cm² for 1 h (c).

Figure 3. FESEM (a, b) and TEM (c) images of Ni nanowires produced at constant density of 1 mA/cm² for 2 h.

Figure 4. FESEM (a, b, d, e), TEM (c) images and XRD (f) patterns of Ni nanotubes synthesized by pulse deposition (pulse current density: 10 mA/cm², t_{on} : 0.1ms, t_{off} : 2ms) after constant density of 5 mA/cm² for half an hour. (a-c) The charge amount of pulse deposition is 1.2 C/cm²; (d-f) The charge amount is 2.4 C/cm²; (f) XRD patterns of Ni nanowire and nanotube arrays. The inset in (c) highlights the HRTEM image of Ni nanotube.

Figure 5. Schematic illustration of growth process of Ni nanowire and nanotube arrays during electrodeposition.

Figure 6. FESEM images of AAO before (a) and after (b) Au sputtering.

Figure 7. FESME images (low magnification) of Ni nanowires (a) and nanotubes (b). Ni nanowires are produced at 1 mA/cm² for 2 h. Ni nanotubes are produced by pulse deposition (pulse current density: 10mA/cm², t_{on} : 0.1ms, t_{off} : 2ms, total charge amount: 2.4 C/cm²) after constant density of 5 mA/cm² for half an hour.

Figure 8. CV (a, b) and chronoamperometry (c, d) curves of Ni nanotube array, nanowire array and Ni plate electrodes in 1 mol/L KOH with 1 mol/L CH₃CH₃OH (a, c) and 1 mol/L KOH with 0.2 mol/L CO(NH₂)₂ (b, d). Ni nanowires are produced at 1 mA/cm² for 2 h. Ni nanotubes are produced by pulse deposition (pulse current density: 10mA/cm², t_{on} : 0.1ms, t_{off} : 2ms, total charge amount: 2.4 C/cm²) after constant density of 5 mA/cm² for half an hour.

Figure 9. FESEM images of Cu nanowires (a) and nanotubes (b), Ag nanowires (d) and nanotubes (e), and XRD patterns of above nanomaterials (c, f). Cu and Ag nanowires are all produced at 1 mA/cm² for 2 h. Cu nanotubes are produced by pulse deposition (pulse current density: 12mA/cm², t_{on} : 0.2ms, t_{off} : 5ms, total charge amount: 2.4 C/cm²) after constant density of 5 mA/cm² for 30mins. Ag nanotubes are produced by pulse deposition (pulse current density: 10mA/cm², t_{on} : 0.1ms, t_{off} : 5ms, total charge

amount: 1.2 C/cm^2) after constant density of 3 mA/cm^2 for 30mins.