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2

3 Abstract

4 Crystalline Co₃O₄ nanowire arrays with different morphologies grown on Ni foam were 5 investigated by varying the reaction temperature, the concentration of precursors, and 6 reaction time. The Co₃O₄ nanowires synthesized under typical reaction condition had a 7 diameter range of approximately 500–900 nm with a length of 17 µm. Electrochemical 8 reduction of hydrogen peroxide (H₂O₂) of the optimized Co₃O₄ nanowire electrode was studied by cyclic voltammetry. A high current density of 101.8 mA cm⁻² was obtained at 9 10 -0.4 V in a solution of 0.4 M H₂O₂ and 3.0 M NaOH at room temperature compared to 85.8 mA cm⁻² at -0.35 V of the Co₃O₄ nanoparticle electrode. Results clearly indicated 11 12 that the Ni foam supported Co₃O₄ nanowire electrode exhibited superior catalytic activity 13 and mass transport kinetics for H₂O₂ electrochemical reduction.

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15 Keywords: Co₃O₄; Nanowire arrays; Ni form; H₂O₂ electrochemical reduction

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1 1. Introduction

2 Recently, the development of hydrogen peroxide (H_2O_2) as an oxidant for low-3 temperature liquid-based fuel cells has attracted significant attention due to lower 4 activation energy, better stability, and ease of handling and storage compared to oxygen 5 based fuel cells [1-3]. Lao et al. has shown that electrochemical reduction of H_2O_2 has 6 faster kinetics than that of oxygen [4]. Yin et al. has demonstrated a direct 7 hydrazine/H₂O₂ fuel cell exhibiting an open circuit voltage (OCV) of \sim 1.6 V and a high power density of 470 mW cm⁻² compared to that with oxygen oxidant (OCV~0.9 V and 8 73.9 mW cm⁻²) [5]. To date, noble metals such as Pt, Pd, Ir, Au, and Ag are the dominant 9 10 catalysts for electrochemical reduction H₂O₂ owing to the high efficiency and stability [6-9]. However, the expensive cost and scarcity of noble metal resources hinder their 11 12 practical applications. Therefore, current research focuses on the electrochemical 13 reduction of H_2O_2 using transitional metal oxides such as nickel oxide, iron oxide, copper 14 oxide due to their low cost, high abundance, and high electrocatalytic reaction [10].

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16 Among the transitional metal oxides, cobalt oxide (Co₃O₄) has been extensively studied 17 because of its superior catalytic properties arise from its efficient electron transportation between Co^{2+} and Co^{3+} ions [11, 12]. However, Co_3O_4 catalysts usually suffer from the 18 19 poor electrical conductivity and the dissolution or agglomeration during electrochemical 20 processes [13]. Therefore, mixing Co₃O₄ catalysts with conductive carbon-based 21 materials such as carbon nanotubes, graphene, and carbon foam is proposed to improve 22 the conductivity of the Co₃O₄ hybrid catalysts [14]. However, such mixing approach 23 involves the use of an organic binder, which will decrease the effective surface area of the Co₃O₄ catalysts [15]. Accordingly, a binder-free approach by directly growing the electrocatalyst materials on a current collector such as carbon-based materials has proved to enhance the cycling stability of the electrocatalysts [16, 17]. Also, one-dimensional (1D) nanostructure have been reported to be a promising morphology for high electrochemical performance owing to their sufficient exposed surface, efficient ion transfer and rapid electron transport [18, 19].

7

8 In this work, various synthesis conditions including the influence of reaction temperature, 9 the concentration of precursors, and reaction time on the morphology of 1D Co_3O_4 10 nanostructures grown on Ni foam were comprehensively investigated. The optimized 11 Co_3O_4 nanowire electrode was selected to study the electrochemical reduction of H_2O_2 in 12 alkaline medium. For comparison, the electrochemical reduction of H_2O_2 in conventional 13 powdery Co_3O_4 nanoparticle electrode was studied. The Co_3O_4 nanowire electrode delivered a high current density of 101.8 mA cm⁻² at -0.4 V in a solution of 0.4 M H₂O₂ 14 and 3.0 M NaOH at room temperature compared to 85.8 mA cm⁻² at -0.35 V of the Co₃O₄ 15 16 nanoparticle electrode.

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18 **2. Experimental**

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20 2.1. Ni Foam Supported Co₃O₄ Nanowire Arrays

Ni foam substrate (110 PPI, 320 g m⁻²; Artenano Company Limited, HK) was cleaned in
acetone for 10 min, then etched with 6.0 M HCl for 30 min. After thoroughly rinsing with
water, the Ni foam was soaked in 0.1 mM NiCl₂ for 8 h and extensively rinsed with water.

1	Various amount of Co(NO ₃) ₂ and NH ₄ NO ₃ were added in a solution consisting of
2	deionized water and ammonia (30 wt%). The homogeneous solution containing 0.2 M
3	$Co(NO_3)_2$ and 0.1 M NH ₄ NO ₃ was magnetically stirred for 20 min in air at room
4	temperature until the pink color solution was gradually turned to black color. Such
5	change of color indicates that Co(II) ions were partially oxidized to Co(III) ions in the
6	solution through the uptake of oxygen. Ammonia added to the solution might enhance the
7	oxidation of Co(II) ions to Co(III) ions [20]. The pretreated Ni foam and the obtained
8	homogeneous solution were then transferred to a Teflon-lined stainless-steel autoclave,
9	which was sealed and kept at different temperatures and maintained for different reaction
10	times. To investigate the impact of various synthesis parameters on the morphology of
11	the nanowire grown on the Ni foam, a series of conditions were tested and summarized in
12	Table 1. After the reaction, the Ni foam with as-synthesized products was taken out from
13	the solution and thoroughly washed with water, dried at 80 °C. Then, the Ni foam with
14	as-grown Co ₃ O ₄ precursors were calcined at 300° C for 2 h. Notably, the merging of
15	Co ₃ O ₄ nanowires occurred when the thermal treatment temperature was higher than 300°
16	C [21]. For comparison, the morphology of the nanowire arrays was examined using
17	scanning electron microscopy (SEM, JEOL JSM-5600) and transmission electron
18	microscopy (TEM, FEI Teccai G2 S-Twin, Philips). The structure was determined using
19	an X-ray diffractometer (XRD, Siemens D500). The 2 θ scan range was from 10° to 80°
20	with a scan rate of 5 $^{\circ}$ min ⁻¹ and a step width of 0.02 $^{\circ}$.

2.2. H₂O₂ Electroreduction

1 Cyclic voltammetric tests were conducted on an IVIUM nSTAT electrochemical station. 2 Ni foam supported binder-free Co₃O₄ nanowire electrode and powdery Co₃O₄ 3 nanoparticle electrode were working electrodes. The powdery Co₃O₄ nanoparticle 4 electrode was prepared by mixing the active material (5 mg), acetylene black, and 5 polytetrafluorene-ethylene (PTFE) binder at a weight ratio of 80:15:5 and dispersing the 6 mixture in ethanol to produce a homogeneous paste. The mixture was carefully placed 7 onto nickel foam (1 cm \times 1 cm \times 0.2 cm), and then dried in a vacuum oven at 80 °C 8 before pressing under a pressure of 20 MPa. A glassy carbon rod behind a D-porosity 9 glass frit and a saturated Ag/AgCl, KCl electrode was employed as the counter and 10 reference electrodes, respectively. All electrochemical tests were performed at room 11 temperature. The electrolyte was a 3.0 M aqueous NaOH solution made using analytical 12 grade chemical reagents.

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14 **3. Results and discussion**

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16 To study the effect of time on the morphology of the nanowire arrays grown on the Ni 17 foam, different reaction times were tested ranging from 3 to 18 h (Table 1, Samples 1–4). 18 Figure 1a-c shows the morphological and structural evolution of the nanowires grown on 19 the Ni foam at different reaction times. The shiny Ni foam substrate turned black after 20 nanowire growth. Both the size and uniformity of the nanowires increased with 21 prolongation of reaction time. For the reaction time of 12 h (Sample 3), the Co_3O_4 22 nanowires were structurally uniform and had diameters of approximately 500–900 nm 23 and lengths of up to 17 μ m. However, when the reaction time reached 18 h, the nanowires 1 (Fig. 1d, Sample 4) became slightly lengthened, and the uniformity became degraded. A 2 number of nanoparticles were deposited onto the surface of the nanowires. The reason 3 might be that some high-energy sites were formed due to the effect of ammonia and 4 vapor-liquid equilibrium, causing Co ions to nucleate spontaneously onto these active 5 sites and to form nanoparticles. It was reported that hydrazine hydrate as a bidentate 6 ligand can play a structure-directed role in the formation of β -Co(OH)₂ nanocolumns [22]. 7 Ammonia is expected to play a similar role in the nanowire growth because ammonia is a 8 unidentate ligand and it can form complexes with Co(II) ions and Co(III) ions.

9

10 The proposed evolution process is as follows. At the early stage of the reaction, the 11 adsorption of Co(II) cations on the Ni foam increased the local cation concentration and 12 formed the nuclei. The dominant β -Co(OH)₂ nanowires were then formed from the nuclei 13 during the initial 6 h reaction [23, 24] (Samples 1–2). When the reaction time was 14 prolonged to 12 h, the surface of nanowire became granular. A clear Co_3O_4 spinel phase 15 was identified, as supported by the XRD pattern (Fig. 4a). The granular morphology of the Co_3O_4 nanowires was due to the solid-state reaction between the β -Co(OH)₂ 16 17 nanowires and the dissolved oxygen in the solution. These results, combined with the 18 XRD results (Fig. 4a), confirm that the as-prepared nanowires consisted of brucite β -19 Co(OH)₂ and spinel Co₃O₄ phases, which suggest the partial oxidation of Co(II) ions to 20 Co(III) ions during the nanowire growth [21]. The oxidation reaction from β -Co(OH)₂ to 21 Co_3O_4 was considered as energetically favored transformation [25]. Notably, the β -22 $Co(OH)_2$ nanowire was transformed to Co_3O_4 nanowire without a significant increase in 23 diameter. Figure 2 shows the Co_3O_4 samples synthesized under different concentrations

1 of precursors (Samples 5–8). The results suggest that low reactant concentration of the 2 reactant (Sample 5) could not sustain the growth of nanowires but only caused the 3 formation of compact and non-uniform nanoplates on the surface of the Ni foam. The 4 mechanism of nanoplate growth was complicated and influenced by various factors. The 5 dominant phase of the as-prepared nanocrystal produced in the initial stage of reaction 6 (non-calcined) was the brucite β -Co(OH)₂ phase, which had a layered structure and 7 comprised sheets of hexagonally close-packed OH ions with one Co(II) ions bonded to 8 six OH ions. These β -Co(OH)₂ sheets were bonded to one another by weak OH-OH 9 dipole interactions. Therefore, brucite crystals have the tendency to grow into thin 10 nanoplates. When the concentration of reactants was low (Sample 5), the amount of 11 reactant could not sustain the growth of nanowires. Thus, a compact thin film of β -12 $Co(OH)_2$ nanoplates were produced. After calcination in air, β -Co(OH)₂ nanoplates were 13 transformed into Co₃O₄ nanoplates without apparent change in morphology. In general, 14 materials with hexagonal structure are favored to form 1-D nanostructures under a 15 suitable reaction condition [24]. When the concentration of reactants increases, uniform 16 nanowires are formed instead of nanoplates. However, a higher concentration of reactants 17 (Fig. 2d, Sample 8) can cause the nanowires to become bigger or several single ones to 18 merge. These phenomena might be caused by the rapid mass transfer and a large amount 19 of high-energy sites on the surface of the as-prepared nanowires. When the concentration 20 of reactants (Fig. 2c, Sample 7) was a little lower than the typical concentration (Sample 21 3), uniform and smooth nanowires were successfully obtained. However, the number density of the nanowires was sparser than the ones synthesized under the typical 22 23 condition (Sample 3). The results suggest that the various morphologies of the nanostructures can be tailored from nanoplates to nanowires by tuning the concentrations
 of Co(NO₃)₂ • 6H₂O, and NH₄NO₃.

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4 The effect of reaction temperature on the morphology of Co₃O₄ nanostructures is shown 5 in Figure 3. In Fig. 3a (Sample 9), nanowires and several leaf-like crystals with diameters 6 of $3-6 \mu m$ (measured in the middle of the leaf-like crystal) and lengths of approximately 7 16 µm were present. The surface of the leaf-like crystal was smooth and flat. Figure 3b 8 (Sample 3) clearly shows that Co₃O₄ nanowires were uniformly covered with Ni foam, 9 which grows densely and vertically from the substrate. The nanowires were uniform, with 10 diameters of 500–900 nm and lengths of approximately 17 µm. In Fig. 3c (Sample 10), 11 some of the nanowires grew bigger and longer, and a few of nanowires integrated into a 12 bigger one. The coexistence of leaf-like crystals and nanowires suggests that the reaction 13 process was not homogeneous when the temperature was 70° C. We do not understand 14 the formation mechanism of the leaf-like crystal; however, we propose that this can be 15 caused by the rapid gathering rate of local Co(II) ions. The reason for the enlargement of 16 nanowires when the temperature was set at 100° C might be the rapid mass transfer, 17 which led to a fast deposit of Co(II) ions on the nuclei. It could also be due to the 18 increasing number of high-energy sites on the surface of nanowires, which led to the 19 growth of nanocrystals among the as-prepared nanowires, thereby causing single 20 nanowires to merge. The results suggest that temperature is a key factor in controlling the 21 morphology of the nanowires. Well-ordered nanowire arrays were formed at the reaction 22 temperature of 90° C.

1 To summarize the above discussions on the growth of Co_3O_4 nanowire arrays, various 2 sizes of nanowires synthesized at different reaction conditions are shown in Table 1. The 3 results suggest that the proper reaction condition for preparation of well-ordered 4 nanowire arrays (Sample 3) were achieved as follows: a reaction time of 12 h, moderate 5 concentration, and a temperature of 90° C. Figure 4 shows the XRD patterns of the 6 samples prepared under this reaction condition. The phase of Ni was found in the pattern 7 because of the Ni foam substrate. The XRD pattern of non-calcined nanowires contained 8 the combined phases of brucite β -Co(OH)₂ and spinel Co₃O₄. Some Co(II) ions were 9 oxidized to Co(III) ions during the nanowire growth in the solution. The pattern of Fig. 10 4b matches the pattern of spinel phase Co_3O_4 well, indicating that the nanowires were 11 Co_3O_4 after calcination. The transformation of β -Co(OH)₂ to Co₃O₄ was due mainly to the 12 oxidation of β -Co(OH)₂ during the calcination. The reaction formula was as follows:

The TEM images (Fig. 5) show that the non-calcined nanowire was structural compact, while the calcined nanowire was loose and consisted of irregularly shaped cracks. Some cracks were formed from the release of water vapor during the calcination (refer to the reaction formula 1).

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Figure 6a shows current-potential polarization curves of the Co_3O_4 nanowire and nanoparticle electrodes for electrochemical reduction of H_2O_2 in 0.4 M H_2O_2 and 3.0 M NaOH solution at scan rate 5 mV s⁻¹. The onset potentials of the two electrodes were quite similar at around -0.15 V. The catalytic activity of H_2O_2 electrochemical reduction is attributed to the redox couple of $Co(OH)_2/Co_3O_4$. The current density on the Co_3O_4

1 nanowire electrode was higher than that of the Co_3O_4 nanoparticle electrode in the tested 2 potential range. More importantly, the Ni foam supported Co₃O₄ nanowire electrode 3 showed a much lower potential at -0.6 V than that of the Co_3O_4 nanoparticle electrode (-0.35 V). The Co₃O₄ nanoparticle electrode delivered current density of 85.8 mA cm⁻² at -4 5 0.35 V, which is comparable to literature [26]. In contrast, the Co_3O_4 nanowire electrode exhibited a higher current density of 101.8 mA cm⁻² at -0.4 V compared to of the Co₃O₄ 6 7 nanoparticle electrode. The high electrocatalytic performance of Co_3O_4 nanowires arises 8 from the unique 1D nanostructures, which provide not only high surface area for 9 electrochemical reaction but also a short diffusion path for ions. Such binder-free 10 approach also results in low internal resistance because Co_3O_4 nanowires were in direct 11 contact with the Ni foam substrate. Results clearly indicated that the Ni foam supported 12 Co_3O_4 nanowire electrode exhibited superior catalytic activity and mass transport kinetics 13 for H₂O₂ electrochemical reduction than binder approach powdery electrode. Figure 6b 14 shows the dependence of the catalytic performance of Ni foam supported Co₃O₄ 15 nanowire electrode (Sample 3) on various concentration of H_2O_2 . The polarization curves 16 demonstrated that H_2O_2 electrochemical reduction occurs at around -0.1 V and the current 17 density increases with the potential going from -0.1 to -0.8 V. The cathodic peak current 18 density increased with the increase of H₂O₂ concentration from 0.1 to 0.6 M. Significant 19 small oxygen bubbles were observed on the electrode surface at an H₂O₂ concentration 20 higher than 0.3 M. Currents began to fluctuate slightly when the potential was decreased 21 from -0.45 to -0.8 V due to the perturbation of oxygen from H₂O₂ decomposition.

22

23 **4.** Conclusions

1 Various Co₃O₄ nanowires with different morphology and sizes grown on Ni foam were 2 successfully prepared via a template-free method. The brucite β -Co(OH)₂ was 3 transformed to spinel Co_3O_4 after calcination in air. The release of water vapor caused 4 some cracks on the surface of the nanowires. Reaction temperature, the concentration of 5 reactants, and reaction time are key variables that determine the final size and 6 morphology of the nanowires. The nanowires grew vertically from the surface of the Ni 7 foam, and both size and uniformity of the nanowires increased with the prolongation of 8 reaction time. The nanowires synthesized at 12 h presented the most uniform morphology. 9 The various morphologies of the nanostructures can be tailored from nanoplates to 10 nanowires by tuning the concentration of reactants. The reaction temperatures lower or 11 higher than 90° C were unfavorable to the growth of well-ordered nanowires. The Co₃O₄ 12 nanowires were structurally uniform and crystalline and had diameters of approximately 13 500–900 nm and lengths of up to 17 μ m in the typical reaction condition (Sample 3). The 14 Ni foam supported Co_3O_4 nanowire electrode showed superior catalytic activity and mass 15 transport property for H_2O_2 electrochemical reduction in an alkaline medium than the 16 Co₃O₄ nanoparticle electrode.

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18 Acknowledgements

This work was supported mainly by the Global Frontier R&D Program
(2013M3A6B1078874) on Center for Hybrid Interface Materials (HIM) funded by
the Ministry of Science, ICT & Future Planning, the Science and Technology
Development Fund from Macau SAR (FDCT-098/2015/A3), and the UEA funding.

1 References

- 2 [1] D.J. Brodrecht, J.J. Rusek, Applied Energy, 74, 113-124,
- 3 [2] X.H. Yan, T.S. Zhao, L. An, G. Zhao, L. Shi, Int J Hydrogen Energ, 41, 5135-5140,
 4 (2016)
- 5 [3] S.M.M. Ehteshami, M. Asadnia, S.N. Tan, S.H. Chan, Journal of Power Sources, **301**,
- 6 392-395, (2016)
- [4] S.J. Lao, H.Y. Qin, L.Q. Ye, B.H. Liu, Z.P. Li, Journal of Power Sources, 195, 41354138, (2010)
- $\begin{array}{c} \mathbf{0} \\ \mathbf{0} \\ \mathbf{151} \\ \mathbf{W} \\ \mathbf{V} \\ \mathbf{V} \\ \mathbf{n} \\ \mathbf{71} \end{array}$
- 9 [5] W.X. Yin, Z.P. Li, J.K. Zhu, H.Y. Qin, Journal of Power Sources, **182**, 520-523,
- 10 (2008)
- 11 [6] D. Cao, L. Sun, G. Wang, Y. Lv, M. Zhang, Journal of Electroanalytical Chemistry,
- 12 **621,** 31-37, (2008)
- 13 [7] F. Miomandre, P. Audebert, M. Maumy, L. Uhl, Journal of Electroanalytical
- 14 Chemistry, **516**, 66-72, (2001)
- 15 [8] D. Cao, Y. Gao, G. Wang, R. Miao, Y. Liu, International Journal of Hydrogen Energy,
- 16 **35,** 807-813, (2010)
- 17 [9] L. Sun, D. Cao, G. Wang, Journal of Applied Electrochemistry, **38**, 1415-1419, (2008)
- 18 [10] X.Z. Li, Y.Y. Fang, X.Q. Lin, M. Tian, X.C. An, Y. Fu, R. Li, J. Jin, J.T. Ma, J
- 19 Mater Chem A, **3**, 17392-17402, (2015)
- 20 [11] A. Aijaz, J. Masa, C. Rosler, W. Xia, P. Weide, A.J.R. Botz, R.A. Fischer, W.
- 21 Schuhmann, M. Muhler, Angew Chem Int Edit, **55**, 4087-4091, (2016)
- 22 [12] L. Xu, Q.Q. Jiang, Z.H. Xiao, X.Y. Li, J. Huo, S.Y. Wang, L.M. Dai, Angew Chem
- 23 Int Edit, **55**, 5277-5281, (2016)
- 24 [13] T.T. Nguyen, V.H. Nguyen, R.K. Deivasigamani, D. Kharismadewi, Y. Iwai, J.J.
- 25 Shim, Solid State Sci, **53**, 71-77, (2016)
- 26 [14] H.Y. Lu, Y.P. Huang, J.J. Yan, W. Fan, T.X. Liu, Rsc Adv, 5, 94615-94622, (2015)
- 27 [15] S.X. Wu, K.S. Hui, K.N. Hui, K.H. Kim, J Mater Chem A, 4, 9113-9123, (2016)
- 28 [16] L. Ren, K.S. Hui, K.N. Hui, J Mater Chem A, 1, 5689-5694, (2013)
- 29 [17] L.J. Zhang, J. Wang, J.J. Zhu, X.G. Zhang, K.S. Hui, K.N. Hui, J Mater Chem A, 1,
- 30 9046-9053, (2013)
- 31 [18] Y.-T. Tseng, J.-C. Lin, Y.-J. Ciou, Y.-R. Hwang, ACS Applied Materials &
- 32 Interfaces, **6**, 11424-11438, (2014)
- 33 [19] S.X. Wu, K.S. Hui, K.N. Hui, J Phys Chem C, **119**, 23358-23365, (2015)
- 34 [20] Z. Guo, W. Liu, B.-L. Su, Nanotechnology, **19**, 1-5, (2008)
- 35 [21] G. Wang, D. Cao, C. Yin, Y. Gao, J. Yin, L. Cheng, Chemistry of Materials, DOI
- 36 10.1021/cm901928b(2009)
- 37 [22] Y. Shao, J. Sun, G. Lian, J Phys Chem C, **113**, 6566–6572, (2009)
- 38 [23] Y. Li, B. Tan, Y. Wu, Nanoletters, **8**, 265-270, (2008)
- 39 [24] Y. Hou, H. Kondoh, M. Shimojo, T. Kogure, T. Ohta, Journal of Physical Chemistry
- 40 B, **109**, 19094-19098, (2005)
- 41 [25] X.W. Lou, D. Deng, J.Y. Lee, J. Feng, L.A. Archer, Advanced Materials, 20, 258-
- 42 262, (2008)
- 43 [26] D. Cao, J. Chao, L. Sun, G. Wang, Journal of Power Sources, **179**, 87-91, (2008)
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Sample	Time (h)	Concentration (mol/l)			Temperature	Structure	tructure Nanowire	
		Cobalt nitrate (mol/l)	Ammonium Nitrate (mol/l)	Ammonia (mol/l)	(℃)		Diameter (nm)	Length (µm)
1	3	0.2	0.1	6	90	Wire	480~530	10~11
2	6	0.2	0.1	6	90	Wire	520~590	11~14
3	12	0.2	0.1	6	90	Wire	500~900	14~17
4	18	0.2	0.1	6	90	Wire	500~900	15~18
5	12	0.05	0.025	1.5	90	Plate		
6	12	0.1	0.05	3	90	Wire	300~400	2.5~3
7	12	0.15	0.75	4.5	90	Wire	400~550	9~11
8	12	0.25	0.125	7.5	90	Wire	Non-uniform	Non-uniform
9	12	0.2	0.1	6	70	Left like crystal + wire	NA	NA
10	12	0.2	0.1	6	100	Wire	800~6000	20~25

1 Table 1. Various sizes of nanowires synthesized on different reaction conditions



- - Fig. 1. SEM images of Co₃O₄ nanowire arrays grown at different times: a 3 h (Sample 1),
- **b** 6 h (Sample 2), **c** 12 h (Sample 3), **d** 18 h (Sample 4)



Fig. 2. SEM images of the nanoparticles or nanowires synthesized with different
precursor concentrations: a Sample 5, b Sample 6, c Sample 7, d Sample 8



- **Fig. 3.** SEM images of nanowires or other structures synthesized at different temperatures:
- **a** 70° C (Sample 9), **b** 90° C (Sample 3), **c** 100° C (Sample 10)



Fig. 4. XRD pattern of the nanowires scratched down from Ni foam substrate (Sample 3):

a non-calcined, **b** calcined

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Fig. 6. Current-potential polarization curves for H_2O_2 electrochemical reduction: **a** Co_3O_4 nanoparticle and nanowire electrodes with electrolyte: 3.0 M NaOH and 0.4 M H_2O_2 at scan rate 5 mV s⁻¹, **b** Co_3O_4 nanowires electrode with electrolyte: 3.0 M NaOH and different concentrations of H_2O_2 at scan rate 5 mV s⁻¹.