Supporting Information

Low-temperature and template-free fabrication of cobalt oxide acicular nanotube arrays and their application for supercapacitors

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S1. EIS spectra of the Co_3O_4 ANRAs and Co_3O_4 ANTAs electrodes

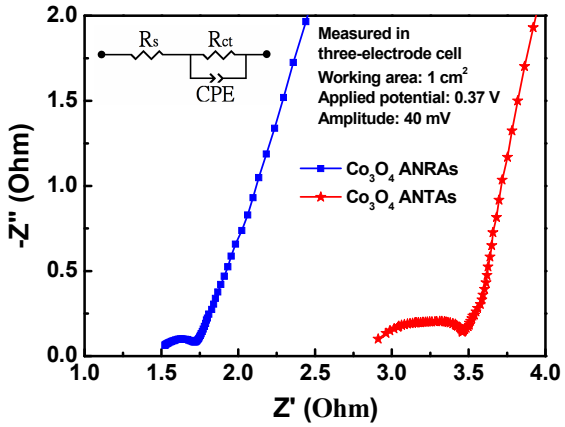

Figure S1. EIS spectra of the Co_3O_4 ANRAs and Co_3O_4 ANTAs electrodes, measured in 5.0 M KOH solution at 0.37 V *vs*. Ag/AgCl/KCl (sat'd) with an amplitude of 40 mV. *Inset*: the equivalent circuit, which is composed of the series resistance (R_s), charge-transfer resistance (R_{ct}), and constant phase element (CPE).

S2. Charge-discharge curves of the bare graphite, Co_3O_4 ANRAs and Co_3O_4 ANTAs electrodes at various charge-discharge current densities

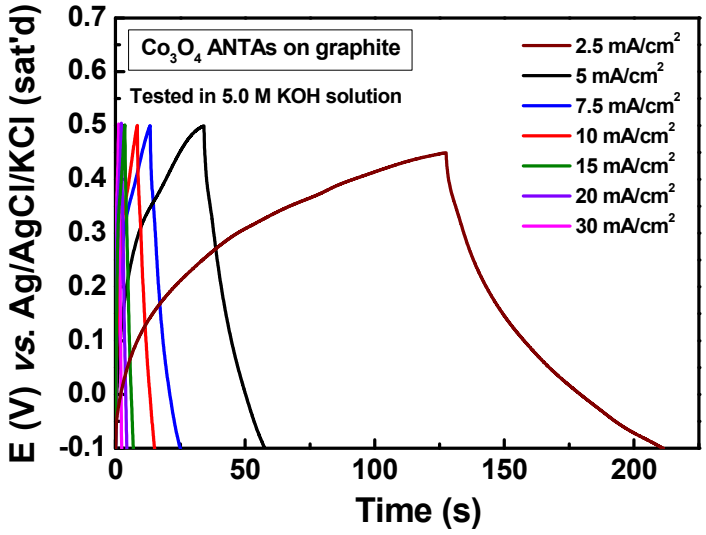

Figure S2. Charge-discharge curves of the Co_3O_4 ANTAs electrode measured in 5.0 M KOH solution at various charge-discharge current densities.

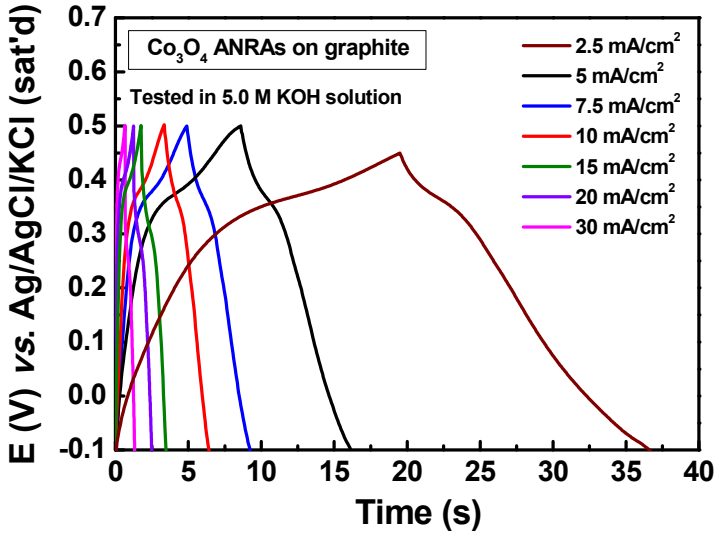

Figure S3. Charge-discharge curves of the Co_3O_4 ANRAs electrode measured in 5.0 M KOH solution at various charge-discharge current densities.

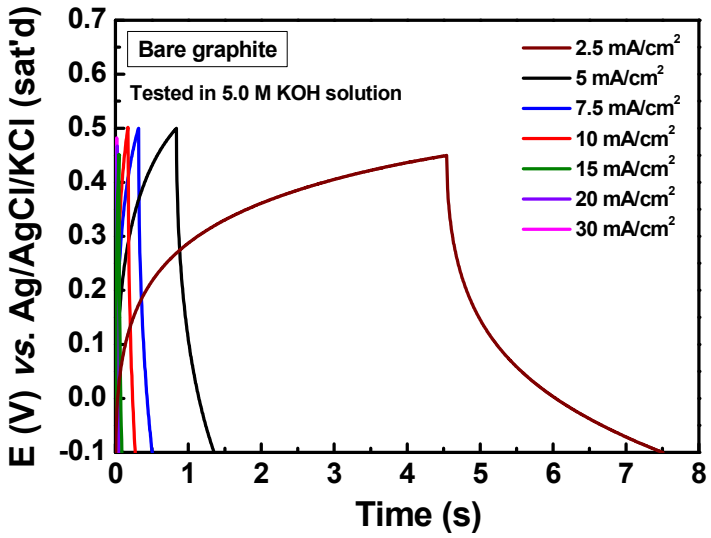

Figure S4. Charge-discharge curves of the bare graphite substrate measured in 5.0 M KOH solution at various charge-discharge current densities.

S3. Estimation of the film mass

The 37% HCl solutions containing various concentrations of $CoCl_2$, with the color ranging from bright blue to transparent, were prepared. The UV-visible spectra of these solutions were measured, and their maximum absorbance at 663 nm was calibrated with the concentration of $CoCl_2$, as shown in Fig. S5(a). Thereafter, the Co_3O_4 ANRAs and Co_3O_4 ANTAs thin films (3 cm^2 for each) were dissolved in two batches of 15 mL fresh 37% HCl solution, respectively. The UV-visible spectra of these two solutions were measured, as shown in Fig. S5(b). According to the absorbance at 663 nm shown in Fig. S5(b), the concentrations of Co^{2+} in the solutions of Co_3O_4 ANRAs and Co_3O_4 ANTAs are 0.84 mM and 0.94 mM, respectively. From the molecular weight of Co_3O_4, the masses of the Co_3O_4 ANRAs and Co_3O_4 ANTAs thin films can be estimated

to be 0.34 mg/cm^2 and 0.38 mg/cm^2, respectively.

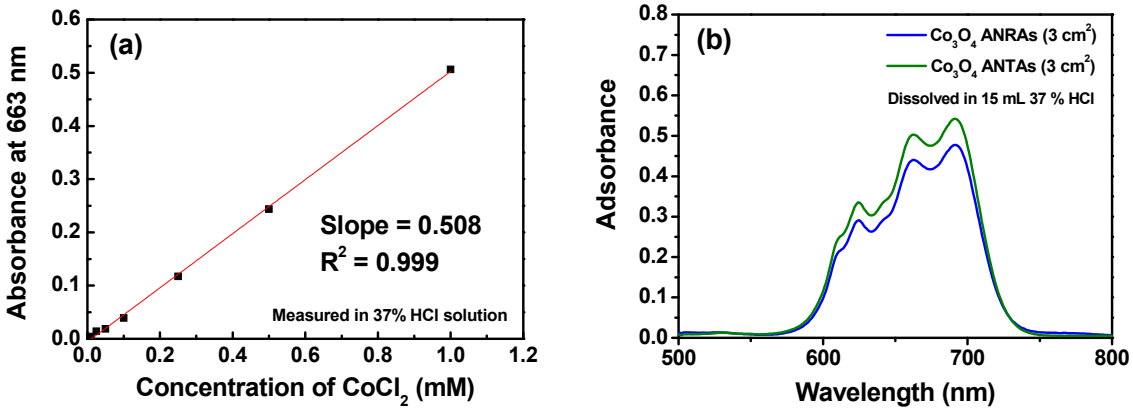

Figure S5. (a) Relationship between the absorbance of the $CoCl_2$ solution in 37% HCl at 663 nm and the concentration of $CoCl_2$. (b) UV-visible spectra of the 37% HCl solutions after digesting the Co_3O_4 ANRAs and Co_3O_4 ANTAs thin films.

S4. Comparison to the reported studies using Co_3O_4 as pseudocapacitive material

Table S1. Partial list of recent reported studies using Co_3O_4 as pseudocapacitive material.

Morphology of Co_3O_4	Substrate	High-temperature treatment to obtain Co_3O_4	Specific capacitance (F/g)	Reference
Co_3O_4 nanosheet arrays	Ni foam	✓	2,735	[S1]
Co_3O_4 thin layer	Porous Ni substrate	×	2,200	[S2]
Co_3O_4 nanoflowers	Ni foam	✓	1,937	[S3]
Co_3O_4 nanowires	Carbon fiber paper	✓	1,525	[S4]
Co_3O_4 nanowire arrays	Ni foam	✓	1,257	[S5]
Co_3O_4 nanowire arrays	Ni foam	✓	1,160	[S6]
Co_3O_4 nanonet	Carbon fiber paper	✓	1,124	[S7]
Co_3O_4 nanosheets	Ti foil	×	1,033	[S8]
Co_3O_4 acicular nanotube arrays	Graphite	×	979	This work
Co_3O_4 nanotubes	Ni foam	✓	574	[S9]
Co_3O_4 microsphere arrays	RGO/CNT paper[a]	×	378	[S10]
Co_3O_4 nanoparticles	Ni foam	✓	363	[S11]
Co_3O_4 hollow-sphere array	Ni foil	✓	358	[S12]
Hollow Co_3O_4 boxes	Ni foam	✓	278	[S13]
Co_3O_4 nanowires	Ni grid	✓	202	[S14]
Hollow Co_3O_4 octahedra	Carbon fiber paper	×	192	[S15]
Porous Co_3O_4	Ni foam	✓	150	[S16]
Co_3O_4 microtubules	Ni foam	✓	131	[S17]
Co_3O_4 nanosheets	Ni grid	✓	92	[S18]

[a] RGO/CNT = Reduced graphene oxide/carbon nanotubes

S5. Charge-discharge curves recorded during 2,000 cycles of measurement

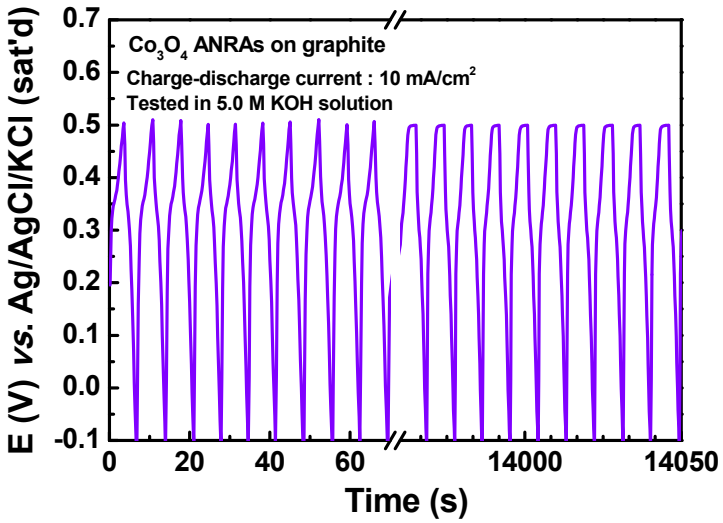

Figure S6. Charge-discharge curve of the Co_3O_4 ANRAs electrode measured in 5.0 M KOH solution at 10 mA/cm^2, recorded during 2,000 cycles of measurement.

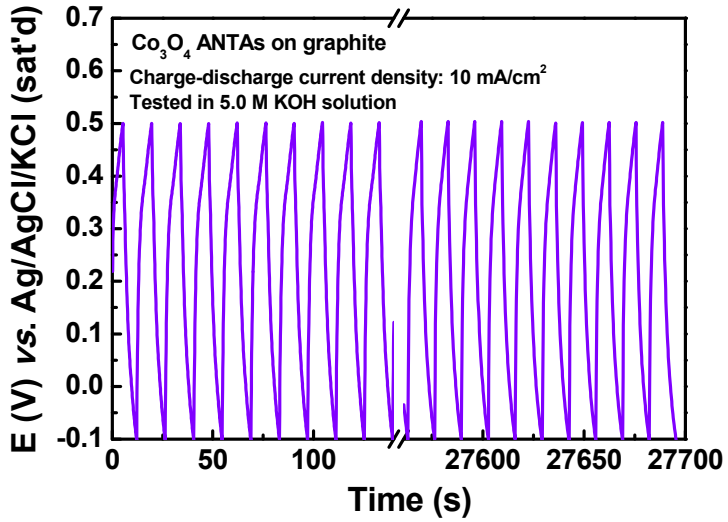

Figure S7. Charge-discharge curve of the Co_3O_4 ANTAs electrode measured in 5.0 M KOH solution at 10 mA/cm^2, recorded during 2,000 cycles of measurement.

S6. Morphologies of the films after 2,000 cycles of the charge-discharge process

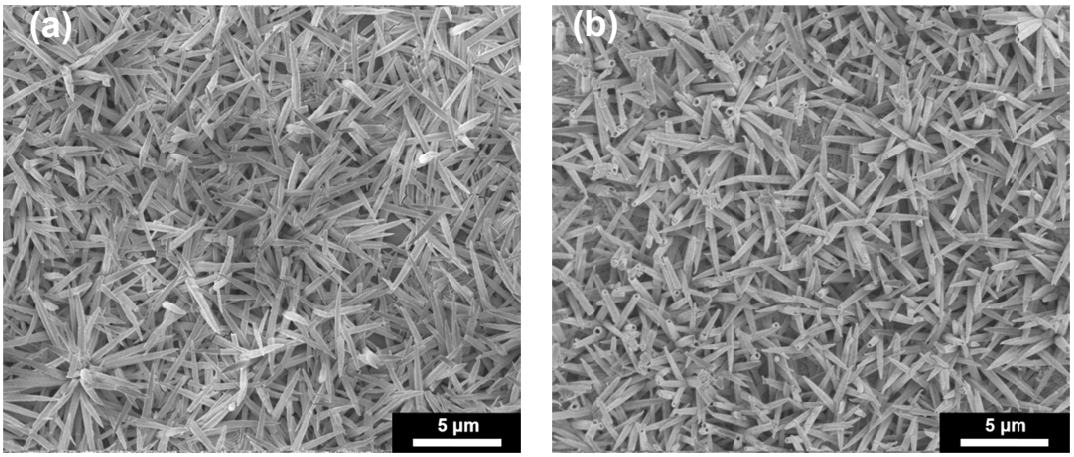

Figure S8. SEM images of the (a) Co_3O_4 ANRAs thin film, and (b) Co_3O_4 ANTAs thin film after 2,000 cycles of the charge-discharge process.

S7. Reference

[S1] C. Z. Yuan, L. Yang, L. R. Hou, L. F. Shen, X. G. Zhang and X. W. Lou, *Energy Environ. Sci.*, 2012, **5**, 7883.

[S2] M. J. Deng, F. L. Huang, I. W. Sun, W. T. Tsai and J. K. Chang, *Nanotechnology*, 2009, **20**, 175602.

[S3] X. X. Qing, S. Q. Liu, K. L. Huang, K. Z. Lv, Y. P. Yang, Z. G. Lu, D. Fang and X. X. Liang, *Electrochim. Acta*, 2011, **56**, 4985.

[S4] R. B. Rakhi, W. Chen, D. Y. Cha and H. N. Alshareef, *Nano Lett.*, 2012, **12**, 2559.

[S5] H. N. Zhang, Y. J. Chen, W. W. Wang, G. H. Zhang, M. Zhuo, H. M. Zhang, T. Yang, Q. H. Li and T. H. Wang, *J. Mater. Chem. A*, 2013, **1**, 8593.

[S6] F. Zhang, C. Z. Yuan, X. J. Lu, L. J. Zhang, Q. Che and X. G. Zhang, *J. Power Sources*, 2012, **203**, 250.

[S7] L. Yang, S. Cheng, Y. Ding, X. B. Zhu, Z. L. Wang and M. L. Liu, *Nano Lett.*, 2012, **12**, 321.

[S8] C. W. Kung, H. W. Chen, C. Y. Lin, R. Vittal and K. C. Ho, *J. Power Sources*, 2012, **214**, 91.

[S9] J. Xu, L. Gao, J. Cao, W. Wang and Z. Chen, *Electrochim. Acta*, 2010, **56**, 732.

[S10] C. Z. Yuan, L. Yang, L. R. Hou, J. Y. Li, Y. X. Sun, X. G. Zhang, L. F. Shen, X. J. Lu, S. L. Xiong and X. W. Lou, *Adv. Funct. Mater.*, 2012, **22**, 2560.

[S11] J. C. Deng, L. T. Kang, G. L. Bai, Y. Li, P. Y. Li, X. G. Liu, Y. Z. Yang, F. Gao and W. Liang, *Electrochim. Acta*, 2014, **132**, 127.

[S12] X. H. Xia, J. P. Tu, X. L. Wang, C. D. Gua and X. B. Zhao, *Chem. Commun.*, 2011, **47**, 5786.

[S13] W. Du, R. M. Liu, Y. W. Jiang, Q. Y. Lu, Y. Z. Fan and F. Gao, *J. Power Sources*, 2013, **227**, 101.

[S14] D. W. Wang, Q. H. Wang and T. M. Wang, *Inorg. Chem.*, 2011, **50**, 6482.

[S15] Y. Cao, F. L. Yuan, M. S. Yao, J. H. Bang and J. H. Lee, *CrystEngComm*, 2014, **16**, 826.

[S16] F. L. Meng, Z. G. Fang, Z. X. Li, W. W. Xu, M. J. Wang, Y. P. Liu, J. Zhang, W. R. Wang, D. Y. Zhao and X. H. Guo, *J. Mater. Chem. A*, 2013, **1**, 7235.

[S17] D. L. Yan, H. Zhang, L. Chen, G. S. Zhu, S. C. Li, H. R. Xu and A. B. Yu, *ACS Appl. Mater. Interfaces*, 2014, **6**, 15632.

[S18] S. L. Xiong, C. Z. Yuan, X. G. Zhang, B. J. Xi and Y. T. Qian, *Chem. Eur. J.*, 2009, **15**, 5320.