Electronic Supplementary Information (ESI†)

Facile synthesis and superior electrochemical performances of $CoNi_2S_4$/graphene nanocomposite suitable for supercapacitor electrodes

Weimin Du,*[a] Zhiyong Wang,[a] Zhaoqiang Zhu,[a,b] Sen Hu,[a] Xiaoyan Zhu,[a] Yunfeng Shi,[a] Huan Pang, *[a] and Xuefeng Qian[c]

[a] *College of Chemistry and Chemical Engineering, Anyang Normal University, Anyang, Henan, 455002, China, Tel: +86-372-2900040; E-mail: duweimin75@gmail.com and huanpangchem@hotmail.com*

[b] *College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou, Henan, 450001, China*

[c] *School of Chemistry and Chemical Technology, Shanghai Jiao Tong University, Shanghai, 200240, China*

1. Synthesis of graphene oxide (GO)

2 g commercial graphite, 1 g $NaNO_3$ and 46 mL concentrated sulfuric acid were mixed together in a 250 mL flask at room temperature. Then，the flask was magnetically stirred in a icewater bath and 6 g potassium hypermanganate was added. The temperature of the whole reaction system does not exceed 15℃. After an hour, the reaction bulb was moved into an oil bath with 35℃ temperature and continuously kept for an hour. Afterwards, the reaction bulb was again transferred into the icewater bath and 80mL de-ion water was slowly added. During this process, the temperature of the whole reaction system was controlled lower than 50℃. Then, the whole reaction system was again heated to 95℃ and kept for 30 minutes. 40mL de-ion water and 10 mL 30% H_2O_2 were added for neutralizing the superfluous potassium hypermanganate. Finally, graphene oxide (GO) was obtained after alternately washed by 5% dilute hydrochloric acid and de-ion water for cleaning up SO_4^{2-} ions, and dried in a vacuum oven at 60℃.

2. Synthesis of graphene

2g as-prepared graphene oxide (GO) was added into 400 mL de-ion water in a 500 mL flask at room temperature. The graphene oxide (GO) was ultrasonic for 30 minute until there is not obvious particulate matter. Then, 0.3 mL hydrazine hydrate (64.2mmol) and 3mL ammonia water were added into GO. Reaction system was placed in an oil bath at 100℃ and refluxed for 8-12 hours. After alternately washed with de-ion water, methanol and acetone, graphene (or: reduced graphene oxide) was obtained.

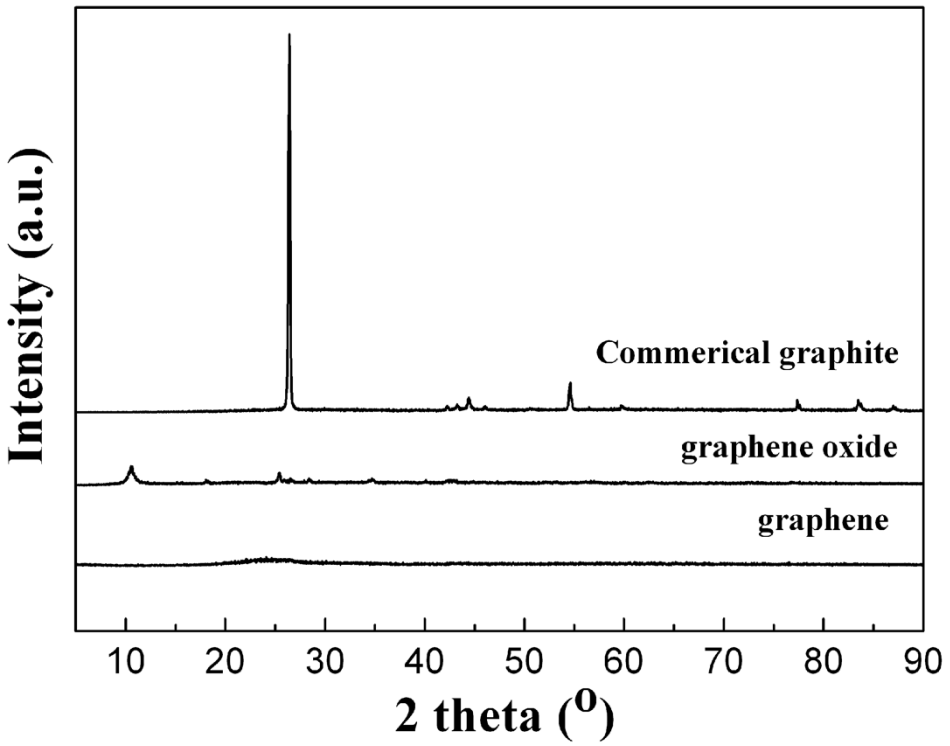

Fig. S1 XRD patterns of commercial graphite, graphene oxide and graphene

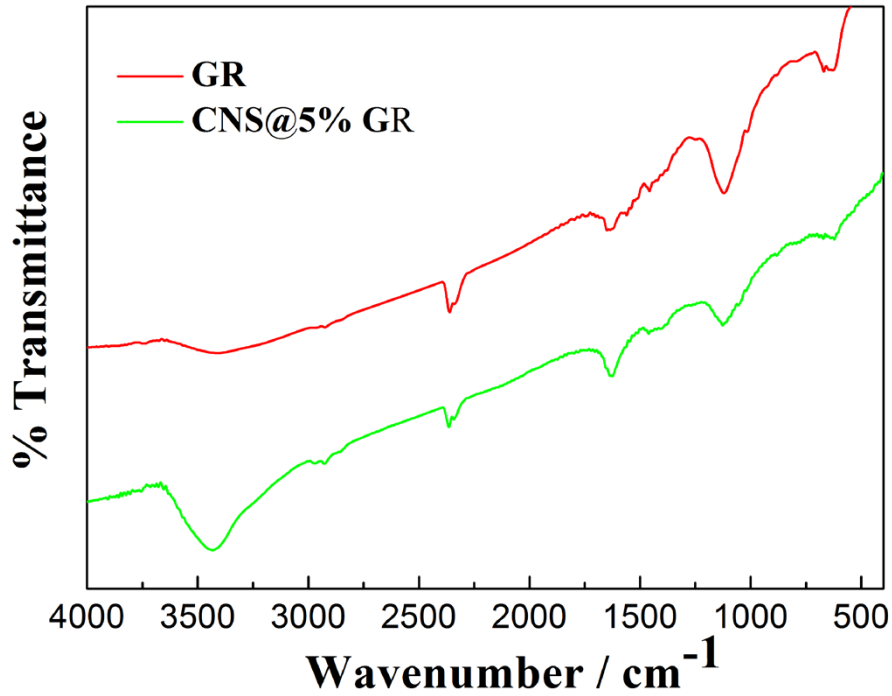

Fig. S2 FTIR patterns of graphene (GR) and $CoNi_2S_4$/graphene nanocomposite with 5% loaded amount of GR (CNS@5%GR)

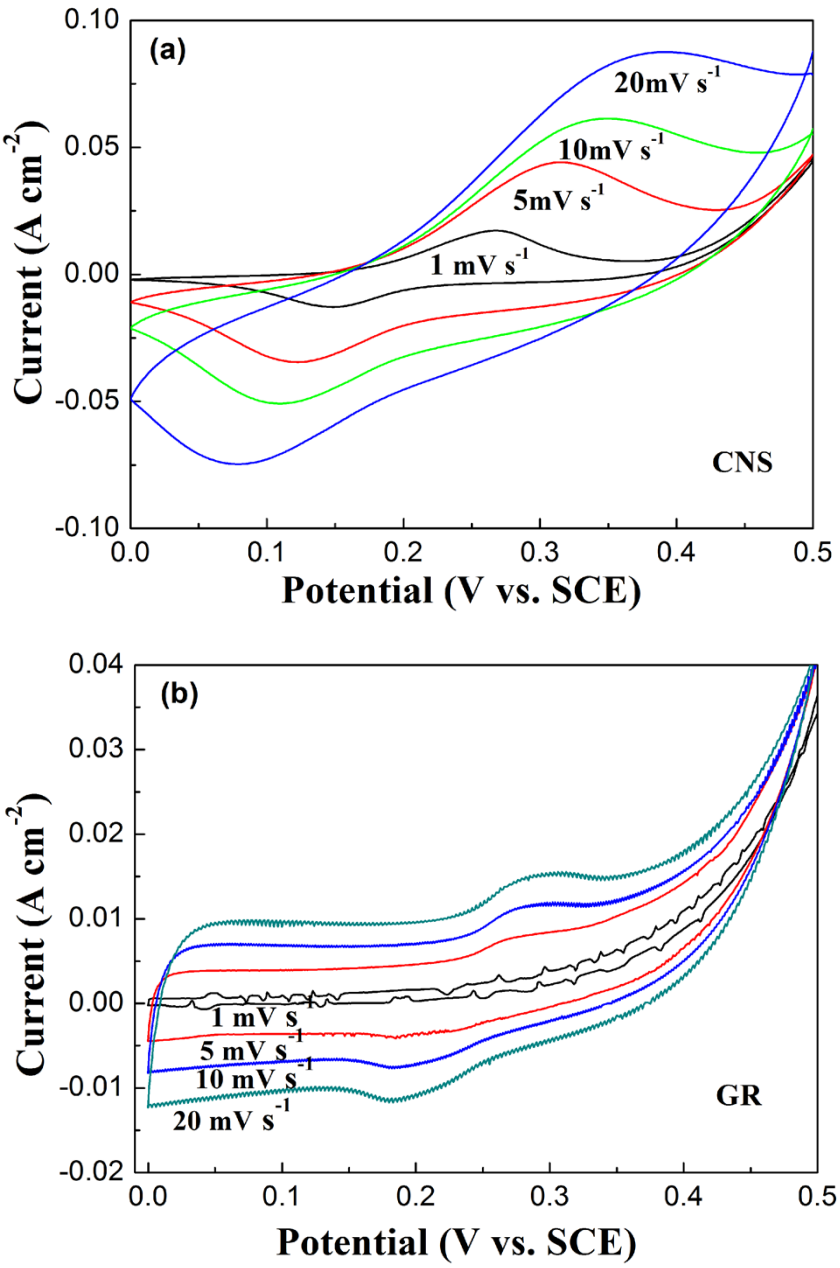

Fig. S3 CV curves at different scan rates recorded from supercapacitor electrodes consisting of (a) CNS nanoparticles and (b) GR

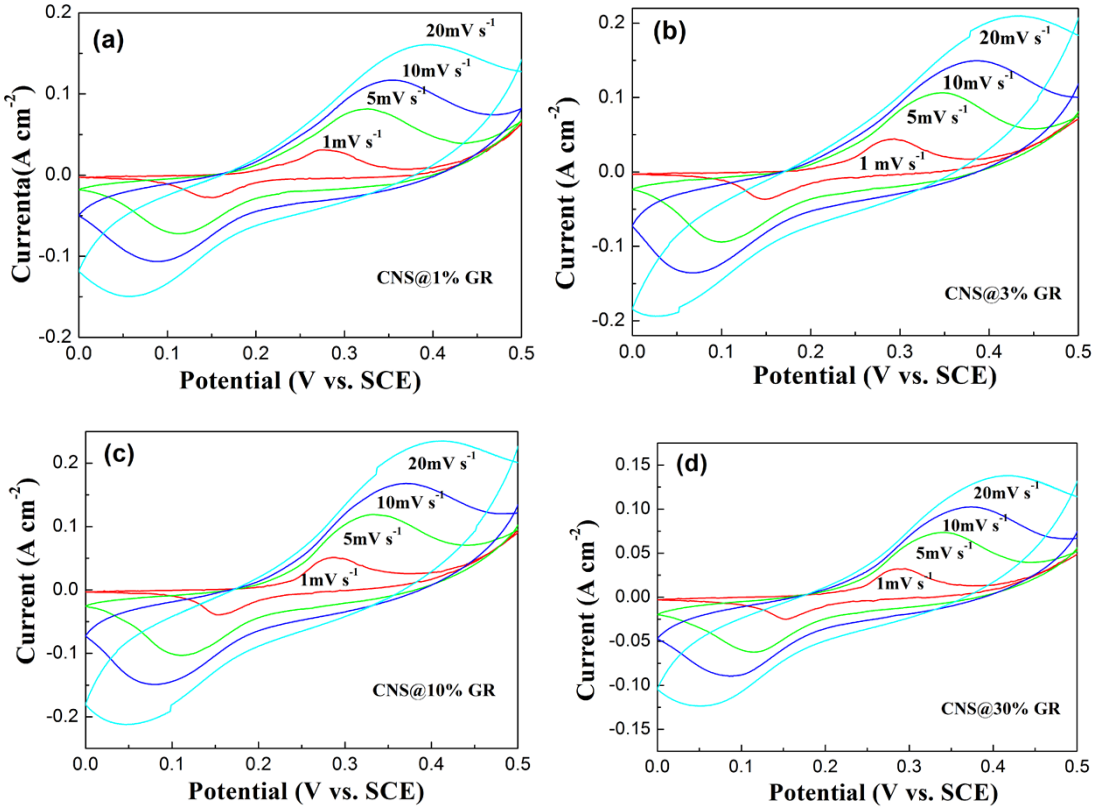

Fig. S4 CV curves at different scan rates recorded from supercapacitor electrodes consisting of $CoNi_2S_4$/graphene nanocomposite with different loaded amount of GR ((a) CNS@1%GR; (b) CNS@3%GR; (c) CNS@10%GR; (d) CNS@30%GR)

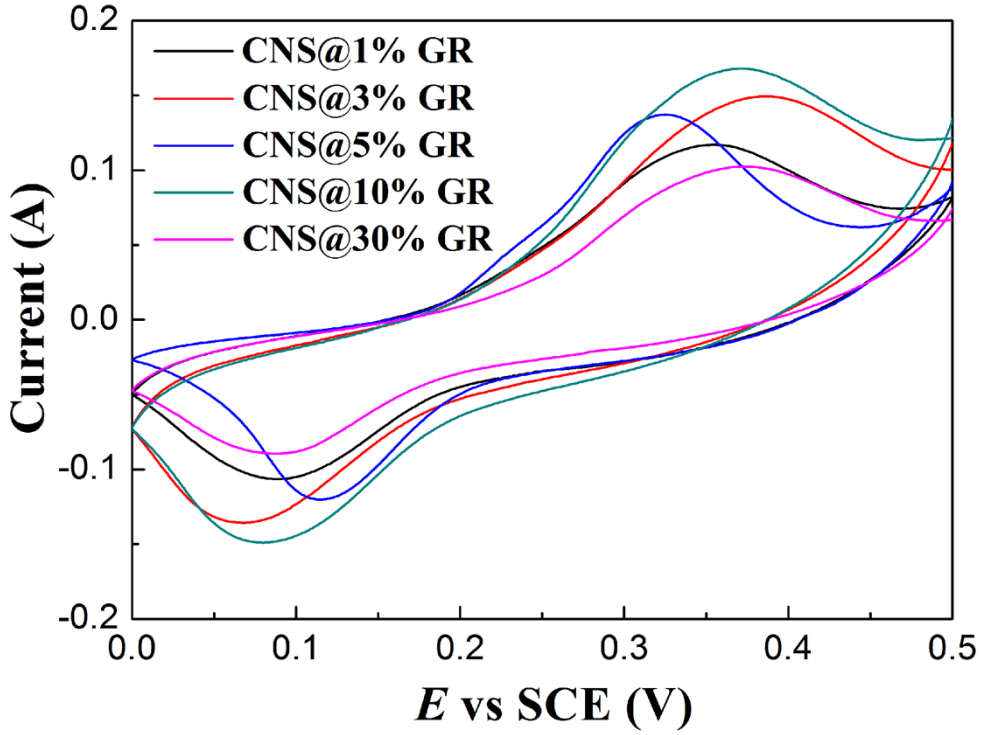

Fig. S5 CV curves at 10 mV S^{-1} recorded from supercapacitor electrodes consisting of $CoNi_2S_4$/graphene nanocomposite with different loaded amount of GR

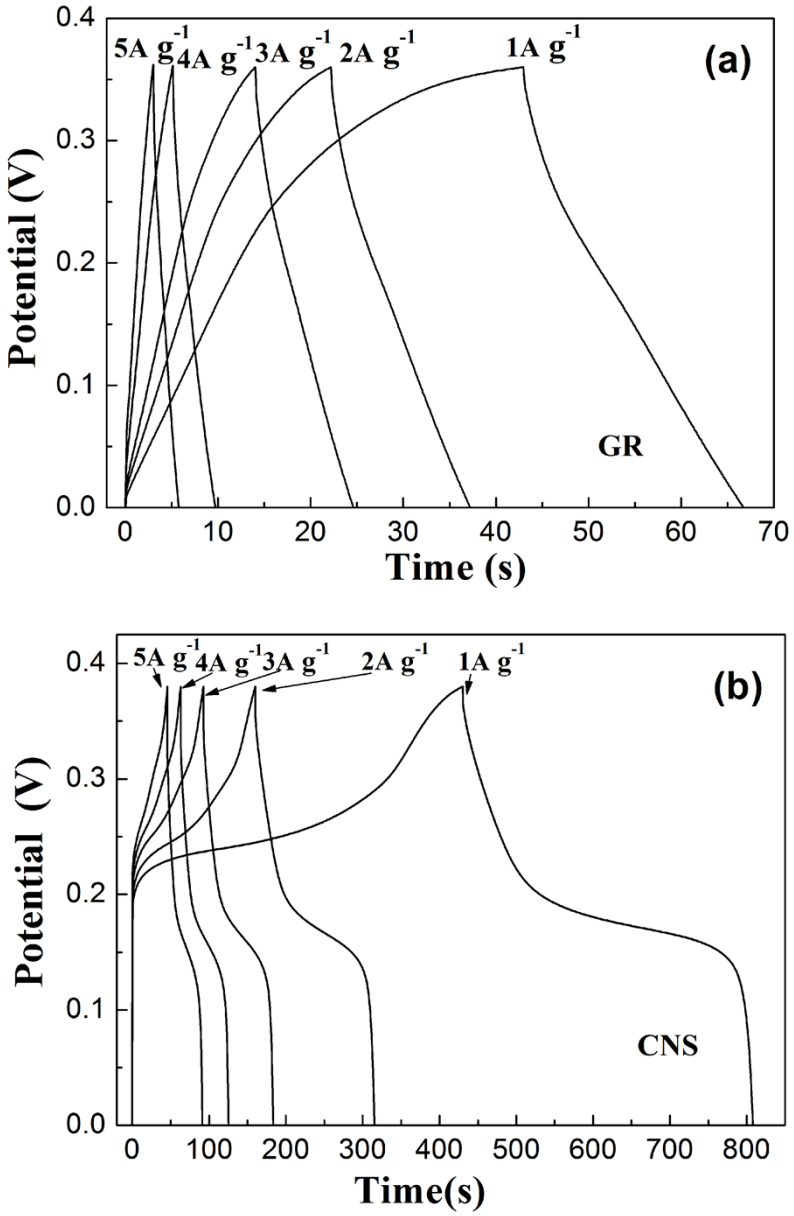

Fig. S6 CD curves of supercapacitor electrodes based on (a) GR and (b) CNS nanoparticles

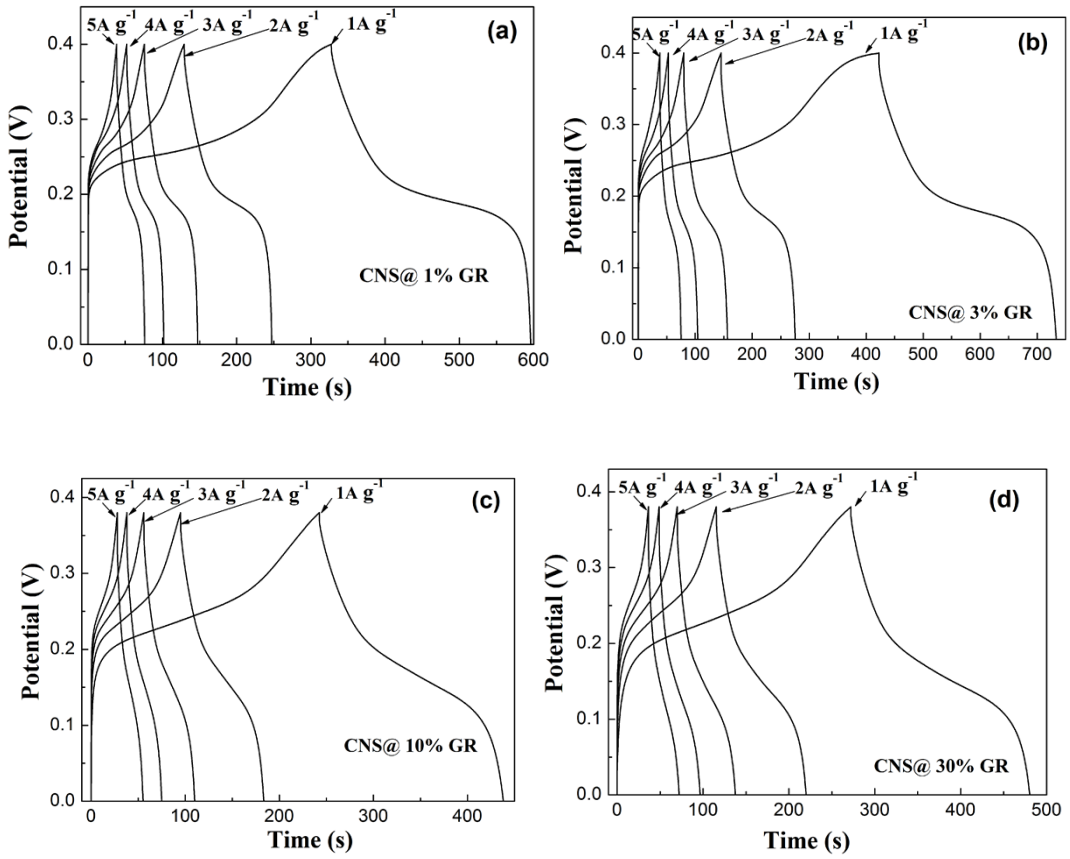

Fig. S7 CD curves of supercapacitor at different current densities recorded from supercapacitor electrodes consisting of $CoNi_2S_4$/graphene nanocomposite ((a) CNS@1%GR; (b) CNS@3%GR; (c) CNS@10%GR; (d) CNS@30%GR)

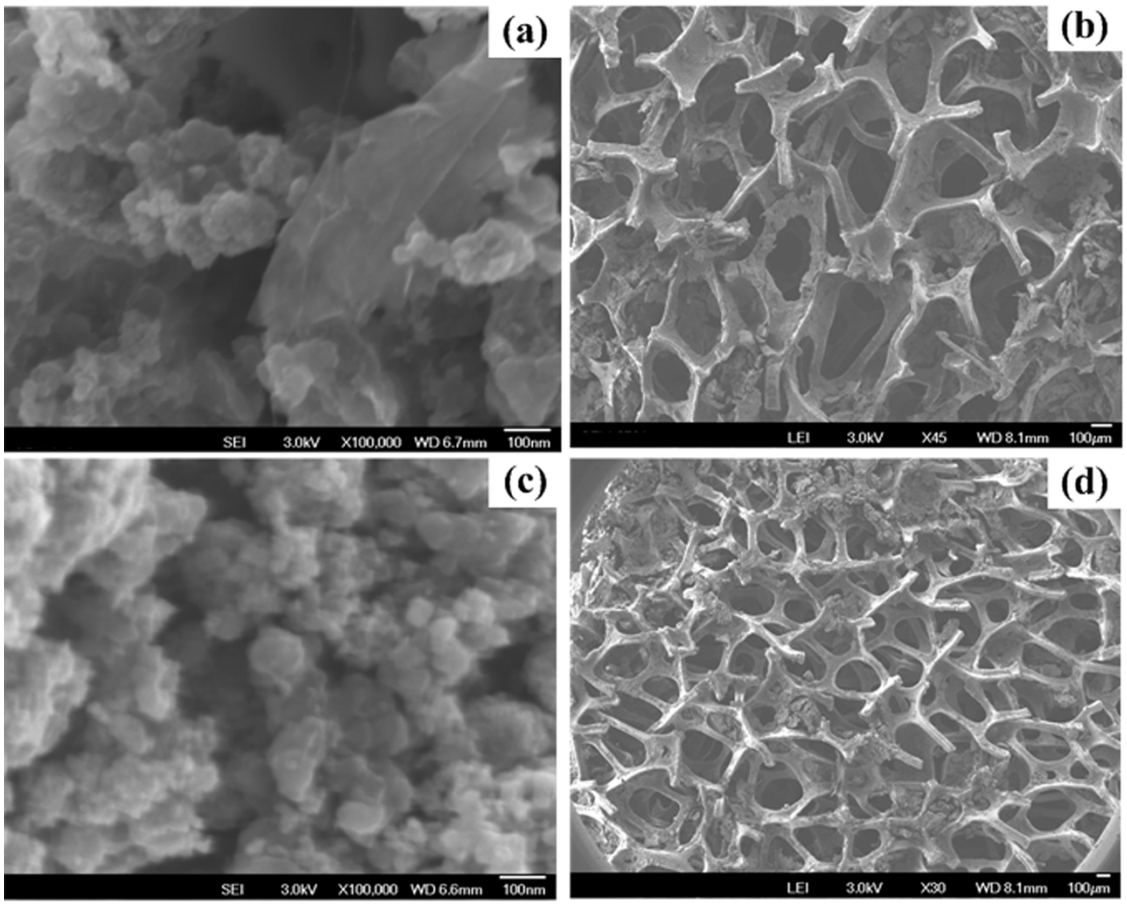

Fig.S8 SEM images of the film morphology of CNS@5% nanocomposite and CNS nanoparticles on the foamed nickel surface, respectively: (a, b) CNS@5% nanocomposite; (c, d) CNS nanoparticles

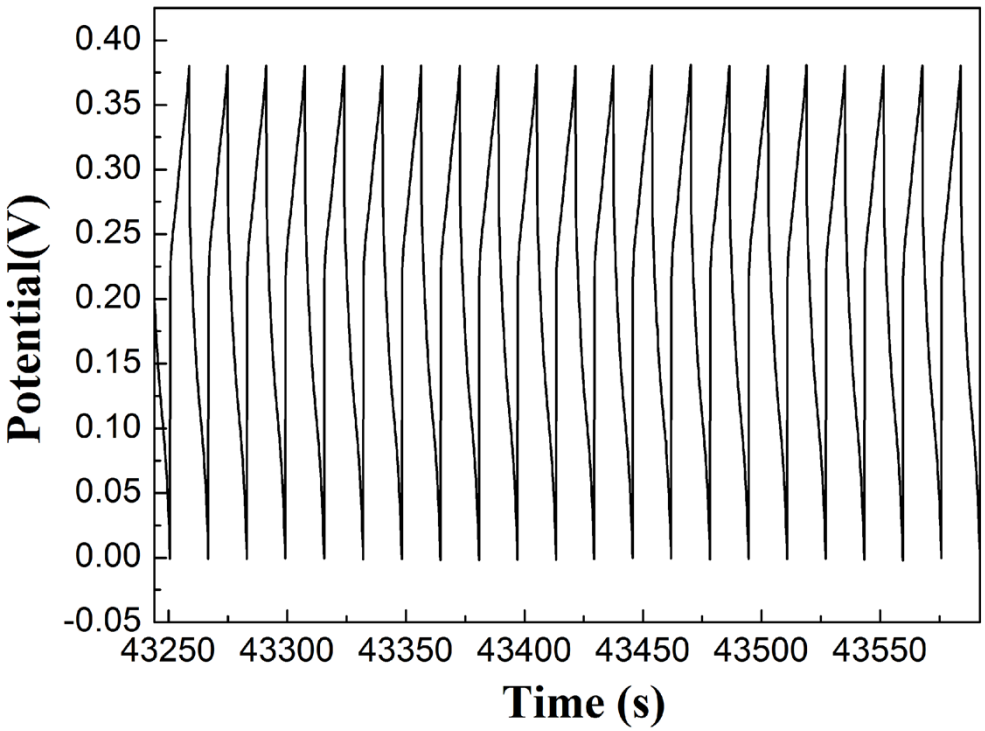

Fig.S9 Typical charge-discharge curves for the last 20 cycles at a current density of 20 A g^{-1} between 0 and 0.4 V of CNS@5%GR nanocomposite

Table S1 Compared electrochemical performance between $CoNi_2S_4$/graphene nanocomposite and other nanomaterials

Samples	**Maximum specific capacitance**	**Rate capability**	**Ref.**
$CoNi_2S_4$/graphene nanocomposite	**2099.1 F g^{-1} at 1 A g^{-1}**	**1046.4 F g^{-1} at 20 A g^{-1}**	**Present work**
$CoNi_2S_4$ nanoparticles	1169 F g^{-1} at 1 A g^{-1}	702.3 F g^{-1} at 5A g^{-1}	1
$NiCo_2S_4$ nanosheets/graphene	1451 F g^{-1} at 3 A g^{-1}	760 F g^{-1} at 20 A g^{-1}	2
$NiCo_2S_4$ porous nanotubes	933 F g^{-1} at 1 A g^{-1}	550 F g^{-1} at 5A g^{-1}	3
urchin-like $NiCo_2S_4$	1149 F g^{-1} at 1 A g^{-1}	888 F g^{-1} at 20 A g^{-1}	4
$NiCo_2O_4$ Nanosheets	***2010 F g^{-1} at 2 A g^{-1}***	***1450 F g^{-1} at 20 A g^{-1}***	*5*
$NiCo_2O_4$ Nanosheets	3.51 F cm^{-2} at 1.8 mA cm^{-2}	1.73 F cm^{-2} at 48.6 mA cm^{-2}	6
$NiCo_2O_4$ nanoneedle arrays	3.12 F cm^{-2} at 1.11 mA cm^{-2}	0.59 F cm^{-2} at 22.24 mA cm^{-2}	7
nickel cobaltite nanowires	401 F g^{-1} at 1 A g^{-1}	301F g^{-1} at 8 A g^{-1}	8
$NiCo_2O_4$ Microbelts	245 F g^{-1} at 1 A g^{-1}	212 F g^{-1} at 10 A g^{-1}	9
$Ni_{0.3}Co_{2.7}O_4$ hierarchical structures	960 F g^{-1} at 0.625 A g^{-1}	805 F g^{-1} at 6.25 A g^{-1}	10
$NiCo_2O_4$ - single wall carbon nanotube nanocomposite	1642 F g^{-1} at 0.5 A g^{-1}	879 F g^{-1} at 20 A g^{-1}	11
$NiCo_2O_4$ – graphene oxide nanocomposites	925 F g^{-1} at 1.5 A g^{-1}	735 F g^{-1} at 33 A g^{-1}	12
cobalt sulfide nanowires	508 F g^{-1} at 2.5 mA cm^{-2}	377 F g^{-1} at 20 mA cm^{-2}	13

Amorphous CoS_x Nanoparticles	910 F g^{-1} at 0.4 A g^{-1}	651 F g^{-1} at 4 A g^{-1}	14
nanosheet-like cobalt sulfide films	***1471 F g^{-1} at 4 A g^{-1}***	***1306 F g^{-1} at 40 A g^{-1}***	15
cobalt sulfide (CoSx)	475 F/g at 5 mA cm^{-2}	369 F/g at 50 mA cm^{-2}	16
cobalt sulfide hierarchitectures	555 F g^{-1} at 5 mA cm^{-2}	464 F g^{-1} at 100 mA cm^{-2}	17
CoS_2 ellipsoids	980 F g^{-1} at 1 A g^{-1}	224 F g^{-1} at 10 A g^{-1}	18
Arrays of CuS ultrafine nanoneedles supported on a carbon nanotube	122 F g^{-1} at 1.2 A g^{-1}	89 F g^{-1} at 7.4 A g^{-1}	19

References:

1. W. Du, Z. Zhu, Y. Wang, J. Liu, W. Yang, X. Qian and H. Pang, *RSC Adv*, 2014, **4**, 6998-7002.
2. S. Peng, L. Li, C. Li, H. Tan, R. Cai, H. Yu, S. Mhaisalkar, M. Srinivasan, S. Ramakrishna and Q. Yan, *Chem Commun*, 2013, **49**, 10178-10180.
3. H. Wan, J. Jiang, J. Yu, K. Xu, L. Miao, L. Zhang, H. Chen and Y. Ruan, *Crystengcomm*, 2013, **15**, 7649–7651.
4. H. Chen, J. Jiang, L. Zhang, H. Wan, T. Qi and D. Xia, *Nanoscale*, 2013, **5**, 8879–8883.
5. C. Yuan, J. Li, L. Hou, X. Zhang, L. Shen and X. W. Lou, *Adv Funct Mater*, 2012, **22**, 4592-4597.
6. G. Zhang and X. W. Lou, *Adv Mater*, 2013, **25**, 976-979.
7. G. Q. Zhang, H. B. Wu, H. E. Hoster, M. B. Chan-Park and X. W. Lou, *Energ Environ Sci*, 2012, **5**, 9453-9456.
8. C. Z. Yuan, J. Y. Li, L. R. Hou, L. Yang, L. F. Shen and X. G. Zhang, *J Mater Chem*, 2012, **22**, 16084-16090.
9. F. L. Zhu, J. X. Zhao, Y. L. Cheng, H. B. Li and X. B. Yan, *Acta Phys-Chim Sin*, 2012, **28**, 2874-2878.
10. H. B. Wu, H. Pang and X. W. Lou, *Energ Environ Sci*, 2013, **6**, 3619-3626.
11. X. Wang, X. D. Han, M. Lim, N. Singh, C. L. Gan, M. Jan and P. S. Lee, *J Phys Chem C*, 2012, **116**, 12448-12454.
12. D. Carriazo, J. Patino, M. C. Gutierrez, M. L. Ferrer and F. d. Monte, *RSC Adv*, 2013, **3**, 13690–13695.
13. S. J. Bao, C. M. Li, C. X. Guo and Y. Qiao, *J Power Sources*, 2008, **180**, 676-681.

14. C. Yuan, B. Gao, L. Su, L. Chen and X. Zhang, *J Electrochem Soc*, 2009, **156**, A199-A203.
15. J. Y. Lin and S. W. Chou, *RSC Adv*, 2013, **3**, 2043-2048.
16. F. Tao, Y. Q. Zhao, G. Q. Zhang and H. L. Li, *Electrochem Commun*, 2007, **9**, 1282-1287.
17. Q. Wang, L. Jiao, H. Du, J. Yang, Q. Huan, W. Peng, Y. Si, Y. Wang and H. Yuan, *Crystengcomm*, 2011, **13**, 6960-6963.
18. L. Zhang, H. B. Wu and X. W. Lou, *Chem Commun*, 2012, **48**, 6912-6914.
19. T. Zhu, B. Xia, L. Zhou and X. Wen Lou, *J Mater Chem*, 2012, **22**, 7851-7855.

Table S2 Calculated values of *R*s, *CPE*, *R*ct, and *C*p of the supercapacitor electrodes consisting of CNS nanoparticles, GR and $CoNi_2S_4$/graphene nanocomposite through fitting of the experimental impedance spectra based on the proposed circuit

Samples	***R*s（Ω·cm^{-2}）**	***CPE*（mF）**	***R*ct（Ω·cm^{-2}）**	***C*p (F)**
CNS	0.6906	0.5011	1.524	0.3035
CNS@1%GR	0.1587	0.4925	1.325	1.353
CNS@3%GR	0.2977	0.53711	0.24882	1.056
CNS@5%GR	**0.1145**	**0.5093**	**0.1749**	**0.8926**
CNS@10%GR	0.1608	0.3987	0.2614	1.083
CNS@30%GR	0.42659	0.50645	0.45276	0.5616
GR	0.6146	0.5518	0.4739	0.2420