

A Novel Nickel Nanocone Array Current Collector for High Performance Supercapacitor

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Abstract—Energy storage devices have become more indispensable in our lives. Among various energy storage devices, supercapacitors have been considered as one of the most promising candidates. In terms of the components of supercapacitor, current collector plays a significant role in enhancing the performance of the supercapacitors. Here we report a novel current collector preparation method through depositing nickel nanocone arrays structure on stainless steel plates. The average height of the nanocones was ~800nm, and its aspect ratio was about 4, which greatly increased the surface area. Owing to its dislocation growth mechanism, the surface of nanocones was rough, which efficiently improved the adhesion with active materials. In order to demonstrate this novel current collector, manganese oxide (MnO₂) was deposited on stainless steel with nickel nanocone arrays. Results showed that the specific capacitance of the nickel nanocone array supported MnO₂ which was investigated in 0.5 M Na₂SO₄ was 351 F/g. It is worth mentioning that the preparation of the novel current collector can be fabricated in large-scale by roll-to-roll process, which greatly promotes the application of the novel current collector.

Keywords—supercapacitor; nickel nanocone array; electrochemical performance

I. INTRODUCTION

With the change of climate, limited availability of fossil fuels, and increasing environmental pollution, there has been an ever increasing and urgent demand for environmentally friendly, high efficient and sustainable sources of energy as well as new energy conversion and storage devices.[1]

Supercapacitor, also known as electrochemical capacitor or ultracapacitor, has drawn much attention, because it stores energy using either ion adsorption (electrochemical double layer capacitors) or fast surface redox reactions (pseudo-capacitors), which result in high power density (>10 Kw kg⁻¹), long cycle life (more than 1,000,000 cycles) and fast charge/discharge rates (within several seconds).[2] Recently, an obvious improvement in performance has been achieved by the design of advanced nanostructured materials, including the nanostructure design of active materials and current collectors.[3-5] A high conductivity current collector with order nanostructure is a good scaffold to load with active material.[6] Some literatures have reported the some novel current collector, and 1D nanowire/nanotube arrays has attracted the worldwide interests (e.g., Cu pillars, CNTs, SnO₂ nanowires).[7-11] However, the poor mechanical properties and high aspect ratio of nano array often result in collapsing to the neighbors, leading to the decrease of useful surface and the limited accessibility to electrolyte.

Here, we report a novel current collector preparation method through electroplating nickel nanocone array structures on stainless steel plates. Excellent mechanical properties and proper aspect ratio (about 4) of NCAs avoid the collapse when loading with active materials The whole thickness of the novel current collector is only 43 μm (the stainless steel plates is 40 μm). The average height of the nanocones is 800nm, and its unique nanocone structure greatly increases the surface area. Owing to its dislocation growth mechanism, the surface of nanocones is rough, which efficiently improves the adhesion with active materials.[12] Compared with the plain stainless steel plate current collector,

the active material is strongly attached to the NCA current collector due to the improved roughness. In order to demonstrate the significance of novel current collector, a typical active material - manganese oxide (MnO_2) is deposited on nickel nanocone arrays (MNN) through the electro-deposition. Calculating from the electrochemical performance of electrode, the specific capacitance of the nickel nanocone array supported MnO_2 investigated in 0.5 M Na_2SO_4 is as high as 351F/g, which is superior to other reported data.[13-15] Furthermore, the novel current collector can be prepared in large-scale by roll-to-roll process, which greatly promotes the extensive use of the novel current collector.

II. EXPERIMENTAL

A. The synthesis of nickel nanocone array current collector

For electro-deposition method, nickel foam was employed as the anodic electrode, and the nickel nanocone arrays were electroplated onto stainless steel plates. Before electro-deposition, stainless steel plates (thickness~40um) were cleaned by ultrasonication for 30 min in a mixed solution of acetone and ethanol (1:1 vol). The stainless steel plates were rinsed with DI waters, and were coated with insulating tapes, leaving an area equal to 1.5 cm X 3 cm of the stainless steel substrates exposed. All chemicals were used as received without further purification. The electrolyte solution contained three components ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 200 g/L, providing Ni^{2+} ; H_3BO_3 , 100 g/L, buffer agent; NH_4Cl , 40g/L, crystal modifier). In addition, the electrolyte pH was adjusted to 4.0 by 10% HCl and 10% NH_4OH solutions and keep temperature at 60°C. The electro-deposition process was performed in electrolyte solution at 1.0 A dm^{-2} current density for 8-12mins to obtain nickel nanocone arrays. After that, the deposited plates were washed by DI water for three times to remove the impurities and dried at 60°C for 30min.

B. The preparation of nickel nanocone array loading MnO_2 material

The stainless steel plates with nickel nanocone array loading MnO_2 were prepared through electro-deposition method.[16,17] The stainless steel plates with nickel nanocone were used as anode and the counter electrode was a

platinum plate. The electrolyte solution was 0.1M manganese (II) acetate (80mL). The electro-deposition process was operated in the electrolyte solution mentioned with a 10.0 DC voltage for 1-10mins. The as-prepared electrodes was rinsed with DI water for several times to remove the impurities and dried at 60°C for 1 hour. As a control sample, MnO_2 was directly deposited on stainless steel plates under the same condition mentioned above. The mass loading of MnO_2 was calculated by weighting the electrode before and after MnO_2 deposition.

C. Materials characterization and electrochemical measurements

The phase analysis was operated on the X-ray diffraction measurements (XRD, BrukerDS RINT2000/PC). The morphology of the nickel nanocone arrays were observed by field emission scanning electron microscopy (FE-SEM, HITACH S4800, Japan). The electrochemical properties of the as-prepared samples were investigated on an electrochemical station (VMP3, BioLogic, France) by a typical three-electrode configuration in a Na_2SO_4 (0.5 M) aqueous electrolyte. The working electrodes were the as-prepared samples with an electrode area of 1.5 X 3 cm^2 , and platinum and a saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively.

The applied potential window of cyclic voltammetry (CV) and galvanostatic charge-discharge (GCD) was in the range from 0.0 V to 0.8 V. The electrochemical impedance spectroscopy (EIS) was conducted in the frequency range between 100 KHz and 0.01 Hz with an amplitude of 5 mV at the open-circuit potential.

The specific capacitance was calculated from the CV curves according to the equations:

$$C = \frac{\int i(V)dV}{mv\Delta V} \quad (1)$$

where, C is the specific capacitance of materials, m is the mass loading on the substrate, v is the scan rate, ΔV is the potential window in the CV curves, $i(V)$ is the voltammetric current.

III. RESULT AND DISCUSSION

Here we successfully synthesized the well-organized NCAs loading with MnO_2 on stainless steel through electro-deposition. According to the X-ray diffraction (XRD) shown in the Figure 1a, three characteristic peaks are consistent with the pattern of JCPDS card (68-0380), suggesting the nickel nanocone array was deposited to the stainless steel plates. Fig. 2a-2c display representative scanning electron microscopy (SEM) images of nickel nanocone array showing their regularity. The nanocones grow perpendicular to the substrate and the average height of the nickel nanocones is 800nm. With the growth of NCAs on stainless steel, the surface area of current collector greatly increases, which enables the loading of dramatically increased amount of active materials, thus improving the energy density per unit area. From the Figure 2d, it's obvious that the surface of the nickel nanocone is rough, which greatly enhances the

adhesion between the deposited active material and the current collector. This may be attributed to its dislocation growth mechanism. There are two main functions of NCAs for the electrode, one is increasing the surface area of current collector; the other is improving the adhesion between deposited material and current collector. Therefore, the presence of NCAs is critical for the performance of the supercapacitor. The thickness of NCAs is calculated by measuring the current collectors before and after the electro-deposition of NCAs. Fig. 3 shows the contrast of thickness of the novel current collector. After the electro-deposition, the thickness of current collector is only 43 μm (the thickness of pure stainless steel plate is 40 μm). Thence, the NCAs are so thin that have negligible impact on the total thickness of this novel current collector, which reveal NCAs are a perfect candidate as novel current collector.

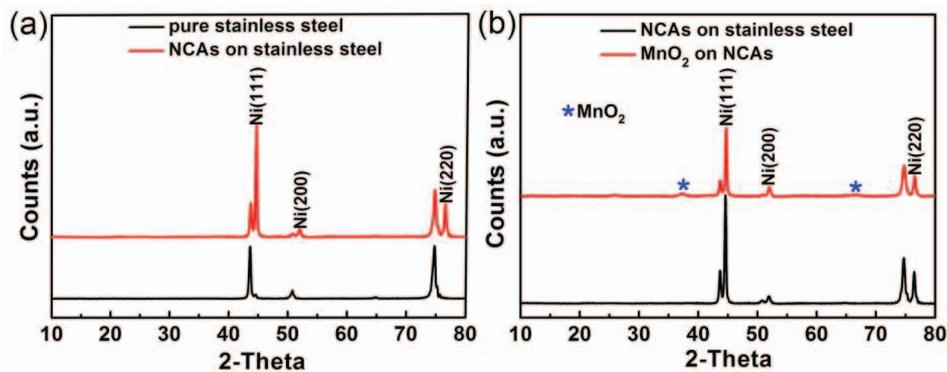


Fig. 1 (a) XRD pattern of pure stainless steel and NCAs on stainless steel. (b) XRD pattern of NCAs on stainless steel and MnO_2 nanostructure deposited on NCAs

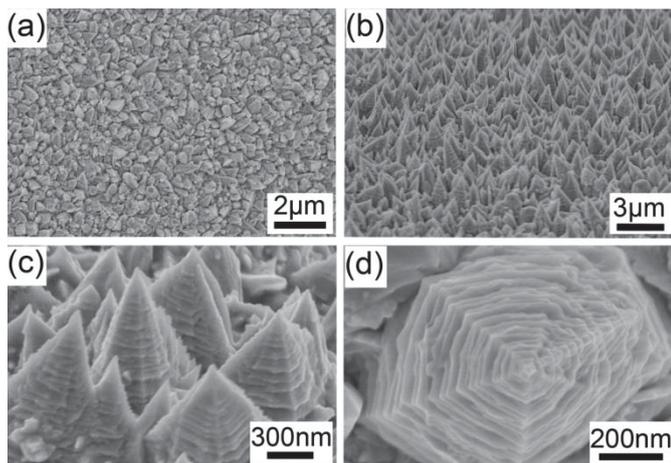


Fig. 2 (a), (b), (c) the different magnification SEM images of NCAs. (d) the top view of a nickel nanocone



Fig. 3 the thickness of current collector before and after electro-deposition

When the electro-deposition of MnO_2 is operated in $\text{Mn}(\text{AC})_2$ solution, the Mn^{2+} surrounding the negative electrode (stainless steel with NCAs) tends to lose two electrons and combines with the O^{2-} to form MnO_2 deposited on the surface of NCAs. When the NCAs were coated with MnO_2 , the representative peaks of amorphous MnO_2 were displayed in XRD pattern (Figure 1b). Fig. 4 shows the morphology of NCAs loading with MnO_2 . Fig. 4a indicates that a uniform layer of MnO_2 active material was deposited to the surface of NCAs. The structure of NCAs have no change and does not collapse owing to its appropriate aspect ratio, which also ensure that electrolyte can easily contact with the active material and sufficiently release the specific capacitance of MnO_2 . Fig. 4b shows the top view of the MNN, MnO_2 deposited on the surface of nickel nanocone looks like nanorod, which can successfully promote the infiltration with electrolyte to take full of MnO_2 .

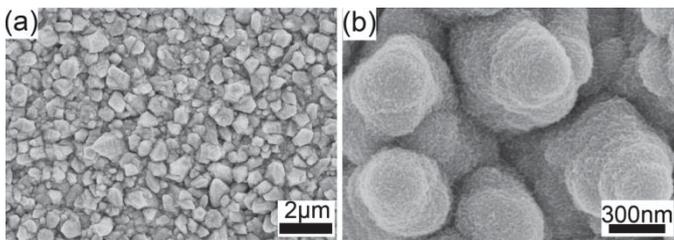


Fig. 4 (a) the low magnification SEM image of MNN. (b) the top view of MnO_2 deposited on nickel nanocone array

In order to assess the electrochemical performance of the novel current collector loading with MnO_2 , the electrodes are investigated with three electrodes system in 0.5 M aqueous Na_2SO_4 electrolytes at scan rate from 10 to 200 mV/s. Fig. 5a shows the CV curves under different scan rates, which shows an ideal symmetric rectangular shape, even the scan rate increases to 200mV/s, suggesting the excellent supercapacitive characteristics. This may be attributed to great access of the electrolyte to the active materials. Fig. 5b shows the GCD curves of MNN under the different current densities. The GCD curves of MNN are nearly triangular, and the IR drop is only 0.04 V at 20 A/g, suggesting the good adhesion between MnO_2 and nickel nanocone array.[18] It is well known that the cycling stability is a critical factor for

supercapacitors in high power applications. The cycling performance of the electrode is given by the fig. 5c, and it is tested at 100 mV/s for 3000 cycles. After the 3000 cycles, the capacitance retention is as high as 99.5%, indicating the excellent cycling stability compared with many other ever-reported transition metal oxide electrodes.[19,20] The specific capacitance of the electrode is calculated from CV curves, and result is displayed in fig. 5d. The specific capacitance of MNN reached up to 351F/g at 6 mV/s, and reach 218 F/g at 200 mV/s, exhibiting the outstanding rate performance. As a control sample, the stainless steel loading with MnO_2 is investigated under the same condition. However, the specific capacitance of the stainless steel loading with MnO_2 just reach to 233 F/g at 6 mV/s and with the increasing of scan rate, the specific capacitance decreased rapidly, which is inferior to the performance of MNN. All the outstanding electrochemical performances we mentioned above are attributed to the NCAs, which greatly increase the surface area and promote the full infiltration between MnO_2 and electrolyte.

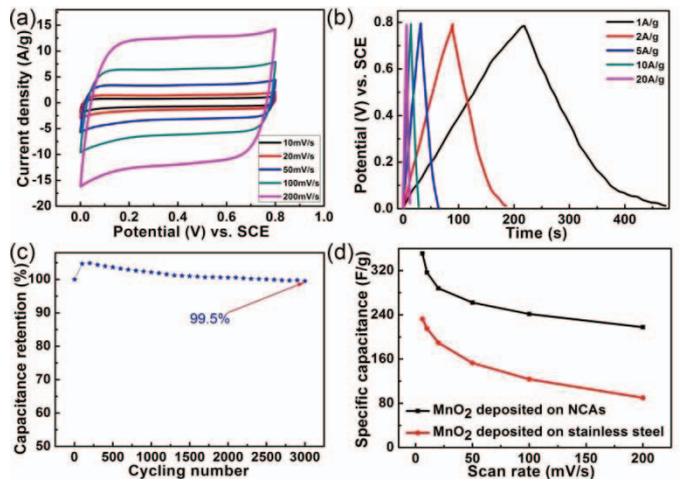


Fig. 5 (a) CV curves of MNN electrode at different scan rates. (b) GCD curves of MNN obtained at different current density. (c) the cycling stability of MNN electrode. (d) Specific capacitance of MNN and MSP at different scan rates.

IV. CONCLUSION

In summary, we report a nickel nanocone array novel current collector fabricated through simple electroplating on stainless steel plates. The whole thickness of novel current collector is 43 μm (the stainless steel is 40 μm). The unique nickel nanocone array structure not only increases the surface area of current collector, but also greatly improves the adhesion with active materials, which is very important for the performance of supercapacitor. When NCAs coated with MnO_2 , it loads more MnO_2 active material compared with the stainless steel in same macro area, and provides the electrolyte with an easy access to MnO_2 rather than collapse, which is attributed to its proper aspect ratio and excellent mechanical property. Therefore, it's no wonder that the specific capacitance of MNN electrode reaches up to 351 F/g, and shows the excellent cycling stability according to a series of electrochemical tests. It is worth mentioning that the preparation of the novel current collector can be fabricated in large-scale by roll-to-roll process, which enables the novel current collector become a promising candidate in future.

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References

[1] P. Simon and Y. Gogotsi, "Materials for electrochemical capacitors," *Nat Mater*, vol. 7, pp. 845-854, November 2008.

[2] B. E. Conway, "Electrochemical supercapacitors," 1999.

[3] X. Zhang, W. Shi, J. Zhu, W. Zhao, J. Ma, S. Mhaisalkar, et al., "Synthesis of porous NiO nanocrystals with controllable surface area and their application as supercapacitor electrodes," *Nano Res*, vol. 3, pp. 643-652, July 2010.

[4] L.-Q. Mai, A. Minhas-Khan, X. Tian, K. M. Hercule, Y.-L. Zhao, X. Lin, et al., "Synergistic interaction between redox-active electrolyte and binder-free functionalized carbon for ultrahigh supercapacitor performance," *Nat Commun*, vol. 4, December 2013.

[5] J. Zang, S. Ryu, N. Pugno, Q. Wang, Q. Tu, M. J. Buehler, et al., "Multifunctionality and control of the crumpling and unfolding of large-area

graphene," *Nat Mater*, vol. 12, pp. 321-325, January 2013.

[6] J. Jiang, Y. Li, J. Liu, X. Huang, C. Yuan and X. W. D. Lou, "Recent advances in metal oxide - based electrode architecture design for electrochemical energy storage," *Adv Mater*, vol. 24, pp. 5166-5180, August 2012.

[7] P.-L. Taberna, S. Mitra, P. Poizot, P. Simon and J.-M. Tarascon, "High rate capabilities Fe_3O_4 -based Cu nano-architected electrodes for lithium-ion battery applications," *Nat Mater*, vol. 5, pp. 567-573, June 2006.

[8] A. L. M. Reddy, M. M. Shaijumon, S. R. Gowda and P. M. Ajayan, "Coaxial MnO_2 /carbon nanotube array electrodes for high-performance lithium batteries," *Nano Lett*, vol. 9, pp. 1002-1006, February 2009.

[9] J. Liu, J. Essner and J. Li, "Hybrid supercapacitor based on coaxially coated manganese oxide on vertically aligned carbon nanofiber arrays," *Chem. Mater*, vol. 22, pp. 5022-5030, August 2010.

[10] J. Duay, E. Gillette, R. Liu and S. B. Lee, "Highly flexible pseudocapacitor based on freestanding heterogeneous MnO_2 /conductive polymer nanowire arrays," *PCCP*, vol. 14, pp. 3329-3337, January 2012.

[11] J. Yan, A. Sumboja, E. Khoo and P. S. Lee, " V_2O_5 loaded on SnO_2 nanowires for high - rate Li ion batteries," *Adv Mater*, vol. 23, pp. 746-750, December 2011.

[12] T. Hang, H. Ling, A. Hu and M. Li., "Growth mechanism and field emission properties of nickel nanocones array fabricated by one-step electrodeposition," *J. Electrochem. Soc*, vol. 157, pp. D624-D627, October 2010.

[13] W. Li, Q. Liu, Y. Sun, J. Sun, R. Zou, G. Li, et al., " MnO_2 ultralong nanowires with better electrical conductivity and enhanced supercapacitor performances," *J. Mater. Chem.*, vol. 22, pp. 14864-14867, June 2012.

[14] Q. Qu, P. Zhang, B. Wang, Y. Chen, S. Tian, Y. Wu et al., "Electrochemical performance of MnO_2 nanorods in neutral aqueous electrolytes as a cathode for asymmetric supercapacitors," *J. Phys. Chem. C*, vol. 113, pp. 14020-14027, July 2009.

[15] F. F. Cao, J. W. Deng, S. Xin, H. X. Ji, O. G. Schmidt, L. J. Wan, et al., "Cu - Si Nanocable Arrays as High - Rate Anode Materials for Lithium - Ion Batteries," *Adv Mater*, vol. 23, pp. 4415-4420, August 2011.

[16] Z. Su, C. Yang, C. Xu, H. Wu, Z. Zhang, T. Liu., "Co-electro-deposition of the MnO_2 -PEDOT:PSS nanostructured composite for high areal mass, flexible asymmetric supercapacitor devices," *J. Mater. Chem A*, vol. 1, pp. 12432-12440, August 2013.

[17] N. Nagarajan, H. Humadi and I. Zhitomirsky, "Cathodic electrodeposition of MnO_x films for electrochemical supercapacitors," *Electrochim. Acta*, vol. 51, pp. 3039-3045, April 2006.

[18] Z. Su, C. Yang, B. Xie, Z. Lin, Z. Zhang, J. Liu, et al., "Scalable

fabrication of MnO₂ nanostructure deposited on free-standing Ni nanocone arrays for ultrathin, flexible, high-performance microsupercapacitor," *Energy Environ. Sci.*, 2014., In press.

[19]S.-L. Chou, J.-Z. Wang, S.-Y. Chew, H.-K. Liu and S.-X. Dou, "Electrodeposition of MnO₂ nanowires on carbon nanotube paper as free-standing, flexible electrode for supercapacitors," *Electrochem. Commun.*, vol. 10, pp. 1724-1727, November 2008.

[20]Z. Lei, J. Zhang and X. Zhao, "Ultrathin MnO₂ nanofibers grown on graphitic carbon spheres as high-performance asymmetric supercapacitor electrodes," *J. Mater. Chem.*, vol. 22, pp. 153-160, October 2012.