

Research Article

Electrodeposition of Mesoporous Co_3O_4 Nanosheets on Carbon Foam for High Performance Supercapacitors

Zhemi Xu,¹ Adnan Younis,¹ Dewei Chu,¹ Zhimin Ao,² Haolan Xu,³ and Sean Li¹

¹ School of Materials Science and Engineering, The University of New South Wales, Sydney, NSW 2052, Australia

² School of Chemistry and Forensic Science, University of Technology Sydney, Sydney, NSW 2007, Australia

³ Ian Wark Research Institute, University of South Australia, Adelaide, SA 5000, Australia

Correspondence should be addressed to Dewei Chu; d.chu@unsw.edu.au

Received 25 October 2013; Revised 27 December 2013; Accepted 5 January 2014; Published 4 March 2014

Academic Editor: Xinhao Li

Copyright © 2014 Zhemi Xu et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Metal oxide nanosheets have promising potential applications in novel energy storage devices. In this work, Co_3O_4 nanosheets/carbon foam with excellent supercapacitor characteristics was successfully fabricated, without using metal substrates. The experimental results demonstrate that the electrochemical tests showed that the as-prepared Co_3O_4 nanosheets exhibited an ideal capacitive behavior with a maximum specific capacitance of 106 F/g in 1 M NaOH solution at a scan rate of 0.1 V s^{-1} .

1. Introduction

Recently, two-dimensional nanosheets have attracted a lot of research interest because of their unique physical and chemical properties. For example, metal hydroxide and oxide nanosheets have been shown to have excellent electrochemical energy storage capabilities in supercapacitors, owing to their large specific surface area, exceptionally small thickness, and quantum size effects [1]. Specially, Co_3O_4 as an attractive pseudocapacitive material has been investigated for a long time because of its high theoretical specific capacitance (3560 F g^{-1}), well-defined electrochemical redox activity, and low cost [2–4].

It is known that only surface atoms or a very thin layer of active electrode materials play a key role during the pseudocapacitive process and the electrochemical activities of electrodes are closely related to the microstructures of active materials. The bulk aggregates of Co_3O_4 limit the full use of the inner active materials. To date, there are many reports on Co_3O_4 with different morphologies (whisker-like, flower-like, hexagonal nanosheets, and nanocone-like) to improve the electrochemical performance, by using hydrothermal approaches. Recently, thin film of Co_3O_4 nanosheets has been electrodeposited on metal (e.g., Ni and Ti) substrates [5]. Electrodeposition represents a facile, low temperature, low

cost, and large scale approach to fabricate various metal hydroxide and oxide thin films, and thus it has great potential applications for depositing supercapacitor materials compared with other methods, for example, hydrothermal, sol-gel, and spin coating. However, most of these reports utilize metal as substrate [6]. For practical applications, metal substrates have some limitations such as cost, weight, and corrosion problems.

Herein, we report a facile method to synthesize Co_3O_4 nanosheets on carbon foam by one step electrochemical deposition followed by annealing, meanwhile, for comparing, annealing was replaced by UV irradiation at room temperature. Carbon foam is inexpensive, lightweight, fire resistant, impact-absorbing, and with good electrical conductivity. As a result, the ultrathin nanosheets obtained here are suitable for industrialization owing to the simple synthetic procedures and reaction conditions.

2. Experimental Section

Electrochemical deposition was carried out by using an Autolab 302N electrochemical workstation. A standard three-electrode setup in an undivided cell was used. Carbon foam (Duocel 80 PPI) was used as the working electrode

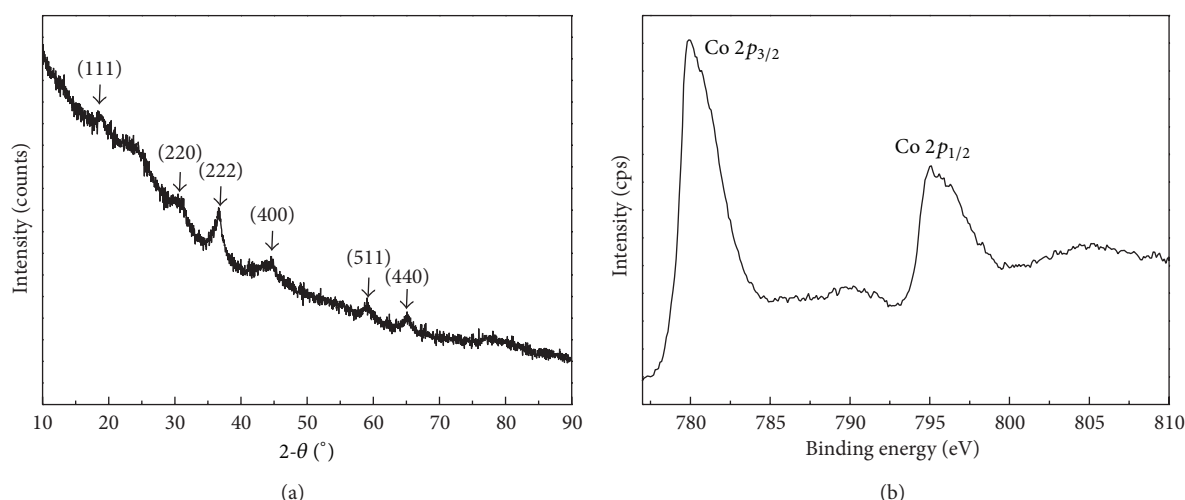


FIGURE 1: (a) X-ray diffraction pattern and (b) Co 2p XPS spectra of mesoporous Co₃O₄ nanosheets on carbon foam.

while platinum foil (0.2 mm × mm 10 mm × 20 mm) was used as the counter electrode. The distance between the two electrodes was 30 mm. The reference electrode was an Ag/AgCl electrode in 4 M KCl solution, against which all the potentials reported herein were measured.

The Co₃O₄ was electrodeposited in a solution of 0.1 M Co(NO₃)₂·6H₂O at −0.8 V for 20 min, at 70°C. The as-deposited films were dried in vacuum oven at 200°C for 2 h, and to compare, films were dried under UV irradiation for 1 h. The phase composition of the samples was characterized by X-ray powder diffraction (PANalytical Empyrean with Cu Kα). X-ray photoelectron spectroscopy (XPS) was performed with an ESCALAB 250Xi spectrometer using a monochromatized Al K-alpha X-ray source (hν) of 1,486.6 eV with 20 eV pass energy. The morphologies of the samples were observed by scanning electron microscopy (Nova NanoSEM 230) and transmission electron microscopy by (Philips CM200). To measure the supercapacitor property of the films, cyclic voltammetry (CV) and galvanostatic charge-discharge measurements were performed on Autolab 302N to evaluate the electrochemical performances of the synthesized nanostructured Co₃O₄ materials.

3. Results and Discussion

Figure 1(a) shows the XRD pattern of mesoporous Co₃O₄ nanosheets prepared on carbon substrate. All peaks are assigned to cubic lattice of Co₃O₄ (*hkl* indices are indicated), which could be indexed to a cubic spinel lattice belonging to the Fd3m space group. Both the position and the relative intensities of the above diffraction lines are in agreement with data corresponding to JCPDS file Number 9-418 with no CoO or other impurities detected.

The chemical composition of mesoporous Co₃O₄ nanosheets was investigated by XPS analysis. The spectrum of Co 2p was acquired and processed using standard XPS peak fitting. Two peaks at binding energies of 780 and 795 eV were observed from the Co 2p spectra. The tetrahedral Co²⁺ and octahedral Co³⁺ can be contributed to the spin-orbit

doublet 2p spectral profile of Co₃O₄. Besides, the relatively sharp peak widths correspond to 2p_{1/2} and 2p_{3/2} with separation of 15 eV, and the weak satellite structure found in the high binding energy side of 2p_{3/2} and 2p_{1/2} transitions indicates the coexistence of Co(II) and Co(III) on the surface of the nanosheet. Therefore, the Co 2p spectrum is well consistent with the XPS spectrum of Co₃O₄.

The surface morphology of electrodeposited Co₃O₄ on carbon foam is shown in Figure 2. As can be found in Figure 2(a), multilayers of Co₃O₄ are formed on carbon foam.

The detailed microstructures of the Co₃O₄ nanosheets were provided by TEM characterizations. Figure 3(a) represents typical TEM images of Co₃O₄ which shows sheet-like structure. Also many small visible pores are observed in the nanosheet. The high-magnification HRTEM in the inset of Figure 3(c) clearly shows lattice fringes with a d-spacing of 0.46 nm (111) which matches well with the XRD pattern. To further elucidate the composition, the SEM-EDS (energy dispersive X-ray spectroscopy) of the Co₃O₄ nanosheet was also conducted, and Co and O elements were detected (not shown here).

Figure 4(a) shows the CV curves of Co₃O₄/carbon foam at the different scan rates of 0.1, 0.2, and 0.5 V s^{−1}. All the CV curves are close to rectangular shape. In addition, the linear increase of the current with the increasing scan rate indicates that the charge is primarily nonfaradic in nature. The charge-discharge behavior of Co₃O₄/carbon foam was examined by galvanostatic charge-discharge method at a constant current density of 0.05 in the potential range from 1 to −1 V. Figure 4(b) shows the typical galvanostatic charge-discharge curve of Co₃O₄/carbon foam. It can be seen that the entire curve is linear, which indicates that the electrode has ideal capacitive characteristics and an excellent electrochemical reversibility. The specific capacitance (F/g) can also be calculated from the galvanostatic charge-discharge curve using the following equation:

$$C = I * \frac{\Delta V}{\Delta t}, \quad (1)$$

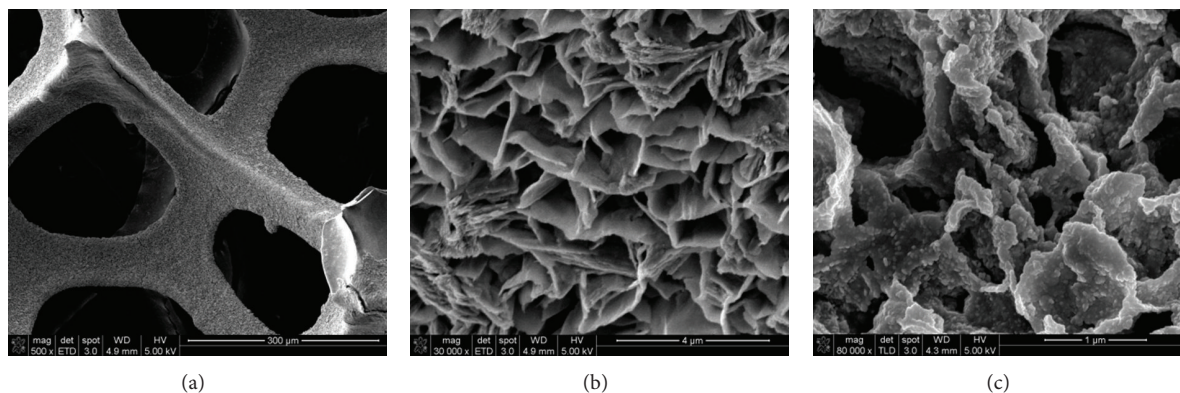


FIGURE 2: SEM images of mesoporous Co_3O_4 nanosheets on carbon foam.

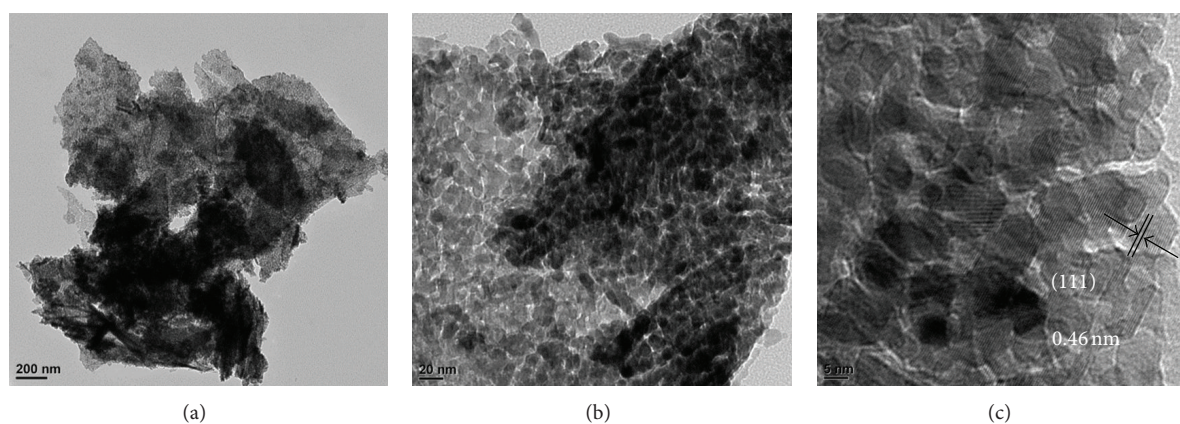


FIGURE 3: (a), (b) TEM images and (c) HRTEM image of mesoporous Co_3O_4 nanosheets.

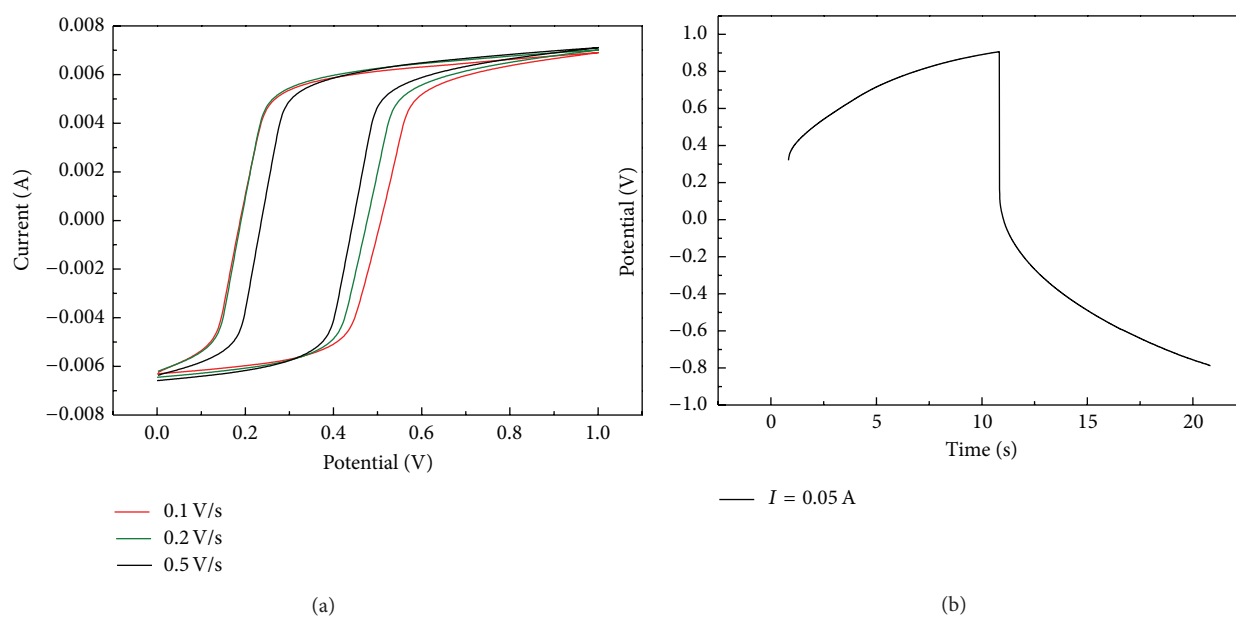


FIGURE 4: (a) Cyclic voltammetric response and (b) galvanostatic charge-discharging curve of Co_3O_4 /carbon foam obtained in 1 M NaOH solution at different scan rates.

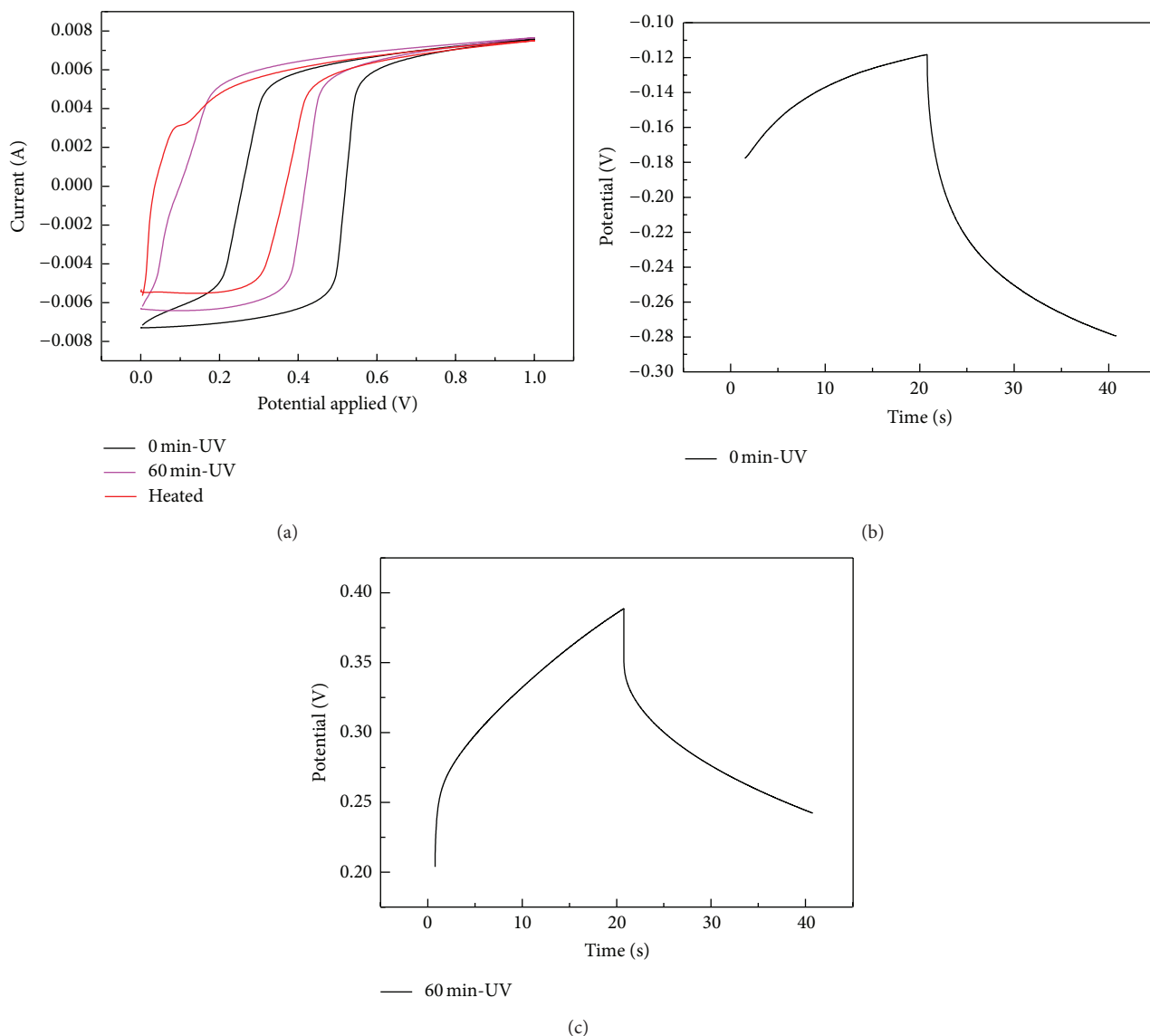


FIGURE 5: (a) Cyclic voltammetric response, (b) galvanostatic charge-discharging curve of $\text{Co}_3\text{O}_4/\text{carbon foam}$ by UV irradiation, and (c) galvanostatic charge-discharging curve of $\text{Co(OH)}_2/\text{carbon foam}$.

where I is the discharge current (A), ΔV is the potential window (V), Δt is the discharge time (s), and g is weight of Co_3O_4 nanosheets (g). The specific capacitances of Co_3O_4 nanosheets are 83, 86, and 106 F/g at constant current densities of 0.02, 0.03, and 0.05 A, respectively.

To compare and ensure the high performance of supercapacitor Co_3O_4 , Co_3O_4 samples from Co(OH)_2 with different reaction conditions were compared. According to the work of others⁴, UV irradiation can induce the transition of Co(OH)_2 to Co_3O_4 as well. Hence, the capacitances of pure Co(OH)_2 , Co_3O_4 , from being heated under 200°C for 1 h, and Co_3O_4 after UV irradiation for 1 h were tested. Figure 5(a) shows the CV curves of $\text{Co}_3\text{O}_4/\text{carbon foam}$ prepared through heart and UV irradiation at the scan rates of 0.1 V s^{-1} , respectively. Near-rectangular shape was observed in all the curves.

Specifically after UV irradiation or heated, Co(OH)_2 transitioned to Co_3O_4 , and a significant stretching in the boundaries of CV curve can be found, which means the capacity of Co_3O_4 is better than that of Co(OH)_2 . The charge-discharge behavior of $\text{Co}_3\text{O}_4/\text{carbon foam}$ by UV irradiation and $\text{Co(OH)}_2/\text{carbon foam}$ was examined by galvanostatic charge-discharge method in the potential range from 0.2 to -0.4 V and from -0.3 to -0.1 V , respectively. Figure 5(b) shows the typical galvanostatic charge-discharge curve of $\text{Co}_3\text{O}_4/\text{carbon foam}$ by UV treatment and Figure 5(c) shows that of $\text{Co(OH)}_2/\text{carbon foam}$. It can be seen that the electrode has ideal capacitive characteristics and an excellent electrochemical reversibility. As it can be calculated as the specific capacitances of Co_3O_4 nanosheets after heated, the specific capacitances of Co_3O_4 nanosheets by UV treatment are 180 F/g and that of $\text{Co(OH)}_2/\text{carbon foam}$ are only 8 F/g.

4. Conclusion

In summary, mesoporous Co_3O_4 nanosheets have been successfully prepared by a simple, green, and inexpensive electrochemical deposition method and employed as a supercapacitor electrode. XRD and TEM results confirmed the phase purity and nanocrystalline structure of Co_3O_4 nanosheets. The electrochemical tests showed that the as-prepared Co_3O_4 nanosheets exhibited an ideal capacitive behavior with a maximum specific capacitance of 106 F/g in 1 M NaOH solution at a scan rate of 0.5 V s^{-1} .

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

Acknowledgment

The authors would like to acknowledge the financial support from the Australian Research Council Project of DP110102391 and DE 120100042.

References

- [1] S. I. Shin, A. Go, I. Y. Kim, J. M. Lee, Y. Lee, and S.-J. Hwang, "A beneficial role of exfoliated layered metal oxide nanosheets in optimizing the electrocatalytic activity and pore structure of Pt-reduced graphene oxide nanocomposites," *Energy & Environmental Science*, vol. 6, no. 2, pp. 608–617, 2013.
- [2] S. K. Meher and G. R. Rao, "Ultralayered Co_2O_4 for high-performance supercapacitor applications," *The Journal of Physical Chemistry C*, vol. 115, no. 31, pp. 15646–15654, 2011.
- [3] X.-H. Xia, J.-P. Tu, Y.-Q. Zhang et al., "Freestanding Co_2O_4 nanowire array for high performance supercapacitors," *RSC Advances*, vol. 2, no. 5, pp. 1835–1841, 2012.
- [4] H.-W. Shim, A.-H. Lim, J.-C. Kim et al., "Scalable one-pot bacteria-templating synthesis route toward hierarchical, porous- Co_3O_4 superstructures for supercapacitor electrodes," *Scientific Reports*, vol. 3, article 2325, 2013.
- [5] H. Zhang, Y. Chen, W. Wang et al., "Hierarchical Mo-decorated Co_3O_4 nanowire arrays on Ni foam substrates for advanced electrochemical capacitors," *Journal of Materials Chemistry A*, vol. 1, no. 30, pp. 8593–8600, 2013.
- [6] C.-W. Kung, H.-W. Chen, C.-Y. Lin, R. Vittal, and K.-C. Ho, "Synthesis of Co_3O_4 nanosheets via electrodeposition followed by ozone treatment and their application to high-performance supercapacitors," *Journal of Power Sources*, vol. 214, pp. 91–99, 2012.

