Dodecyl Sulfate Induced Fast Faradic Process in Nickel Cobalt Oxide/Reduced Graphite Oxide Composite Material and Its Application for Asymmetric Supercapacitor Device

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Supercapacitors are a kind of important energy devices, which provide transient but high power output for various machines and devices. Early transition metal oxides, such as MnO_2, V_2O_5, NiO, and Co_3O_4, are a group of very promising supercapacitor electrode materials to replace expensive and toxic RuO_2. However, the intrinsic low conductivity of these metal oxides limited the performance of supercapacitor. Graphene, a two dimensional carbon material, has attracted plenty of interests due to its high conductivity.[1] Especially for supercapacitor application, it has been well established that the relatively high conductivity of rGO in electrode material matrix gives rise to enhanced electrochemical performance. Despite enhancing the conductivity of material matrix, little work has been reported dealing with enhancing the conductivity of metal oxide. $NiCo_2O_4$ has two orders higher electron conductivity compared with pure NiO or Co_3O_4 (10^{-3}~10^{-2} S cm^{-1}). It is documented to have 62 S cm^{-1} for single crystal $NiCo_2O_4$ nanoplate at room temperature.[2] This makes it highly attractive for the rGO composite electrodes.

Here, we present a facile preparation of nickel cobalt oxide/reduced graphite oxide ($NiCo_2O_4$/rGO) composite material with enhanced electrochemical performance.[3] Dodecyl sulfate anion intercalated NiCo layered double hydroxides-graphite oxide composite material was synthesized first. During heat treatment, the decomposition of long alkane chain triggers the formation of ultrasmall $NiCo_2O_4$ nanocrystals anchored on rGO sheet (Figure 1a). Electrochemical impedance investigation shows that SDS helps to reduce the equivalent series resistance of composite material. Moreover, a fast Faradic process is enabled as demonstrated by Trasatti procedure.[4] As shown in Figure 1b, the instant charge storage (outer charge) is increased from 181.5 C g^{-1} to 491.5 C g^{-1}, indicating an enhancement in readily accessible material for electrochemical reaction. Meanwhile, the total charge stored by Faradic reaction is also greatly improved due to the effect of SDS.

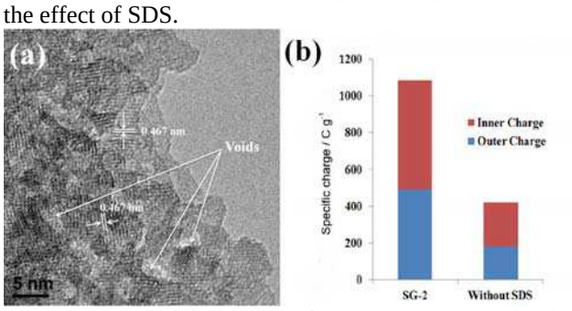

Figure 1. (a) HRTEM image of $NiCo_2O_4$/rGO sample; (b) comparison of fast Faradic process (outer charge storage) and slow faradic process (inner charge storage) between $NiCo_2O_4$/rGO sample prepared with/without SDS.

As a result, this composite material gives a high specific capacitance of 1222 F g^{-1} at 0.5 A $g^{-1}$and 768 F g^{-1} at 40 A g^{-1}, showing an outstanding rate capability. Moreover, the longtime cycling stability of $NiCo_2O_4$/rGO composite material is also excellent (91.6 % retention after 300 cycles).

Asymmetric supercapacitor device with high energy and power densities has been successfully assembled based on $NiCo_2O_4$/rGO composite material and activated carbon. As shown in Figure 2a and b, an optimized asymmetric device shows a high capacitance of 99.4 F g^{-1} at 0.5 A g^{-1} and 44.6 F g^{-1} at 20 A g^{-1}, operating within 0~1.3 V. Ragone plot is shown in Figure 2c. This device shows high energy density of 23.3 Wh kg^{-1} at a power density of 324.9 W kg^{-1}, while maintains a high energy density of 10.5 Wh kg^{-1} at a power density of 12.99 kW kg^{-1}. This result shows a much improved energy density at high power density comparing with previous reports.[5, 6, 7] Moreover, this asymmetric device shows a good stability towards multistage current charge-discharge cycles, as shown in Figure 2d.

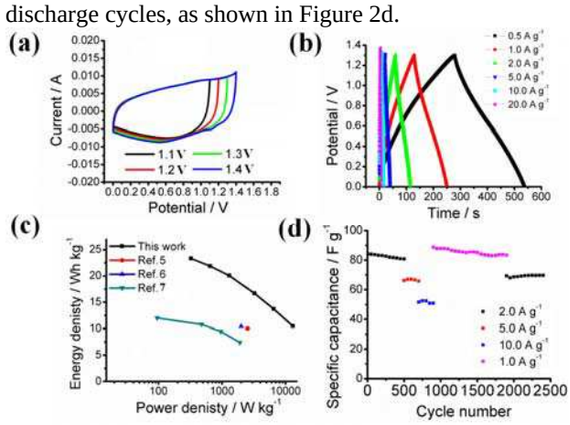

Figure 2. (a) CV curves of $NiCo_2O_4$-rGO/AC asymmetric supercapacitor cell measured at different potential window in 2M KOH electrolyte; (b) charge-discharge curves of different current densities; (c) Ragone plot of $NiCo_2O_4$-rGO/AC asymmetric supercapacitor; (d) cycling test of $NiCo_2O_4$-rGO/AC asymmetric supercapacitor at different current densities.

In summary, we have successfully synthesized $NiCo_2O_4$-rGO composite material with enhanced electrochemical performance. Dodecyl sulfate is beneficial to reduce the resistance in the material and increase the charge storage ability of the composite material.

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