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RAPID COMMUNICATION

Chlorine-doped carbonated cobalt hydroxide for supercapacitors with enormously high pseudocapacitive performance and energy density

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Abstract
Development of supercapacitors which exhibit high energy density without much compromise on power density is a great challenge. Although the pseudocapacitors are very promising in this regard but only surface redox reactions are not sufficient to solve future energy demands. Thus the involvement of the entire electrode materials in Faradaic redox reaction is necessary for excellent results. Here, we have synthesized well-defined and self-stabilized chlorine-doped carbonated cobalt hydroxide ($Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$) nanowires (NWs) composed of discrete particles (which allow the involvment of entire NW) *via* a facile hydothermal method for supercapacitors to introduce the concept of deep Faradaic redox reaction. The engineered structure and unique composition along with define porosity, existence of structure stabilizer counter anions and hydrophilic nature of NWs allow deep diffusion of electrolyte ions. The NWs have shown extraordinary capacitance (9893.75 F/g at 0.5 A/g) and excellent energy density (220 W h/kg) along with high rate capability and stability for 10,000 cycles. We believe that higher energy density devices can be developed using our concept of deep Faradaic redox reactions which will help the practical realization of supercapacitors.

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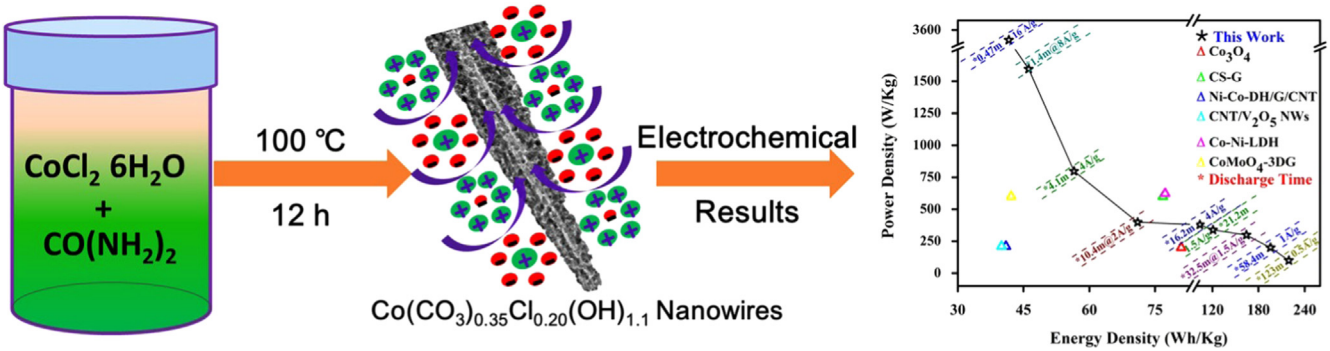
Introduction

Efficient and environmentally benign resources of energy are critical to overcome the limited availability of fossil fuels and concerns regarding the environment. The most pressing challenge is to develop fast and efficient energy storage devices so that the numerous applications of energy resources can be extended from portable electronics to electrical vehicles [1-3]. Nanoscience is of a critical importance in the advancement of energy storage by developing new materials with low cost and stringent safety requirements to fulfill the high desire of energy storage. Among various energy storage devices, lithium ion batteries (LIBs) with high energy density (150-200 W h/kg) and supercapacitors (SCs) with excellent power densities (10 kW/kg) are two of most promising candidates [4,5]. Especially, SCs have attracted tremendous attentions as a promising energy storage device owing to their high power densities, light weight and high portability [6,7]. However, the major bottleneck in the applications of SCs is their low energy densities regardless of high power densities in contrast to LIBs [8-10]. Generally there are two types of SCs, classified by the underlying energy storage mechanisms: electrical double layer capacitors (EDLCs) which store energy by accumulation of charges in the electrical double layer *via* electrostatic interactions at the electrode-electrolyte interface [11-15], and pseudocapacitors which store energy *via* Faradaic redox reaction at electrode surface with enhanced capacitance [16-19]. Many researchers make endeavors to improve the energy density of SCs for practical utilization, offering fast and safe availability of energy at low cost [20]. Initially, carbon-based materials are investigated but limited energy density remains great challenge to develop EDLCs with high capacitance because of simple accumulation of charges on the surface of electrode [7,13,21-23]. To increase the energy density of SCs, pseudocapacitors with Faradaic redox reaction were utilized and offered largely enhanced capacitance [24-29]. However, the reported highest energy density of SCs is still much lower than that of LIBs [30], where the energy density of the SCs depends on the capacitance (C) and the cell potential (V), $E=1/2CV^2$ [31]. Thus the enhancement of energy density mainly depends on the above two parameters (C and V) which are strongly affected by the size, morphology, porosity, structure, crystallinity and composition of the electrode material [1,12,17,32].

Transition metal oxides, hydroxides such as RuO_2, MoO_2, NiO, Co_2O_3, MnO_2, $Co(OH)_2$ and $Ni(OH)_2$ *etc*. and their binary systems can deliver high capacitance and energy densities are advantageous alternatives to EDLCs [9,28,29,33-39]. To improve the conductivity, life cycles and capacitance, these materials are composited with conducting substrates like carbon, graphene, carbon nanotubes and gold [1,16,40]. Recently, there are intensive interests in metallic layered double hydroxides (LDHs) with general formula $[M^{2+}_{1-x}M^{3+}_x(OH)_2]^{x+}[A^{n-}_{x/n}\cdot mH_2O]^{x-}$, where M^{2+} and M^{3+} are divalent and trivalent metal ions and A^{n-} is charge balancing counter anion [41], because LDHs with such a unique structure and compositions bring higher energy density and capacitance values. However, to best of our knowledge, there is no report of SCs with compatible energy densities to LIBs or with exceptional values of capacitance that guarantee SCs towards practical energy storage devices for electric vehicles. Recently, Chen et al. reported cobalt-nickel layered double hydroxide nanosheets as electrode for SCs with energy density of 77.3 W h/kg at a power density of 623 W/kg as best example for ultrahigh energy density, but it is still much lower than energy density of LIBs [41]. Yu et al. reported energy density 42.2 W h/kg at power density of 600 W/Kg for $CoMoO_4$-3D graphene hybrid electrode [42]. The SCs show low energy densities due to the fact that only the surface materials take part in the Faradaic redox reaction, while most of the bulk materials play no role in the reaction, consequently leading to limited capacitance and energy density [43]. Furthermore, Mai et al. introduced a new concept to utilize the redox-active electrolyte by the addition of $CuCl_2$ in electrolyte to enhance the surface redox reaction and got 10-fold improved capacitance (4700 F/g) using carbon as electrode [44]. Similarly, Zhao et al. reported the use of $K_3Fe(CN)_6$ as redox-active additive to improve the capacitance of $Co(OH)_2$/graphene hybrid and achieved high values of capacitance up to 7514 F/g but complex system here is the main hurdle for their real applications [45]. Thus, to achieve both maximum capacitance and energy density, electrode materials should be synthesized precisely with unique composition and structure where entire material can take part in redox reaction and also should exhibit good cyclic stability [1,3,39,41].

To reach the above ideology, we have synthesized chlorine-doped carbonated cobalt hydroxide ($Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$) nanowires (NWs) with unique structure *via* facile, effective and scaled-up approach without tedious step involvement, as shown in Scheme 1. These engineered cobalt hydroxide NWs were used as SCs electrodes and showed unprecedentedly high



Scheme 1 Schematic representation of hydrothermal synthesis of $Co(CO_3)_{0.35}Cl_{0.20}(OH)_{1.10}$ NWs, resulted unique structure with illustration of deep ionic diffusion and outstanding electrochemical performance.