Preparation of $Co(OH)_2$/HY composite and its electrochemical capacitance characteristics

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Physical and chemical properties of substances can be considerably altered when they are exhibited on a nanoscopic scale, thus, nanoscale technology is not simply a miniaturization in sizes, but an in-depth revolution in physical concepts, system design, materials synthesis and manufacturing [1]. Now expectations concerning the application of nanomaterials as the upcoming functional material for the 21st century are rising [2]. In the present report a new composite material (designated as $Co(OH)_2$/HY) of cobalt hydroxide and HY zeolite molecular sieves with anisotropic inorganic nanostructure was prepared. A self-organization-like process was used. The performance as an active electrode material for electrochemical capacitors (or supercapacitors) was studied. These combine the advantages of both dielectric capacitors that can deliver high power within a very small period and rechargeable batteries that store high energy [3].

Cobalt hydroxide is usually added for the purpose of enhancing the performance of $Ni(OH)_2$ as a battery active material. Many electrochemical studies of $Ni(OH)_2$ have been reported, whereas studies of $Co(OH)_2$ are quite sparse [4, 5]. In this report the new composite material was studied as an active electrode material for its electrochemical capacitor characteristics. As a result, we obtained a very high specific capacitance of 483 F/g from our prepared bulk composite in the solution of 2 M KOH, which to our knowledge, is far higher than the highest reported [4, 6] so far for supercapacitors using pure $Co(OH)_2$ electrodes. In addition, a possible anisotropic morphology formation mechanism by which the growth proceeds is tentatively worked out.

HY was prepared by repeated sodium exchange of zeolite NaY (LZPCC, Lanet-Y30), Si/Al = 3, with aqueous of NH_4NO_3 at 35 °C for 14 h. The composite was prepared by a coprecipitation-like method. In the first case, 6.7 ml cobalt chlorite hydrate solution ($CoCl_2{\cdot}6H_2O$; 1.5 M) was mixed with 35 ml emulsoid liquid of HY (6 wt%) with continuous magnetic stirring. 30 min later, the pH of the mixture system was slowly adjusted to 9 with 5 wt% ammonium hydroxide at a temperature of 10 °C and the mixture system obtained was deposited at the same temperature for 3 h. Then, the resulting composite powder was filtered, washed with distilled water several times and dried at a temperature of 100 °C. Finally, the composite of 30% $Co(OH)_2$ loading was prepared. The working electrodes were prepared according to the literature [7]. The surface area of the obtained composite electrode was about 1 cm^2. Electrochemical tests of the working electrodes were carried out with an electrochemical working station (CHI-660 model, Shanghai) in a standard three-electrode cell at room temperature. A platinum gauze and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. 2 M KOH in aqueous solution worked as the electrolyte. The specific capacitance of the test electrode was calculated by $I \times \Delta t/(\Delta V \times m)$, where I is the constant discharging current, Δt is the discharging time, which was measured from −0.15 to 0.45 V in the V-t cure, the voltage change ΔV at a constant current discharge, and m the mass of composite (for the specific capacitance of the composite) or single $Co(OH)_2$ (for the specific capacitance of the effective component) loaded on the working electrode. Their morphology and microstructure were investigated by both scanning electron microscope and transmission electron microscopy (HREM, JEDL-2010 model).

As shown in Fig. 1A and B, the pure HY has a morphology of irregular particles, with a typical particle diameter of ~800 nm and shows a good dispersity characteristic. The irregular particle morphology implies that the HY has a high crystallization structure. This can be further testified by the selected area electron diffraction (SEAD) pattern recorded from pure HY. Comparing both Fig. 1A and B with Fig. 1C and D reveals that after HY was loaded with the $Co(OH)_2$ compound, a fundamental morphology change had taken place on the outer surface of the HY, which means that there were amounts of a whisker-like compound on it. It is important to note that the whisker-like compound showed anisotropic morphology characteristics and a loosely packed microstructure that has been down to nanometer.

To identify the prepared compound on the surface of HY, FTIR spectroscopy (Cu K_α, 30 V–30 mA, Rint2000, Rigaku, Japan), which is sensitive to the short-range order present in a compound, is used. As shown in Fig. 2A, with increasing $Co(OH)_2$ content, the stretching absorbance of the OH (including the α-cage OH, β-cage OH and the OH group of H_2O absorbed by HY) was intensively split by the very

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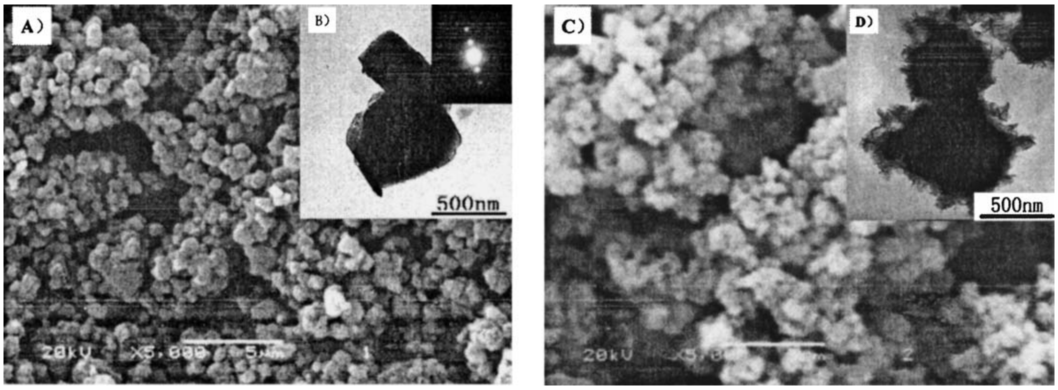

Figure 1 SEM and TEM images of pure HY and $Co(OH)_2$/HY composite. (A) and (B) Pure HY; (C) and (D) $Co(OH)_2$/HY composite with 30 wt% $Co(OH)_2$ loading.

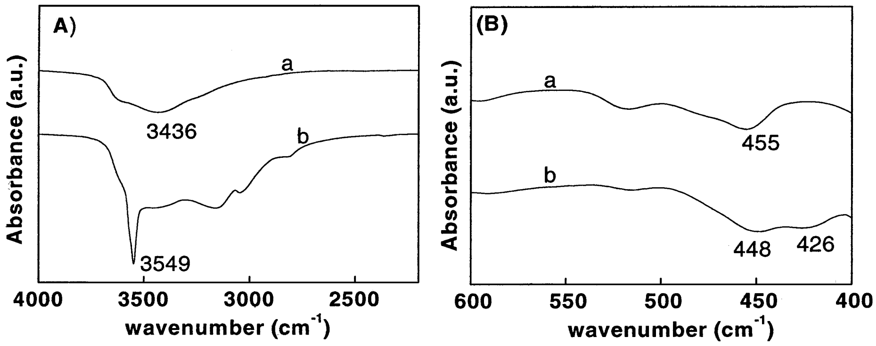

Figure 2 FTIR spectrum of pure HY and composite. (Curve a): pure HY; (Curve b): $Co(OH)_2$/HY composite.

strong OH stretching absorbance of $Co(OH)_2$ that appeared at a frequency of 3549 cm^{-1} and the another characteristic peak, Co-O stretching absorbance of $Co(OH)_2$, appeared at a frequency of 426 cm^{-1} (Fig. 2B). Thus, the $Co(OH)_2$, the molecule of the loaded compound, was obtained. Owing to too small a crystallite size, XRD reflection of $Co(OH)_2$ was not detected for the composite powder.

To understand the reasons why the resulting $Co(OH)_2$ can grow around the outer surface of HY rather than largely forming a single phase, it is necessary to first acknowledge some related characteristics of a HY molecule sieve. Besides amounts of SiO_4 tetrahedral units, it is well known that there are also many tetrahedral units of AlO_4^- embed in the structure of HY. These AlO_4^- can absorb positive ion (such as H^+ ions) in order to keep the electroneutrality condition of the HY system. More importantly, according to the ion and potential selectivity rule of HY [7], when Co^{2+} ions were introduced into the reaction system, some Co^{2+} ions would be preferably be absorbed by AlO_4^-. As a result, a decreasing concentration gradient toward the solution would emerge. Then, with the increasing pH, the $Co(OH)_2$ precipitation would form on the surface of the HY. Sequentially, the first resultant precipitation would provide nucleation centers resulting in more and more $Co(OH)_2$ precipitation.

Based on the above discussions, we can use Fig. 3 to describe the growth mechanism of $Co(OH)_2$ on the surface of HY.

As with any other electrochemical system, supercapacitors also essentially involve process at the interface between an electrode and an electrolyte solution. The larger the area of the interface, the larger will be the rate of the process. Considering the microstructure characteristics of the prepared composite and the electrochemical property of $Co(OH)_2$, we directly use this material to make the electrode of supercapacitors. The applicability of the electrode was evaluated by means of chrono-potentiometric, cyclic voltammograms. Fig. 4A

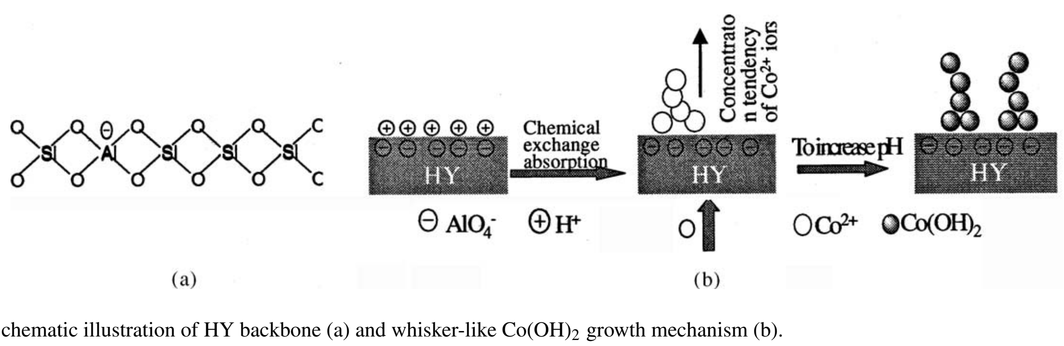

Figure 3 Schematic illustration of HY backbone (a) and whisker-like $Co(OH)_2$ growth mechanism (b).

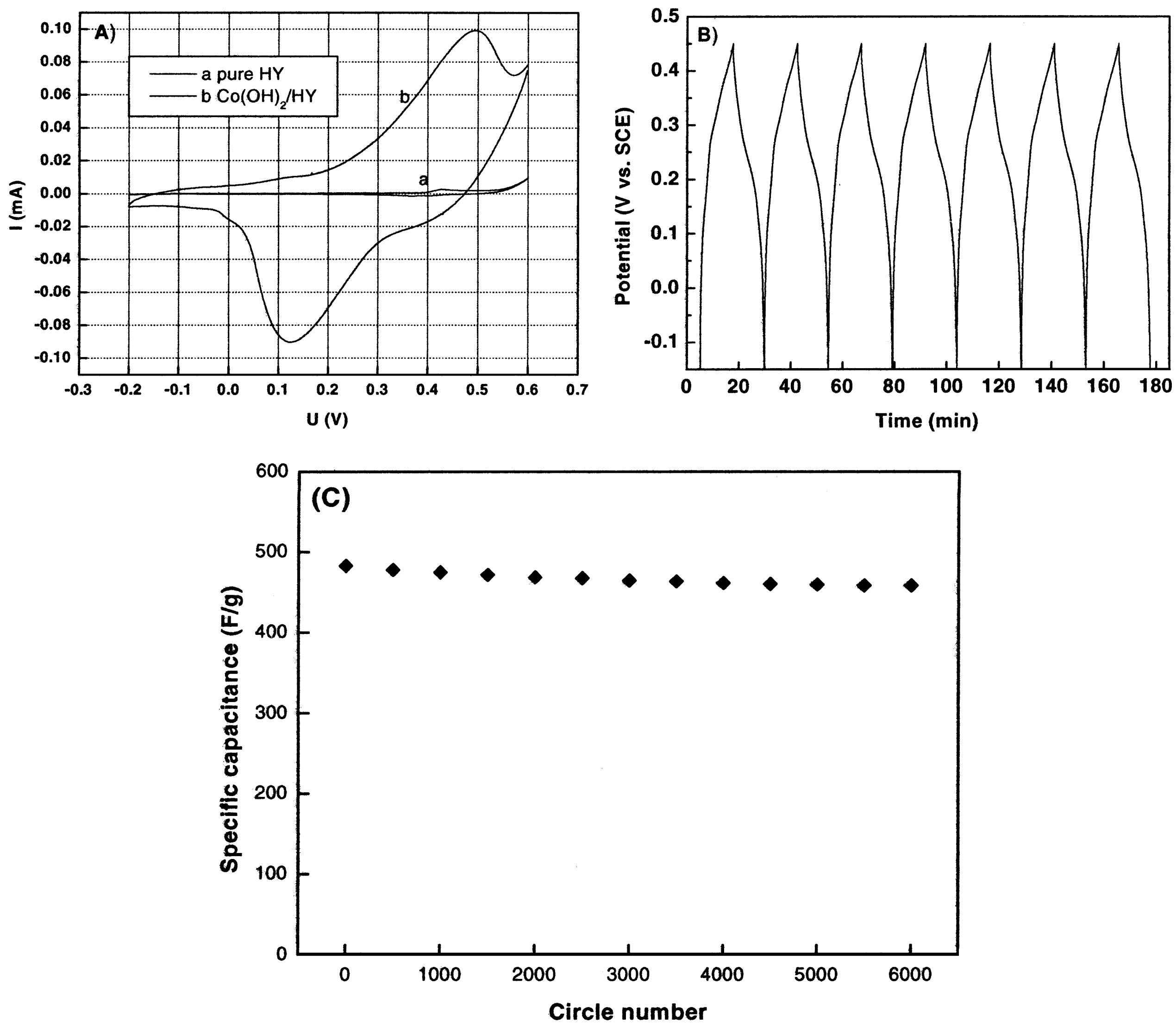

Figure 4 Electrochemical properties of pure HY and composite. (A) Cyclic voltammetric (CV) behavior at sweep rates of 10 mV/s; (B) discharging curves of $Co(OH)_2$/HY composite electrode in 2 M KOH within a potential window of −0.15 to 0.45 V vs. SCE at a discharging current of 4 mA/cm^2. (C) Specific capacitance of $Co(OH)_2$/HY in 2 M KOH as a function of the cycle number. The working electrodes contain 30 mg pure HY or composite.

shows the cyclic voltammetic (CV) behavior of the fabricated HY (curve a) and composite electrode (curve b). Obviously, the negligible integral area (curve a) indicates that the $Co(OH)_2$ of the composite is responsible for the measured capacitance. Furthermore, the shape of the CV (curve b) reveals that the capacitance characteristic is very distinguished from that of the electric double layer capacitance, in which case the CV curve is close to the ideal rectangular shape. This indicates that the measured capacitance is mainly based on the redox mechanism. According to the average value of peak potential of P_1 vs. P_2, peak P_1 is due to the oxidation of $Co(OH)_2$ to COOH and peak P_2 is for the reverse process. Furthermore, as shown in curve b, the potential difference of P_1 and P_2 is larger than the 0.2 V, which is far higher than the theoretic ΔE_p value of 0.058 V for a reversible, single-electron transfer process. It is thereby inferred that this reaction occurs as a quasi-reversible process during the cathodic potential sweep of the composite electrode.

Fig. 4B shows the charge-discharge behavior of the composite electrode. The shape of the charge-discharge curve displays the typical characteristic of faradaic deposition, which results in the three-dimensional absorption of the electroactive species into the bulk solid electrode material by an insertion reaction. This confirms that the measured capacitance is attributed to the supercapacitance. Furthermore, the very high specific capacitance of 483 F/g for our prepared composite is obtained from this figure, which implies the specific capacitance of effective component responsible for supercapacitance, namely single $Co(OH)_2$, is 1610 F/g.

To further obtain the utilization of $Co(OH)_2$ in composite, its theoretical specific capacitance, C_t, must be obtained. Considering that the single electron exchange redox reaction is assumed to take place in the bulk material, the C_t was estimated from: $C_t = n \times F/(\Delta V \times m)$. Where n is 1, the charge transferred, F is Faraday's constant, m is the mole mass of $Co(OH)_2$ in composite, and ΔV is the potential range from −0.15 to 0.45 V corresponding to the current measured. Then, the C_t, the theoretical specific capacitance of 1724 F/g can be obtained, a fact that reveals the very high utilization of 93 wt% for $Co(OH)_2$ in the composite (the limiting electric double-layer capacitance is neglected).

Taking account of the amphiprotic property of AlO_4^- embedded in the HY zeolite framework, there is a need to examine the electrochemical stability of the composite in 2 M KOH aqueous electrolyte. As shown in Fig. 4C, the capacitance loss rate after 6 000 consecutive cycles was negligible, about 5%, a fact that reveals the excellent electrochemical stability. This could be explained by the high Si/Al ratio of the prepared HY.

In summary, a novel strategy, which is better-suited for preparing materials with microscopic structure is described, and a composite of $Co(OH)_2$/HY was prepared using this strategy. In addition, the mechanism by which the growth proceeds are not very rigorous was worked out. Due to the high disperse capability of HY towards $Co(OH)_2$ resulting in loose whisker-like microstructures of $Co(OH)_2$, small channels became available for the diffusion of OH^- electrolyte ions through all $Co(OH)_2$ thin layers. Consequentially, the prepared composite showed very high specific capacitance. This further validated the preparation strategy presented by us.

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