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Preparation of novel nano-composite $Ni(OH)_2$/USY material and its application for electrochemical capacitance storage†

Lin Cao, Ling-Bin Kong, Yan-Yu Liang and Hu-Lin Li*
Department of Chemistry, Lanzhou University, Lanzhou 730000, China. E-mail: lihl@lzu.edu.cn

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A novel nano-composite material of $Ni(OH)_2$/USY was prepared in our lab. This nanostructure creates electrochemical accessibility of electrolyte OH^- ions to $Ni(OH)_2$ thin layers and a fast diffusion rate within the redox phase.

Numerous research groups in both academia and industry around the world are consciously increasing efforts to design and develop advanced materials with dimensions down to a few to several hundred nanometers.[1–3] Expectations of the industrial application of nanomaterials in various fields have been rising rapidly over the past few years. Materials at nanometer scales in electrochemical capacitor applications have received attention.[3–6] Even though noble metal oxides or hydrous oxides (*i.e.* ruthenium oxides) yield remarkably high specific capacitance or power density, capacitors based on this material are quite more costly when compared to other technologies.[7–10] Thus, developing alternative electrode materials with improved characteristics and performance is the next logical step. In this communication, we report for the first time a strategy to prepare nano-composite material of nickel hydroxide on ultrastable Y (USY) zeolite molecular sieves (designated $Ni(OH)_2$/USY) and its application as a novel electrochemical capacitor.

Our strategy is to use a high surface area USY zeolite as the template on which the redox active $Ni(OH)_2$ inorganic nanostructure is synthesized through ion exchange, chemical precipitation and self-directed growth processes. We demonstrate that the unique structure of the nano-composite, which presents synergistic effects of loose whisker-like $Ni(OH)_2$ phase of the order of ~ 10 nm and the fast faradaic reactions accessible to the bulk of the $Ni(OH)_2$ phase, is crucial for its high energy density as an electrochemical capacitor (or supercapacitor). As a result, we obtained a maximum specific capacitance of 583 F g^{-1} (or 1740 F g^{-1} when corrected for the weight percent of $Ni(OH)_2$ phase). This is close to the theoretical limit of the psuedo-capacitance of the redox active phase.

The preparation procedure of $Ni(OH)_2$/USY composite is described as follows: ultrastable Y (USY) was prepared by repeated proton exchange of zeolite NaY (LZPCC, China. Si : Al = 3, BET surface area = 803 $m^2\ g^{-1}$) with aqueous solution of NH_4NO_3 at 35 °C for 15 h followed by steaming at 650 °C for 3 h. $Ni(OH)_2$/USY composite was prepared by the coprecipitation method. In the first step a stoichiometric (with respect to USY) amount of nickel chloride hydrate solution (1.5 M) was mixed in a glass beaker with USY water suspension (6 wt%) using a magnetic stir bar. Thirty minutes later the pH of the mixture was slowly adjusted to 9 by dropwise addition of 5 wt% NH_4OH at a temperature of ~ 10 °C. The resulting suspension was stirred at the same temperature for an additional 3 h. Then the solid was filtered, washed with copious amounts of distilled water and dried at a temperature of 100 °C in air for 5 h. Compositions of the composite are controlled by changing the relative ratio of $NiCl_2·6H_2O$ and USY support in the starting mixture.

The working electrodes were prepared according to the literature.[11] Each electrode contains 10 mg of electroactive material measured and has a geometric surface area of about 1 cm^2. Electrochemical measurements were carried out in 2 M KOH at room temperature with a half-cell set up. A platinum gauze electrode and a saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. The electrochemical reaction is expressed as:[12]

$$Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e$$

As shown in Fig. 1A, pure USY has a morphology of granular particles with a typical particle diameter of ~ 800 nm. Comparing Fig. 1A with 1B and 1C reveals that after USY is loaded with $Ni(OH)_2$, a salient morphology change has taken place on the outer surface of USY. Morphology of $Ni(OH)_2$/USY composite appears fuzzy due to the presence of freshly deposited $Ni(OH)_2$.

When the $Ni(OH)_2$ loading is kept as low as 16.9 wt%, whiskers can anchor on the exterior of USY, Fig. 1B. We conclude that the amount of $Ni(OH)_2$ loading would impact the balance of nucleation and starburst-like whisker growth. As the loading increases, whiskers grow toward the outer space while maintaining a desired, loosely packed structure, Fig. 1C. With very high loading, such as 46.8 wt% (Fig. 1D), $Ni(OH)_2$ forms in solution due to too high a Ni^{2+} ion concentration, which thereby results in the formation of a separate $Ni(OH)_2$ phase (indicated by the arrows in Fig. 1D). It is important to note that the whisker structure shows anisotropic morphology extending from the exterior of USY to interparticle open space, and forming a loosely packed microstructure sizing down to a few nanometers with ample space in between adjacent whiskers. This unique structure provides an important morphological basis for the reversibility and bulk accessibility of faradaic reactions discussed above.

To understand the reasons why the $Ni(OH)_2$ phase can grow around the outer surfaces of USY rather than largely forming an isolated phase, it is necessary first to acknowledge some related characteristics of USY molecular sieve. During the first 30 minutes of reaction, Ni^{2+} ions undergo ion exchange with H^+ to balance the charge on AlO_4^- based on the rule that the zeolite preferentially absorbs high value cations.[13] As a result, a decreasing Ni^{2+} concentration gradient towards solution was created. Thus, with the increasing pH by NH_4OH titration, $Ni(OH)_2$ precipitation will firstly form close to the surfaces of the USY particles. Sequentially, initial precipitations provide nucleation centers that result in more and more $Ni(OH)_2$ buildup extending towards interparticle open space.

Based on the above discussions, we summarize a proposed mechanism in Fig. 2 to describe the growth of $Ni(OH)_2$ nanowhiskers on the surface of USY particles.

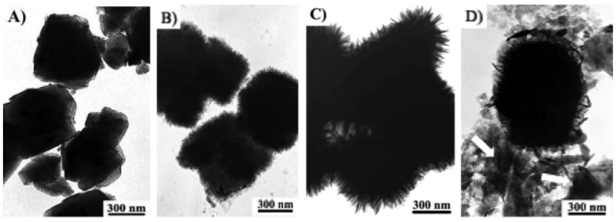

Fig. 1 TEM images of pure and composites. (A) Pure USY; (B) 16.9 wt% $Ni(OH)_2$ loading; (C) 33.5 wt% $Ni(OH)_2$ loading; (D) 46.8 wt% $Ni(OH)_2$ loading.

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† Electronic supplementary information (ESI) available: calculation method of the measured and theoretical specific capacitance. See http://www.rsc.org/suppdata/cc/b4/b401922a/

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Fig. 3A shows the cyclic voltammetric (CV) behavior of electrodes fabricated from USY (curve a) and $Ni(OH)_2$/USY composite (curve b). Obviously, the extremely small area integrated under I–V (curve a) suggests that USY alone has very small specific capacitance. Thus, the $Ni(OH)_2$ phase 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 electric double layer capacitance in which case it is normally close to an ideal rectangular shape, indicating that measured capacitance is mainly based on redox mechanism.

As shown in Fig. 3A (curve a), specific capacitance of the composite increases almost linearly with the increasing $Ni(OH)_2$ loading at low loading and reaches a maximum of 583 F g^{-1} at 33.5 wt% $Ni(OH)_2$. It is noticeable that curve b reveals the specific capacitance corrected for the weight percent of redox effective phase $Ni(OH)_2$ gradually increases to reach a peak of ~ 1740 F g^{-1} when $Ni(OH)_2$ content is 33.5 wt%. Further increase in $Ni(OH)_2$ loading above 33.5 wt% encounters a sharp decrease in both curves. The specific capacitance of pure $Ni(OH)_2$, not induced USY, is only 96 F g^{-1}. This result implies that the excess $Ni(OH)_2$ cannot be effectively dispersed by USY support and, therefore, results in the low utilization of $Ni(OH)_2$. We rationalize highly dispersed, loosely packed $Ni(OH)_2$ phase and its nanometer-sized whiskers on the exteriors of USY provide an important morphological foundation for the extraordinary high specific capacitances. This strategy to use high surface area USY zeolite as a template for the directed synthesis of redox active nano-composite plays a critical role in increasing the specific capacitance of the composite material.[2] It is interesting to note that the highest specific capacitance for $Ni(OH)_2$ phase measured, 1740 F g^{-1}, is slightly bigger than the theoretical value (1735 F g^{-1}) assuming all $Ni(OH)_2$ in the bulk is electrochemically accessible and contributes to capacitance (see ESI†). This can be explained by the contribution from double layer capacitance that may supply additional boost of observed specific capacitance.[14]

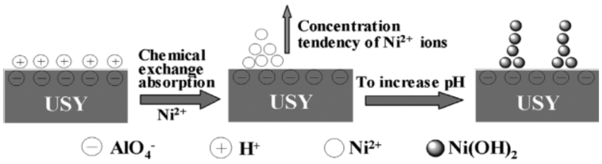

Fig. 2 Schematic mechanism of whisker-like $Ni(OH)_2$ growth on USY zeolite support.

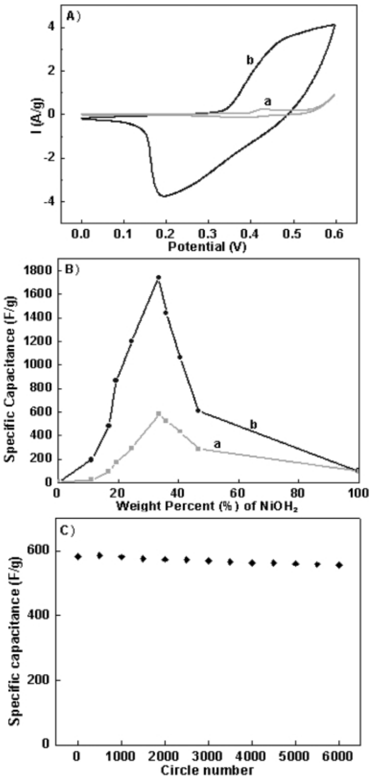

Fig. 3 Electrochemical behavior of $Ni(OH)_2$/USY composite and USY electrode in 2 M KOH. The working electrodes are about 1 cm^2 and contain 10 mg of composite or USY. (A) Cyclic voltammetric (CV) curves (curve a for pure USY; curve b for the composite of 33.5 wt% $Ni(OH)_2$ loading) at sweep rates of 10 mV s^{-1} within a potential window of 0 to 0.6 V *vs.* SCE; (B) specific capacitance of $Ni(OH)_2$/USYcomposite (curve a) and effective component (curve b) corrected for weight percent of $Ni(OH)_2$ phase as a function of $Ni(OH)_2$ loading at a discharging current of 400 mA g^{-1}; (C) the specific capacitance of $Ni(OH)_2$/USY in 2 M KOH as a function of the cycle number.

Taking account of the amphiprotic property of AlO_4^- embedded in the zeolite backbone, there is a special importance to examine the electrochemical stability of the composite in 2 M KOH aqueous electrolyte. As shown in Fig. 3C, specific capacitance loss after 6 000 consecutive cycles was negligible, at about 4.6%, a fact that proves its excellent long-term electrochemical stability. This experiment indicates repetitive cyclings do not induce noticeable degradation of the microstructure.

In summary, a new strategy to prepare materials with very unique microstructure is described. A novel $Ni(OH)_2$/USY nano-composite was successfully prepared using this strategy. Loosely packed $Ni(OH)_2$ whiskers of nanometer scale create electrochemical accessibility of electrolyte OH^- ions and fast diffusion rate through bulk $Ni(OH)_2$ thin layer, which is fundamental for materials showing characterisitics of supercapacitors rather than general batteries. Consequently, we achieved a maximum specific capacitance of 583 F g^{-1} (or 1740 F g^{-1} after correction for weight percent of $Ni(OH)_2$ phase). Even though a high concentration of precursors will result in isolated phase $Ni(OH)_2$ and lower specific capacitance of prepared material, the strategy reported should be viable to extend to other zeolitic materials and transition metal hydroxide systems. Work in this direction is ongoing in our lab.

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