Formation of one-dimensional Ag–Au solid solution colloids with Au nanorods as seeds, their alloying mechanisms, and surface plasmon resonances

One dimensional Ag–Au solid solution nanoalloys were synthesized in the form of colloids in the presence of preformed Au nanorod seeds at ambient conditions. This room-temperature spontaneous alloying process results from the vacancy/defect-motivated interdiffusion of Ag and Au atoms coupled with oxidative etching based on the deduction from high resolution transmission electron microscopy imaging. In particular, the AgAu alloy nanowires possess the Boerdijk-Coxeter-Bernal helical structure composed of twisted lattice.

As featured in:
Cobalt phosphate microarchitectures assembled by ultralong nanoribbons and their application as effective electrochemical capacitor electrode materials†

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COMMUNICATION

Cobalt phosphate (Co11(HPO3)8(OH)6) microarchitectures assembled by ultralong nanoribbons are successfully synthesized by a mild hydrothermal condition without any additives. The uniform ultralong nanoribbon has a width of 100 nm and length of 20–30 μm. More importantly, Co11(HPO3)8(OH)6 microarchitectures are also successfully applied as an electrochemical supercapacitor with a good specific capacitance (312 F g⁻¹ at 1.25 A g⁻¹), good rate capability and excellent cycling property (maintaining about 89.4% at 1.25 A g⁻¹ after 3000 cycles).

1 Introduction

Due to fast redox reactions, high specific surface areas and shortened diffusion paths in the solid phase, synthesized nanomaterials have been an important and hot field of research in electrochemical capacitors. Once Nanoribbons, one of the one dimensional (1D) nanostructures, are perfect building blocks for functional nanodevices and represent a small dimension for efficient electron transport. Commonly, the electrical conductivity is one of the most important aspects of electrode materials, which can effectively enhance the utilization of active materials and mitigate the internal resistance of the capacitors. Therefore the synthesis of one dimensional nanostructures to be used in the field of nanoelectrode materials is highly desirable for materials scientists and researchers in materials engineering who study material properties.

Recently, many efforts have been devoted to synthesize ordered superstructures and hierarchical architectures due to their interesting properties and their potential applications in many fields, including catalysis, optoelectronics, supercapacitors, lithium-ion batteries, drug delivery systems, sensors and antibacterial agents. However, methods of manipulation of these superstructures often use solid templates, which have to be removed after the reaction, but impurities can be introduced from the solid templates which can affect the properties adversely. Therefore, there is a significant interest in developing spontaneous generation of novel patterns with tailored structures and shapes by facile, hard template-free, solution-based, morphology controlled approaches to build novel self-generated architectures.

Metal phosphates exhibit broad and potential applications in catalysis. A preparation process has been used to synthesize an array of transition-metal phosphate amorphous colloidal spheres by Li et al. Therefore, they have received considerable attention, and some progresses have been made. In addition, transition metal phosphates such as cobalt phosphate can act as promising positive electrodes for rechargeable ion batteries, heterogeneous catalysts, sorbents, ion exchangers, and magnetic materials due to the layers of connected CoOx and PO4 polyhedra, the structures of known zeolite types, and are responsible for the outstanding electronic or magnetic properties. However, there are few reports about the electrochemical capacitor properties of cobalt phosphate micro/nanomaterials.

In this work, a cobalt phosphate (Co11(HPO3)8(OH)6) microarchitecture assembled by ultralong nanoribbons has been successfully synthesized by a mild hydrothermal condition without the use of any templates or surfactants. The Co11(HPO3)8(OH)6 microarchitecture is assembled by many uniform ultralong nanoribbons (width of 100 nm and length of 20–30 μm). More importantly, the Co11(HPO3)8(OH)6 microarchitecture is also applied as an electrochemical supercapacitor electrode material, which has a good specific capacitance (312 F g⁻¹ at 1.25 A g⁻¹), good rate capability and excellent cycling property (maintaining about 89.4% at 1.25 A g⁻¹ after 3000 cycles).

2 Experimental

2.1 Synthesis of Co11(HPO3)8(OH)6 microarchitecture

In a typical synthesis, 0.28 g cobalt chloride and 0.30 g sodium pyrophosphate were mixed with 20 mL deionized water. The above mixture was stirred at room temperature. Then the mixture was transferred into a 50 mL stainless-steel autoclave lined with

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polytetrafluoroethylene (PTFE, Teflon), which was sealed and maintained at 200 °C for six days. The obtained precipitates were washed several times by deionized water, ethanol, and dried in air.

2.2 Electrochemical measurement

The electrochemical study on Co11(HPO3)8(OH)6 microarchitecture electrodes was carried out on a CHI 660D electrochemical work station (Shanghai Chenhua Instrument, Inc.). All electrochemical performances were carried out in a conventional three-electrode system equipped with platinum electrode and a saturated calomel electrode (SCE) as counter and reference electrodes, respectively. Before electrochemical measurements, we purged O2 from the solution by the inert gas, Ar. The working electrode was made from the mixture of active material (Co11(HPO3)8(OH)6 micro-architecture), acetylene black, and PTFE (polytetrafluoroethylene) with a weight ratio of 80 : 15 : 5, coated on a piece of foamed nickel of about 1 cm², and pressed into a thin foil at a pressure of 5.0 MPa. The typical mass load of electrode material is 5.0 mg. The electrolyte was 3.0 M KOH solution. Cyclic voltammetry and galvanostatic charge–discharge methods were used to investigate the capacitive properties of the Co11(HPO3)8(OH)6 microarchitecture electrode. And electrochemical impedance spectroscopy measurements of all the samples were conducted at open circuit voltage in the frequency range of 100 kHz to 0.01 Hz with an AC voltage amplitude of 5 mV by using a PARSTAT2273.

2.3 Characterizations

The morphology of as-prepared samples was observed by a JEOL JSM-6701F field-emission scanning electron microscope (FE-SEM) at an acceleration voltage of 5.0 kV. The phase analyses of the samples were performed by X-ray diffraction (XRD) on a Rigaku-Ultima III with Cu Kα radiation (λ = 1.5418 Å). Nitrogen adsorption–desorption measurements were performed on a Gemini VII 2390 Analyzer at 77 K using the volumetric method. The specific surface area was obtained from the N2 adsorption–desorption isotherms and was calculated by the Brunauer–Emmett–Teller (BET) method. Transmission electron microscopy (TEM) images and HRTEM images were captured on the JEM-2100 microscopy instrument at an acceleration voltage of 200 kV.

3 Results and discussion

Fig. 1a shows the XRD patterns of the sample. Powder XRD characterizations confirm that Co11(HPO3)8(OH)6 nanocrystallites have been obtained under our experimental conditions with high purity and good crystallinity in Fig. 1a, which are indexed to be in agreement with Co11(HPO3)8(OH)6 [JCPDS NO. 44-1326]. The optical photo of the product is shown in Fig. 1b, and Co11(HPO3)8(OH)6 powder is lavender. Good crystallinity of Co11(HPO3)8(OH)6 might be good for improving the cycle life of electrodes, because its stable crystal structure is not easy to destroy during the electrochemical process.† Fig. 1c shows schematic crystal structures of the unit cell of Co11(HPO3)8(OH)6 projected based on the data of ICSD-72431. And such a one dimensional crystal structure might improve diffusion of ions or electrons.†

Fig. 1d–f shows FE-SEM images of obtained Co11(HPO3)8(OH)6 microarchitectures, and the size of the microarchitectures is 40–50 μm in Fig. 1d. It indicates that the microarchitecture almost completely consists of many ultralong nanoribbons in Fig. 1d. In the image of Fig. 1e, we can see that ultralong nanoribbons have arrayed uniformly. When assembling, there are also many nanopores formed by many overlapped layers of ultralong nanoribbons in Fig. 1e. These nanopores might offer many channels to let ions and electrolytes go through, which might enhance the travelling speed and thus bring good specific capacitances.† The width of ultralong nanoribbons is about 100 nm and the length is dozens of micrometers, which means a large aspect ratio of these ultralong nanoribbons in Fig. 1f.

We also explored the formation mechanism of the micro-architecture and found the reaction time affected the morphology of the product. The product was synthesized under different hydrothermal conditions (seen in ESI Fig. 1†). From ESI Fig. 1a and b,† micropolyhedra were obtained under 24 hours hydrothermal condition and there were some micropores on the surface of the micropolyhedra. After 72 hours hydrothermal condition, some microflower assembled nanorods were observed among these micropolyhedra in ESI Fig. 1c and d,† And after 6 days of hydrothermal condition, Co11(HPO3)8(OH)6 microarchitectures were successfully synthesized which might have formed based on the Co11(HPO3)8(OH)6 microflowers, see ESI Fig. 1e and f.† When further maintained for 10 days, the Co11(HPO3)8(OH)6 microarchitectures have been destroyed and some slices of one dimensional structures can be seen in ESI Fig. 1g and h.†

Transmission electron microscopy (TEM) images in Fig. 2a and b show the uniform ultralong nanoribbons from the Co11(HPO3)8(OH)6 microarchitecture. High-resolution TEM (HRTEM, Fig. 2c) and selected area electron diffraction (SAED) in Fig. 2d show that the nanoribbons are structurally uniform and may be described as a single crystal with [001] growth direction. The marked interplanar d-spacings of ca. 0.249 nm correspond to the (001) lattice planes of a hexagonal Co11(HPO3)8(OH)6.
To gain further insight into the surface and interface structures of samples, Brunauer–Emmett–Teller (BET) measurements were performed to examine their specific structural properties. The product shows a distinct hysteresis in the larger range ca. 0.75–1.0 \( P/P_0 \) in ESI Fig. 2,† indicating the presence of mesopores possibly formed by the stacking of component nanoparticles. The BET surface area of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitectures is 71.6 m\(^2\) g\(^{-1}\), which ensures an efficient contact of activated materials with electrolyte. The corresponding Barrett–Joyner–Halenda (BJH) pore size distribution curve (in inset of ESI Fig. 2,†) shows that the pore size of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) is uniform, within the range of mesopores (3–20 nm), and the porous structures of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitectures could offer high surface areas, which make an efficient contact of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitectures with electrolyte.

Cyclic voltammetry (CV) was used to evaluate the electrochemical properties and quantify the specific capacitance of as-prepared Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitecture electrodes. A new Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) capacitor in an alkaline solution relies on charge storage in the electric double layer at the electrode–electrolyte interface and charge storage in the host material through redox reactions on the surface and hydroxyl ion diffusion in the host material.\(^{51,52}\) Fig. 3a shows CV curves of the Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitecture at different scan rates. The potential span is from 0 to 0.60 V (vs. SCE) in 3.0 M KOH aqueous solution. It is clear that the Faradaic pseudocapacitive property of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitecture is based on the surface redox mechanism of Co\(^{2+}\) to Co\(^{3+}\) at the surface.

![Fig. 2](image) (a and b) TEM images of the sample; (c) HRTEM image; (d) selected area electron diffraction (SAED).

![Fig. 3](image) (a) Cyclic voltammetry curves of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitecture electrodes at different scan rates; (b) chronopotentiometry (CP) curves of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitecture electrodes at different current densities; (c) the specific capacitances calculated by the CP curves and current densities of Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitecture electrodes; (d) the relationships of the specific capacitance against cycling number for Co\(_{11}\)(HPO\(_3\))\(_8\)(OH)\(_6\) microarchitecture electrodes with a current density 1.25 A g\(^{-1}\).
of the Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture. Chronopotentiometry (CP) curves at different current densities are shown in Fig. 3b. The symmetrical characteristic of charging–discharging curves is good, which means that the Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrodes with excellent electrochemical capability and redox process are reversible. The relationships between the specific capacitances calculated by CP curves and current densities are given in Fig. 3c. Based on the CP curves, Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrodes have a large specific capacitance and reach 312 F g$^{-1}$ at a current density of 1.25 A g$^{-1}$ and remain at 198 F g$^{-1}$ even at 12.5 A g$^{-1}$. It is also very important for electrode materials to have good specific capacitance retention. The supercapacitors should work steadily and safely, which requires the specific capacitance of electrode materials to change as little as possible. The relationship of the specific capacitance against cycling number of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture materials is shown in Fig. 3d. It shows its excellent specific capacitance retention under large current density 1.25 A g$^{-1}$. After 100 continuous charge–discharge cycles, the Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture almost retains the same specific capacitance as its initial value. More importantly, the Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture still retains more than 89.4% of its specific capacitance after 3000 continuous charge–discharge cycles. A slight reduction in the capacitance of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrodes possibly results from the slight collapse of the microarchitecture structure when the ions are intercalated/extracted into the microarchitecture structures. And as a comparison with our previous work,$^{41}$ the specific energy and specific power of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrodes are larger than those of NH$_4$CoPO$_4$·H$_2$O nano/microstructures (seen in ESI Fig. 3,†), which are two key factors for evaluating the practical industrial power applications of electrochemical supercapacitors.

The electrode kinetics of the as-prepared material electrodes were estimated by electrochemical impedance spectra (EIS). Fig. 4a shows the EIS of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrodes at room temperature and the calculated result by ZSimWin software. The EIS data can be fitted by an equivalent circuit consisting of a bulk solution resistance $R_s$, a charge-transfer resistance $R_{ct}$, a pseudocapacitive element $C_p$ from the redox process of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$, and a constant phase element (CPE) to account for the double-layer capacitance, as shown in Fig. 4b. The solution resistance $R_s$ of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrodes was measured to be 2.6 ohm, while the charge-transfer resistance $R_{ct}$ was calculated to be 4.6 ohm. This clearly demonstrates the reduced charge transfer resistance of the Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrode. In addition, the charge-transfer resistance $R_{ct}$, also called Faradaic resistance, is a limiting factor for the specific power of the supercapacitor.$^{29-35}$ It is the low Faradaic resistance that results in the high specific power of the Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture electrode. These phase angles are $>$45° in the low frequencies clearly, which means that the structure of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture allows ions or electrolyte transfer to occur quickly.

4 Conclusions

A Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture assembled by ultralong nanoribbons has been successfully synthesized by a mild hydrothermal condition without any templates or surfactants being used. More importantly, the measurement of electrochemical properties of Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture is an important study, which illustrates the Co$_{11}$(HPO$_3$)$_8$(OH)$_6$ microarchitecture might be applied as an outstanding electroactive material with an excellent cycling property (maintaining about 89.4% at 1.25 A g$^{-1}$ after 3000 cycles) for supercapacitor applications. However, compared with other cobalt based supercapacitor electrode materials, the improvement of specific capacitance and rate performance is our further work. Exploring the electrochemical characteristics of novel nano/micromaterials might direct a new generation of supercapacitor materials.

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