

Au-doped Co_3O_4
nanotubes as
electrode materials
for lithium ion
batteries



**ASSIGN
BUSTER**

The use of transition metal oxides, such as Co_3O_4 , as positive electrode materials in lithium ion batteries (LIBs) has attracted great interest due to their high discharge-charge capacity. However, the poor capacity retention of the materials caused by large volume changes during the cycling process limits their cycle life time. Therefore I propose gold nanoparticles doped Co_3O_4 nanotubes as a new electrode material to improve the battery life time, which largely depends on the size and shape of the anode materials.

This proposed study aims at synthesizing Au-doped Co_3O_4 nanotubes and investigating the effect of the nanotubular structure on the battery performance. In this proposal, Co_3O_4 nanotubes will be synthesized by a surfactant-assisted method for the first time. The nanotubular structure with a high surface area and porous wall surfaces can provide increased active sites for lithium ion diffusion, which will greatly elongate the cycling lifetime. The Au nanoparticles incorporated in the nanostructure are expected to further enhance the electrochemical performance by facilitating the lithium ions intercalation.

This noble-metal-doped nanotubular structure can also be applied to other transition metal oxides as electrode materials to facilitate the development of LIBs with higher rate capacity and longer cycle life. Introduction Lithium ion batteries (LIBs) have been the dominant power source for portable electronics because of their high energy density and design flexibility. However, the ever-growing global need for high-power energy source, especially for large-scale applications, such as electric cars, has driven much research efforts towards the development of next generation LIBs with better performance electrode materials. -3 As a member of spinel-type transition
<https://assignbuster.com/au-doped-co3o4-nanotubes-as-electrode-materials-for-lithium-ion-batteries/>

metal oxides, Co_3O_4 possesses excellent electronic and chemical properties. In particular, Co_3O_4 is an important ceramic material in electrochemical, catalytic and magnetic applications. As anode materials for LIBs, Co_3O_4 can deliver capacity three times that of the commonly used graphite (350 mA h g^{-1}) in theory.

However, they usually suffer from poor capacity retention upon cycling and poor rate capability, which remains major challenges in cell applications. , 5 These problems have been attributed to the large volume changes during repeated lithium uptake and removal reactions, which can cause local stress and eventually lead to electrode failure. One promising remedy is to prepare nanomaterials with designed structures, as growing evidence shows that the nanostructured materials can improve the electrochemical properties compared to the bulk counterpart. 6-11 It is also consistent with the current trend to develop batteries in smaller dimensions

Recently researchers demonstrated that Co_3O_4 nanomaterials with different shapes possessed different electrochemical properties as anode materials in LIBs. 12 Tuning the morphology to obtain porous and high surface area can greatly enhance the capacity of the electrode. 13 Therefore it is desirable to investigate Co_3O_4 nanostructures with different parameters, such as shape and size, to find out the optimum Co_3O_4 anode materials. The creation of pores and channels is a natural way to the thermodynamic stabilization of complex structures.

Correspondingly, material researchers have made a lot of effort in porous materials^{14, 15} and nanotubular structures^{16, 17}. Mesoporous materials are

known for their ultra large surface areas and highly ordered pore structures, and they have shown potential applications in catalysis, gas storage and optics. 15 Shaju and coworkers synthesized mesoporous Co_3O_4 for electrochemical use⁵, however, after several cycles, the materials lost their mesoporosity and become more like bulk Co_3O_4 , therefore the fragile mesoporosity did not practically improve the capacity of conversion reactions on extended cycling.

The geometry of nanotubes has been an important conceptual novelty and also versatile candidates in materials research since the discovery of carbon nanotubes. Different synthetic strategies have been explored to generate numerous inorganic nanotubes, for example, solvothermal/hydrothermal method, misfit rolling (also known as the rolling-up method), and vapor phase reactions. The misfit rolling is a mechanism inspired directly from the discovery of carbon nanotubes, and it has been applied to many material systems to form tubular structures.

To follow the philosophy, it is very important to choose the right starting materials bearing layered structure, or create a layered structure for the rolling-up process. Considering the cubic spinel structure of Co_3O_4 , it is not quite possible for it or other Co(III) compounds to form nanotubes directly through the rolling-up mechanism. However, it is possible to circumvent this intrinsic problem by adopting an indirect strategy. Co(OH)_2 , together with some other Co(II) compounds such as halides, possess a CdI_2 -type layered structure (Space group $P-3m1$, , shown in Figure 1).

The OH^- ions form a hexagonal close packed arrangement while the Co^{2+} fill all of the octahedral sites in alternate layers. The resultant structure consists of a layered lattice. Similar to other layered structure such as graphite, $\text{Co}(\text{OH})_2$ could make an excellent precursor material for the synthesis of corresponding oxide nanotubes. Figure 1. The rhombohedral structure of CdI_2 . To be noted, there are few reports on the synthesis of Co_3O_4 nanotubes by solvothermal method up to date. 18, 19 However, there are two major drawbacks.

First, due to the lack of structural control, the products contain various shapes including plates, particles, rods and tubes, which greatly impede the study on the Co_3O_4 nanotubes, as it is always favorable to synthesize monodisperse, homogeneous nanomaterials. Second, the high temperatures required to force the rolling-up to happen, given no other assistance in the system. Herein, I propose a controllable synthesis route for the preparation of homogeneous Co_3O_4 nanotubes in the lyotropic media. Lyotropic liquid crystals (LLC) are a group of materials that compose amphiphilic molecules with a long-range order upon the addition of a solvent.

LLC phases are formed by a self-assembly process that is driven by the hydrophobic effect. For most LLC systems, aggregation or formation of micelles occurs only when the concentration exceeds a critical micelle concentration (CMC). Therefore CMC is an important feature to consider when using surfactants in material synthesis. Below CMC, the surface tension changes strongly with the surfactant concentration; after the concentration reaches CMC, the micelle concentration increases while the monomer

concentration stays more constant. It is usually in the range of 10^{-5} - 10^{-2} mol/L.

The as-synthesized Co_3O_4 nanotubes will enhance the electrolyte/electrode (Co_3O_4) contact area, shorten the lithium ion diffusion length in the Co_3O_4 layers, and accommodate the strain induced by the volume change during the electrochemical reaction. One of the many merits contributed by the “bottom-up” approach is the concept of manipulating the building blocks. Searching the materials library containing types of low dimensional nanoscale building blocks with different functions, many multifunctional nanostructures can be constructed.

The complex nanostructures with two or more components usually exhibit unique physical properties compared to their single component peers. Particularly, some dopants may potentially enhance the properties of the other component and even generate new properties. For example, hybrid nanoparticles consisting of Au and Fe_3O_4 combine plasmonic and magnetic properties, and each property may be tuned by the composition, shape, and interface interaction. The increased components or integrated properties usually lead to wider applications with enhanced sensitivity and accuracy.

Therefore, we propose a doping for the Co_3O_4 nanotubes to enhance the electrochemical performance as anode material. Au-containing electrode systems have exhibited improved electrochemical performance remarkably, including higher reversible capacity and rate capability. 11, 20 Thanks to the effort of many researchers, the Au nanoparticles can be fabricated into very

small diameters. The gold nanoparticles thus can migrate spatially within and outside of the host nanostructures and affect the overall properties.

As an electronic conductor, the Au nanoparticles in the electrode can improve the insertion and extraction reversibility of the lithium ions.

Combining the effect of Au doping and the architecture of the host nanotubes, the improvement of battery performance can certainly be expected. 2. Specific Aims This proposal is to develop Au nanoparticles doped Co_3O_4 nanotubes as anode materials in LIBs. Our interests in designing this doped nanotubular nanocomposites originate from the ever growing demands for smaller and longer-life batteries used in portable electronics.

This proposed material features several advantages: 1) Co_3O_4 materials have high rate capability and long cycle life as anode material in LIBs; 2) the nanotubular architecture of Co_3O_4 possesses larger surface area to enhance its contact area with the electrolyte, smaller dimensions for shortened lithium ion diffusion length in the Co_3O_4 layers, and can accommodate the strain induced by the volume change during the electrochemical reaction; 3) the introduction of gold nanoparticles as dopants on the nanotubes can further enhance the electrochemical properties through the interaction with the intercalated lithium species.

This multicomponent nanostructured system may retain the merits of both components and also obtain integrity for electrochemical uses. We anticipate this material design philosophy will open a door for new anode materials and help develop the next generation of LIBs. Therefore, the specific aims for this

proposed research are: 1. To develop a synthetic strategy to develop Au nanoparticles doped Co_3O_4 nanotubes. 2. To evaluate the electrochemical performance of the doped Co_3O_4 nanotubes as anode materials in LIBs. 3. Research Design and Methods.

1 The first aim of the proposal is to develop a synthetic scheme for gold nanoparticles doped Co_3O_4 nanotubes. To better demonstrate the effect of the nanotubular structure and Au nanoparticles doping, three types of samples are synthesized: Co_3O_4 nanoparticles (CoNP), Co_3O_4 nanotubes (CoNT) and Au nanoparticles doped Co_3O_4 nanotubes (Au-CoNT). The synthesis of CoNP. The Co_3O_4 nanoparticles are synthesized following the reported hydrothermal method with little modification. The synthesis of CoNT.

To produce Co_3O_4 nanotubes with high surface area, the following templating methods are designed. [pic] Figure 2. The schematic model for the formation of Co_3O_4 nanotubes. (a) Co(II) ions and surfactant monomers; (b) and (c) are the cross-sectional and top view of the assembled Co(OH)_2 layered structure; (d) the Co_3O_4 nanotube. The items in the scheme are not drawn to scale. As previously mentioned, to circumvent the difficulty of synthesizing spinel nanotubes via rolling-up process, we choose Co(OH)_2 as Co precursor material.

Co(OH)_2 possesses a CdI_2 -type layered structure with an interlayer spacing of 0.47 nm. The Co atoms in the layered sheets are hexagonally arranged as the top layer shows. The formation of tubular structures could be divided into several steps. First, the surfactant anions condensed into aggregations with

Co^{2+} ions intercalated into their hydrophilic head to form lamellar micelles, as shown in Figure 2(a) to (b)/(c). The Co^{2+} layers are confined in the aqueous interface of the micelles.

Second, the sheet-like structures start to loosen at the edge and then gradually scroll up to form nanotubes (Figure 2(c)). The driving force for this scrolling behavior can be attributed to the change of external conditions, such as elevated temperatures, drastically changed pressure, and the introduction of foreign species. This is the breaking of equilibrium for the metastable 2D sheets, and also generating of more stable 1D tubes in a changed physical and chemical conditions. It is always intriguing to understand the mechanism for nanostructure formations.

In this proposed scheme, the lyotropic media created by the surfactant aggregation provides an ideal soft template for the intermediate sheet-like structure. The thermal stress induced by the external high temperature, will initiate the rolling-up of the layered sheets to reduce the surface energy. In nanotubes synthesis, during and after the synthesis, it is important to retain the nanotubular structure integrity so that the high surface area is maintained. Particularly in this case, it is crucial to avoid potential structural collapse by using templates.

Herein we propose two anionic surfactants to be used templating agents. One is sodium dodecyl sulfate ($\text{C}_{12}\text{H}_{25}\text{SO}_4\text{Na}$, [pic] SDS), and the other one is sodium (+)-10-camphorsulfonate ($\text{C}_{10}\text{H}_{15}\text{SO}_4\text{Na}$, [pic] SCS). SDS is commonly used in detergents, while the acid form of SCS, CSA is an important organic agent. In this particular use, both surfactants have similar

condensation mechanism, the difference is that SDS is a linear molecule with the tail length (from the first carbon atom to sulfur atom) about 16.5 Å (semi-empirical method, Gaussian), while SCS has a much shorter hydrophobic end about 5 Å.

Therefore the corresponding interplanar distance of the lamellar micelles will be different, which will lead to nanotubes with different diameters. In the aqueous media, the condensation mechanism of the surfactants is like this. First, surfactant molecules are compactly packed to form tail-to-tail bilayer arrangements, forming directing arrangements between the Co^{2+} layers. In the lamellar layers, the Co^{2+} ions undergo ionic interactions with the hydrophilic heads of the surfactants, and can be crystallized without structural collapse as a result of the addition of OH^- .

Thus Co(II) precursors can be dissolved in the SDS solution to form $\text{Co}(\text{H}_2\text{O})_6^{2+}$, and soon combine with the OH^- hydrolyzed from urea to form intermediate Co(OH)_2 . After the surfactant layers being removed by rinsing with DI water and ethanol, the Co(OH)_2 sheet-like structures will be obtained. The coexistence of nanotubes and nanosheets is expected to be seen when the reaction time is not long enough, or the reaction is not carried out thoroughly. Another advantage of using surfactants such as SDS and SCS is that it makes possible large-scale synthesis using nontoxic reactants and low-cost processing.

Anisotropic crystal growth with surfactants is limited by dynamic properties of the surfactants. In many cases, spherical crystallization is preferred over soft-template directed process; however, within a certain window of

surfactant concentration, the template directing process could dominate. The ionic interactions between the surfactant and the metal ions drive the metal ions concentrated on the heads of SDS in the layer of the lamellar phases. The nucleated crystals become attached to the hydrophilic head parts of the bilayers to decrease the surface energy.

On the other hand, the SDS bilayers also fix the growing crystals and make it preferential crystallization along the lateral direction due to the geometrical confinement. The oxidation from Co(II) to Co_3O_4 happens during the hydrothermal treatment. In Co(OH)_2 , the Co atoms in the layered sheets are hexagonally arranged. Spinel Co_3O_4 has a cubic structure with three-fold symmetry viewed along $[111]$. As shown in Figure 3, during the oxidation, some preoxidized Co^{3+} species diffuse into the interlayer space to form Kagome net, while some of the Co^{2+} ions in the hexagonal sheets are oxidized into Co^{3+} .

Since the rearrangement of Co atoms takes place within or tightly around the sheets-structures, no significant diameter change is involved, thus after the oxidation process, the Co_3O_4 nanotubes were obtained without apparent size increase. [pic] Figure 3. Crystal structure model of the transformation from Co(OH)_2 to Co_3O_4 . Blue and yellow spheres denote Co^{2+} and Co^{3+} respectively. Only Co atoms are shown in the structure for simplicity. 22 3. 1. 3 The synthesis of Au-CoNT. There are two primary approaches to incorporate gold nanoparticles into the host nanostructures.

One is through the one-pot reaction, or to generally mix the Au precursors into the reaction system at the beginning of the reaction. This is the most

trouble-saving method to perform decent dopings, however, in this case, though Au has a face-center cubic structure and is less likely to form layered structure in the presence of surfactant, the Au species are likely to enter the hydrophilic end of the micelles and interrupt the formation of the $\text{Co}(\text{OH})_2$ sheets. This may lead to complex structures, such as core-shell structures²³.

Moreover, the surfactant removal step will inevitably cause the removal of Au nanoparticles, resulting in a low doping efficiency, or low Au concentration in the final products. The other approach is to mix in Au precursor after the intermediate $\text{Co}(\text{OH})_2$ sheets are formed. The highly-active Au nanoparticles will be spontaneously generated in the hydrothermal environment through the reduction by ethanol. Depending on the available attaching sites, the Au nanoparticles will be partly wrapped into the nanotubes, and partly outside the nanotubes.

By varying the reaction time, the size of nanotubes/particles will be tuned accordingly. The relative concentrations of the Co and Au precursors can also be adjusted by changing the amount/ratio of the precursors. 3. 1. 3 Material Characterization The samples (CoNP, CoNT and Au-CoNT) and the intermediate $\text{Co}(\text{OH})_2$ can be characterized using the following techniques. The Phase identification can be characterized using x-ray diffraction (XRD). However, due to the structure similarity between Co_2O_3 and Co_3O_4 , some other techniques that can differentiate Co(II) and Co(III), such as x-ray photoelectron spectra (XPS), are needed.

In the XPS spectra, peaks for both Co^{2+} and Co^{3+} should be found for Co_3O_4 . Au species, depending on the relative concentration, may also be

detected by XPS. The morphologies of the samples can be examined by transmission electron microscope (TEM). The chemical composition can be estimated by the energy-dispersive spectroscopy (EDS). The microstructure including the average pore size can be measured from the N_2 adsorption isotherm, and the surface area can be derived using Brunauer-Emmett-Teller (BET) model. The thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) measurements can sensitively detect the composition change from $\text{Co}(\text{OH})_2$ to CoO and Co_3O_4 by weight change.

TGA can also verify the removal of the surfactant. The complete surfactant removal can also be detected by the infrared (IR) spectrum, showing no CH bending/stretching bands. Utilizing the magnetic property of Co_3O_4 , the nanoparticles and nanotubes can also be imaged by the magnetic force microscopy. 3. 2 The second aim of the proposal is to examine the electrochemical performance of the doped nanotubular Co_3O_4 as anode materials in the LIBs.

This can be evaluated by a standard method based on $\text{Co}_3\text{O}_4/\text{Li}$ half cell. 3.

2. 1 Experimental scheme and design In the battery industry, the motivation for using Li in the pursuit of high energy density is based on the facts that Li is the most electropositive (-3.04 V versus standard hydrogen electrode) and the lightest (equivalent weight $M = 6.94 \text{ g mol}^{-1}$, and density $\rho = 0.53 \text{ g cm}^{-3}$) metal. In a typical LIB, the anode and cathode are materials into which lithium ions can migrate. When a cell is charging, the Li ions are extracted from the cathode and inserted into the anode.

When the cell is discharging, the reverse process occurs. At the same time, the cobalt species are oxidized from Co^{3+} to Co^{4+} during charging, and reduced from Co^{4+} to Co^{3+} during discharge. The battery performance is closely related to the intrinsic property of the materials that form the positive and negative electrodes. The cycle life also depends on the nature of the interfaces between the electrode and electrolyte. In our proposed work, the electrochemical measurements will be carried out using Au- $\text{Co}_3\text{O}_4/\text{Li}$ half cell (shown in Figure 4).

The working electrode contains 80 wt% of the Co_3O_4 samples (CoNP, CoNT and Au-CoNT), 10 wt% of conductivity agent (carbon black, Super-P), and 10 wt% of binder (polyvinylidene difluoride, PVDF). The Li foil serves as the counter electrode and reference electrode. The standard electrolyte LiPF_6 is used in a 50: 50 w/w mixture of ethylene carbonate and diethyl carbonate. The cell must be assembled in a glove box with strictly controlled moisture and oxygen level. [pic] Figure 4. The block diagram of the cell device in the discharging process.

3. 2. 2 Electrochemical measurements and expected outcomes

The electrochemical properties of the Co_3O_4 samples (CoNP, CoNT and Au-CoNT), including the capacity and the cycle performance, will be evaluated by using galvanostatic cycling and cyclic voltammetry. The galvanostatic measurement will be performed between 0. 01 and 3. 0 V at a constant current density of 50 mA g^{-1} (equivalent to 1 Li per formula unit in 2. 2 h). Two voltage plateaus at around 1. 3 and 1. 0 V are expected to be observed for the first discharge process, corresponding to the reduction processes to CoO (or $\text{Li}_x\text{Co}_3\text{O}_4$) and metallic Co, respectively.

2, 24 A high charge

<https://assignbuster.com/au-doped-co3o4-nanotubes-as-electrode-materials-for-lithium-ion-batteries/>

capacity should be attained in the first cycle and is not expected to change after a considerable 30 cycles. It is also expected that there will be a small fading rate.

22 The high capacity retention is believed to benefit from the nanotubular structure, particularly the robust nanotubes walls. 9, 25 The Co_3O_4 nanotubes, compared to nanoparticles should obtain higher capacity, due to the larger surface area and smaller effective diffusion length for Li^+ . The cell using Au-CoNT as positive electrode material is expected to show better plateau capacity retention than the undoped samples.

This could be attributed to two possible reasons: 1) the formation of AuLi_x alloy; 2) the catalytic effects of Au nanoparticles on the Li- Co_3O_4 reaction. Owing to the relative small concentration of Au, the effect of the Au-Li alloy is probably negligible. It is probably due to the catalytic effect of Au as decreasing the binding energy of Li_2O and further facilitating Li_2O reversible formation or decomposition during the charge or discharge process. Even small amount of Au dopants is proved to enhance the specific capacity by 30%, compared to the undoped counterparts, which makes it a cost-friendly solution.