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Polyvinylpyrrolidone-assisted Solvothermal Synthesis of Porous $LaCoO_3$ Nanospheres as Supercapacitor Electrode

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A polyvinylpyrrolidone (1-ethenylpyrrolidin-2-one or PVP)-assisted solvothermal method has been developed to synthesize porous $LaCoO_3$ nanospheres. Appropriate PVP addition may effectively prohibit the growth of nanospheres and plays an important role in reducing the size of $LaCoO_3$. The porous morphology of $LaCoO_3$ nanospheres can be obtained by an annealing process to achieve a specific capacitance of 203 F g^{-1} at a current density of 1 A g^{-1} with good cyclic stability for $LaCoO_3$ which has been prepared with 0.5 g PVP. This attributes to the synergistic effect of both size reduction and porous morphology.

Keywords: perovskite; porous; $LaCO_3$ nanospheres; supercapacitor; polyvinylpyrrolidone

1. INTRODUCTION

In recent years, transition metal oxides (TMOs) have attracted much attention as electrode materials for use as supercapacitors due to their multiple oxide states, rapid reversible Faradaic surface reaction and satisfactory electrochemical stability [1-4]. $LaMnO_3$ as one of a number of typical TMOs with perovskite structure has recently been developed and investigated as a pseudocapacitor electrode, and an anion-based fast-charge electrical storage mechanism has been introduced [5]. Similarly, $LaCoO_3$ possessing the crystalline structure of rhombohedral R-3c may be adopted as an electrode material for supercapacitor [6, 7]. Although an unaggregated spherical oxide with a nanometer-size distribution is the most desirable state for improved capacitance, it is difficult to obtain spherical nanopowder particles through hydrothermal synthesis due to the formation behavior of perovskite [8]. A surfactant such as polyvinylpyrrolidone (1-ethenylpyrrolidin-2-one or PVP) is normally used to modify materials' morphology and microstructure [9]. PVP is a polar molecule and binds very well to

other polar molecules [10, 11]. PVP can be used in hydrothermal synthesis, as a stabilizing agent to prevent the aggregation of metal particles and retain a uniform colloidal dispersion [12].

In this work, porous $LaCoO_3$ nanospheres have been successfully synthesized by a solvothermal method under the assistance of PVP. The addition of PVP can effectively reduce the size of $LaCoO_3$ nanospheres, and the uniform distribution of ~300 nm $LaCoO_3$ nanospheres have been obtained using 0.5 g PVP. The size reduction of $LaCoO_3$ by adding 0.5 g PVP leads to enhanced electrochemical performance and a specific capacitance of 203 F g^{-1} has been achieved at a current density of 1 A g^{-1} with good cyclic stability.

2. EXPERIMENTAL

2.1 Preparation of porous $LaCoO_3$ nanospheres

The precursor to $LaCoO_3$ was prepared with a single-step solvothermal method. One mmol of cobalt (Ⅱ) nitrate hexahydrate (98%, ACS reagent) and 1 mmol of lanthanum (Ⅲ) nitrate hexahydrate (99.9%-La, REO) were dissolved in a mixture of 160 ml isopropyl alcohol and 32 ml glycerinum and stirred for half an hour. Various aliquots of PVP (average molecular mass of 8000) at 0.5 g and 1g were added to the solution along with a sample without PVP for comparison. The mixed solution was transferred into a stainless steel autoclave and heated at 180°C for 6 h. The obtained product was washed three times prior to centrifuge collection, and then dried at 60°C. The precursor powders were annealed at 600°C for 6 h in a pure O_2 atmosphere.

2.2 Materials characterization

The samples' morphology was determined by using a Hitachi S4800 (Japan) scanning electron microscopy (SEM) with a 5.0 kV accelerating voltage. Transmission electron microscopy (TEM) characterization was done using a JEM 3100 (JEOL, Japan) operated at 200 kV. X-ray diffraction (XRD) patterns were accomplished using a Bruker D8 (Cu Kα radiation λ=1.54056 Å). Cycling voltammetry (CV) and chronopotentiometry (CP) were performed using a CHI660D (Shanghai Chenhua, China) electrochemical workstation.

2.3 Electrochemical measurements

The work electrode slurry was prepared by mixing annealed $LaCoO_3$, carbon black (Super P) and polytetrafluoroethylene (binder) at a mass ratio of 8:1:1. The mixed slurry was pasted onto Ni foam with 2 mg cm^{-2}, followed by vacuum dessication at 80°C. The electrochemical measurement was performed using a traditional three-electrode system at room temperature with platinum foil as the counter electrode and Hg/HgO as the reference electrode in an aqueous 6 M KOH electrolyte. The CV curves were measured in a potential range of 0-0.5V vs Hg/HgO and CP was measured in a potential range of 0-0.45V vs Hg/HgO. The cyclic performance was conducted with LAND (Wuhan, China).

3. RESULTS AND DISCUSSION

The XRD patterns (Fig. 1A) shows the crystalline structure of $LaCoO_3$ prepared with 0, 0.5 and 1 g PVP, respectively. All of the reflections can be readily indexed to rhombohedral $LaCoO_3$ (JCPDS No. 48-0123) while no other phase can be detected. This indicates that the $LaCoO_3$ single phase has been achieved successfully after annealing at 600°C for 6 h in an O_2 atmosphere, and the phase purity is not affected by the addition of PVP.

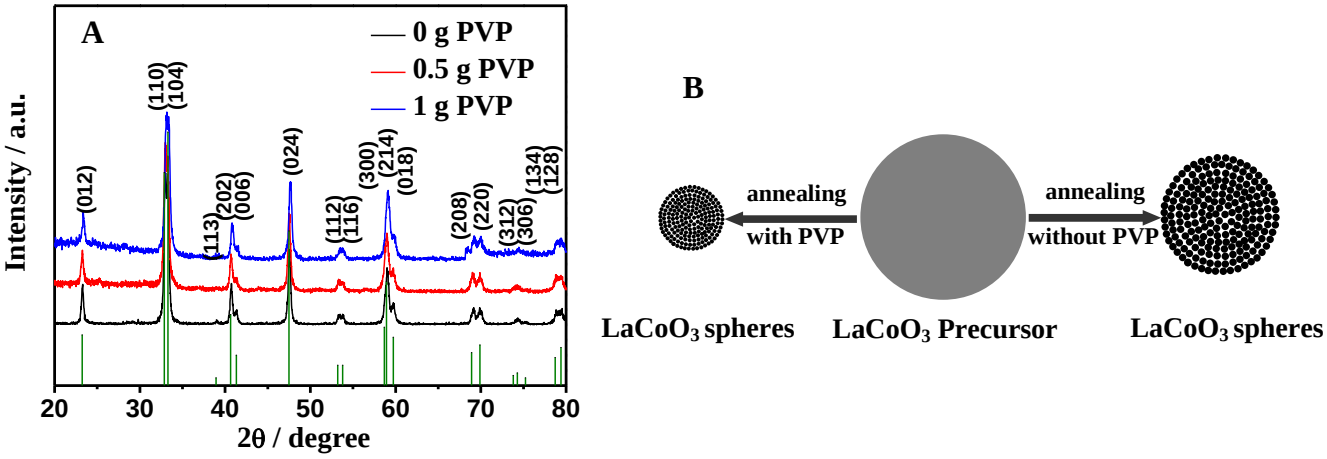

Figure 1. XRD patterns of $LaCoO_3$ prepared with various amounts of PVP (A), Schematic illustration for the formation of porous $LaCoO_3$ nanospheres (B).

The microstructures of $LaCoO_3$ precursor and $LaCoO_3$ annealed for 6 h in O_2 are revealed by SEM. The as-prepared $LaCoO_3$ precursor without PVP (Fig. 2A) consists of uniform micro-spheres with diameters of ~1 μm. The spherical morphology is well maintained after annealing (Fig. 2B), however, the diameters of the spheres are reduced to ~500 nm because of the shrinkage during annealing. The surface roughness of the spheres becomes more significant after annealing, suggesting that the spheres might be composed of $LaCoO_3$ nanoparticles. By adding 0.5 g of PVP, the morphology of most $LaCoO_3$ nanospheres is retained with a dramatic reduction in their average size to ~300 nm after annealing (Fig. 2C). The size of $LaCoO_3$ is reduced further by increasing the amount of PVP to 1 g, however, the spherical structure can not be retained and tends to deteriorate, leading to the collapse of the $LaCoO_3$ nanospheres (Fig. 2D). TEM images (Fig. 2E, F) clearly demonstrate that the porous morphology of the $LaCoO_3$ nanospheres after annealing and the porous structure is not affected by the addition of 0.5 g PVP. As illustrated in Fig. 1B, the formation of porous $LaCoO_3$ nanospheres may be attributed to the annealing process of the $LaCoO_3$ precursor, with which the nucleation and growth of $LaCoO_3$ nanoparticles continues during annealing, eventually forming the porous nanospheres. The physical absorption of PVP on the nanoparticles surface may prohibit the nanospheres' growth. Therefore, PVP is used here as an important agent in reducing the size of $LaCoO_3$ [13-15]. It is importnt to note that from the cavity of the broken parts in Fig. 2D, the $LaCoO_3$ nanospheres obtained might be hollow inside.

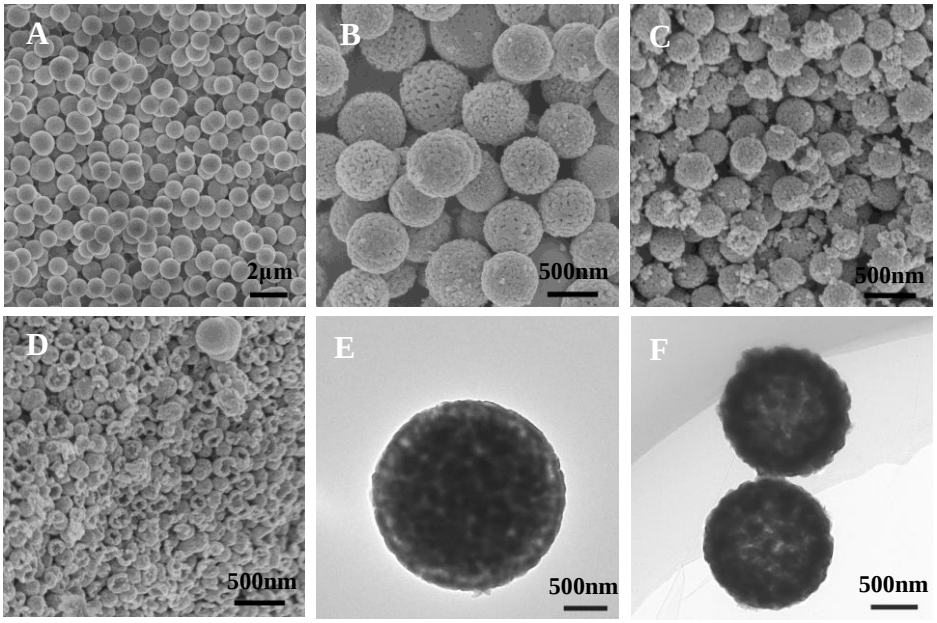

Figure 2. SEM images of $LaCoO_3$ precursor prepared without PVP (A), $LaCoO_3$ prepared with 0 (B) , 0.5 (C), 1 g (D) PVP after annealing, TEM images of porous $LaCoO_3$ nanospheres prepared with 0 (E), 0.5 (F) g PVP after annealing.

Fig. 3A shows the cyclic voltammetry (CV) tested in 0-0.5 V at a scanning rate of 10 mV s^{-1} for $LaCoO_3$ prepared with 0, 0.5 and 1 g PVP respectively. All the samples display distinct redox peaks during the anodic and cathodic sweeps, showing characteristics of the electrochemical supercapacitors delivering reversible capacitance based on the surface reactions [16, 17]. $LaCoO_3$ prepared with 0.5 g PVP demonstrates the largest area enclosed under the CV curve, indicating the greatest specific capacitance. The chronopotentiometry (CP) measurements are performed in the 0-0.45 V voltage range at a charging-discharging current of 1 A g^{-1} (Fig. 3B). $LaCoO_3$ prepared with 0.5 g PVP exhibits the longest charging and discharging duration, indicating the excellent electrochemical performance of the porous $LaCoO_3$ nanospheres. Fig. 3C shows specific capacitances as a function of current densities of $LaCO_3$ prepared with various additions of PVP. It reveals that $LaCoO_3$ prepared with 0.5 g PVP exhibits the highest specific capacitance of 203 F g^{-1} at a current density of 1 A g^{-1} and a capacitance as high as 123 F g^{-1} can be achieved at a current density of 20 A g^{-1}. This performance is comparable to perovskite such as $La_{0.85}Sr_{0.15}MnO_3$ [19] and double pervoskite Y_2NiMnO_6 [20] and it could be further optimized by controlled doping on the B-site of the perovskite structure [21-22] (Table. 1). However, $LaCoO_3$ prepared with 0 and 1 g PVP show a capacitances reduction of 51.7 and 162 F g^{-1} at a current density of 1 A g^{-1}, and 11.5 and 88.4 F g^{-1} at a current density of 20 A g^{-1}, respectively. The cyclic stability of porous $LaCoO_3$ nanospheres is evaluated by repeated charging and discharging for 5000 cycles at a current density of 1 A g^{-1} (Fig. 3D). The specific capacitance increases slightly from 203 F g^{-1} to 225 F g^{-1} during the first 200 cycles, which might be due to electrochemical activation [18].

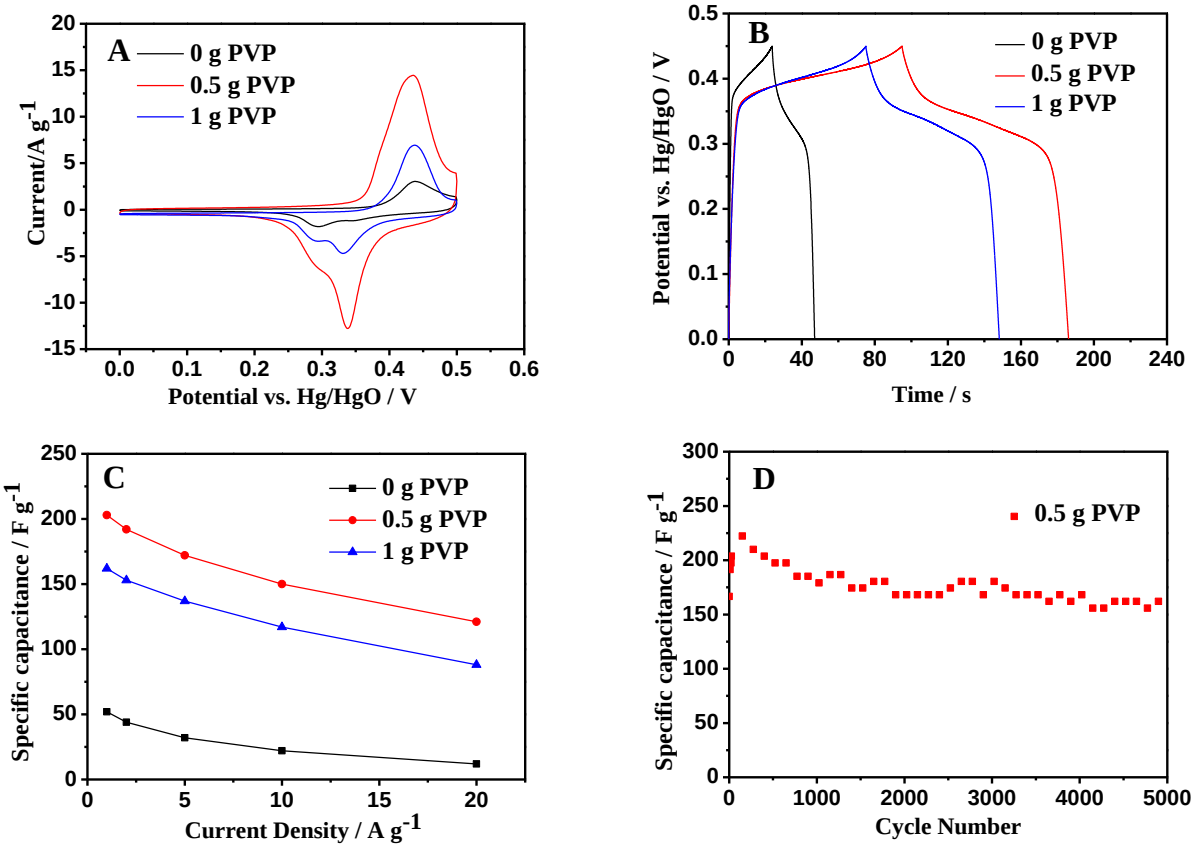

Figure 3. CV curves of $LaCoO_3$ electrodes prepared with various additions of PVP at a scanning rate of 10 mV s^{-1} (A), charge-discharge curves at a current density of 1 A g^{-1} (B), specific capacitance as a function of current density (C), cyclic performance of $LaCoO_3$ prepared with 0.5 g PVP at a current density of 1 A g^{-1} (D).

Table 1. Performances comparison of some perovskite oxides as supercapacitor electrodes.

Perovskite oxides	Specific capacitance	Electrolyte
$La_{0.85}Sr_{0.15}MnO_3$ [19]	198 F g^{-1} at 0.5 A g^{-1}	aqueous KOH
Y_2NiMnO_6 [20]	77.76 F g^{-1} at 30 mA g^{-1}	aqueous KOH
$SrCo_{0.9}Nb_{0.1}O_{3-\delta}$ [21]	773.6 F g^{-1} at 0.5 A g^{-1}	aqueous KOH
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [22]	572 F g^{-1} at 1 A g^{-1}	aqueous KOH
porous $LaCoO_3$ in this work	203 F g^{-1} at 1 A g^{-1}	aqueous KOH

Porous $LaCoO_3$ nanospheres demonstrate good specific capacitance and cyclic performance due to the synergistic effect of porous morphology and size reduction. On one hand, the porous structure significantly improves ionic and electronic transfer, which is beneficial to rapid ion and electron transfer, leading to enhanced electrochemical performance. On the other hand, the size reduction of $LaCoO_3$ caused by the addition of PVP might provide more active sites to produce the electrochemical reaction due to an increase in specific surface area. EIS measurements (Fig. 4) further confirm that porous $LaCoO_3$ nanospheres with reduced size exhibit the smallest real axis intercept (merely 0.375 Ω) and a negligible semicircle, indicating the lowest recorded internal resistance and charge transfer resistance.

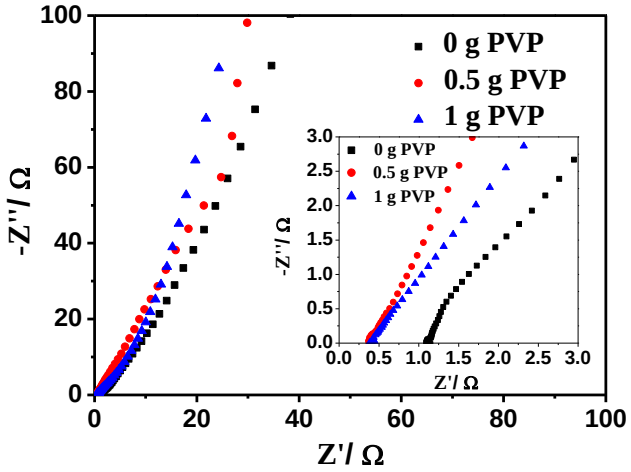

Figure 4. Electrochemical impedance spectroscopies of $LaCoO_3$ prepared with various aliquots of PVP.

CONCLUSIONS

We have successfully utilized PVP as a promising agent in solvothermal synthesis to obtain porous $LaCoO_3$ nanospheres. The proper utilization of PVP can significantly reduce the size of $LaCoO_3$ with maintaining its spherical structure, and this porous morphology can be obtained by the annealing process. Electrochemical measurements indicate that porous $LaCoO_3$ nanospheres manifest promising electrode for application as supercapacitors with satisfactory capacitance and cyclic stability. The results of this work will hopefully propagate the design of other porous oxides in various applications.

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