Preparation of dense ZIF-67 layer wrapping PPy nanotubes via assistance with triethylamine

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Abstract: The high dispersity and conductivity of materials are of great significance in the field of energy conversion and storage. In this work, a highly dispersed ZIF-67 anchored onto polypyrrole nanotubes precursor with good crystalline is prepared via self-assembly through coordination between cobalt cation and 2-methylimidazole assisted with deprotonating agent of triethylamine. The as-synthesized precursor displays a dense coating layer wrapping high aspect ratio polypyrrole nanotubes as clearly observed by scanning electron microscope. This work provides a rational route in construction of hierarchical composites with high conductivity and outstanding catalytic property applied in electrocatalysis and energy storage device.

1. Introduction

Metal-organic frameworks (MOFs) are highly ordered porous crystalline materials formed by self-assembly of central metal ions and organic ligands. Zeolitic imidazolate framework-67 (ZIF-67), a typical MOFs, has attracted extensive attentions in the catalysis field due to its cobalt ions and nitrogen-rich linkers which could transform into cobalt-based composites and nitrogen doped carbon skeleton, respectively. But individual ZIF-67 derivatives cannot form a continuous conductive network, resulting in inferior charge transfer efficiency. The introduction of polypyrrole (PPy) is considered to be an effective strategy to enhance the conductivity of composites, which has outstanding intrinsic conductivity and can be transformed into high conductive nitrogen-doped carbon[1-3].

Yuan et al[4] prepared hollow CoFe2O4 and carbon nanotubes composites adding little amount of PPy nanoparticles at the same time, which have performed excellent power conversion efficiency used as a counter electrode of dye sensitized solar cells. The presence of PPy nanoparticles contributing to filling the space have further improved the conductivity and catalytic efficiency of the materials. Chen et al[5] synthesized LiNi0.8Co0.1Mn0.1O2 cathode materials and then surface-coated with Li3PO4 and PPy layer, which delivered a high discharge capacity and better cycle stability. The PPy coating significantly enhanced the electrical conductivity of the cathode materials and effectively hindered the direct contact between electrode and electrolyte which dramatically improved the structure stability. Compared with the two existing state of PPy, coating layer and interstitial particle usually used for post-modification, high aspect ratio PPy nanotubes can provide radial direction paths of charge transfer and could also utilize its alone electrons of nitrogen to anchor metal ions to prepare variety of materials with low interfacial contact impedance. Xu et al[6] obtained ZIF-67 nanocrystals connected by PPy nanotubes through electrostatic attraction between the negatively charged PPy nanotubes and Co2+ ions and
following in situ growth of ZIF-67. The PPy not only increased the overall electrical conductivity, but also used as a support to disperse well the polyhedral. However, most of size of the ZIF-67 loaded on PPy through in situ growth was much bigger than tube diameter of PPy, which limited the rapid charge transfer from ZIF-67 to collector PPy and also restricted nano-size effect of ZIF-67-derived materials.

In this work, a dense coating layer of ZIF-67 wrapping PPy precursors was successfully prepared via controllable nucleation and growth of ZIF-67 onto the surface of PPy. This material can be further transformed into variety of derivatives with high nitrogen doping, excellent conductivity and outstanding catalytic performance.

2. Experimental Section

The preparation of ZIF-67/PPy is shown in Scheme 1. The detailed experimental procedure is depicted as followed. First of all, PPy nanotubes (75 mg), prepared according to the work of Zhang et al with some modification, were dispersed in methanol (50 mL) under ultrasonication. Then, appropriate Co(NO₃)₆·6H₂O were added into above dispersion under magnetic stirring at room temperature to ensure Co²⁺ fully adsorbed by PPy, which was denoted as A. Meanwhile, 2-methylimidazolate (2-mIm, mole ratio of 1:4 with cobalt nitrate hexahydrate) were added into another beaker with 50 mL methanol and stirred to form clear solution, which was denoted as B. Latterly, B was quickly poured into A under constant stirring for 15 min and then put into an incubator chamber at 25 ℃ for 4 hours. The mixture was separated by centrifugation and washed with methanol several times. ZIF-67/PPy precursor was obtained after the precipitate dried at 60 ℃ in vacuum overnight.

3. Results and discussion

3.1. The crystalline structure of ZIF-67/PPy composites

The crystalline structure and purity of the as-synthesized materials were characterized by XRD, as displayed in Fig. 1. A broad peak at the range of 20-30 degree for the pure PPy could be observed, which
was assigned to the amorphous nature of PPy. The intensity and location of sharp diffraction peaks of ZIF-67/PPy were well in line with the simulated data of ZIF-67 by diamond software, indicating a high crystalline degree of ZIF-67 in ZIF-67/PPy composites. Meanwhile, the disappearance of broad amorphous peaks of PPy in ZIF-67/PPy was likely caused by the high crystalline degree of ZIF-67.

![XRD image of ZIF-67/PPy and stimulation ZIF-67](image)

Figure 1. XRD image of ZIF-67/PPy and stimulation ZIF-67

3.2. Effect of addition amount of Co cation

The amount of substance of Co cation was adjusted to 1.5 mmol, 2.5 mmol, and 3.5 mmol, respectively, for studying the effect of addition amount of Co cation upon the morphology of ZIF-67/PPy. Figure 2 showed the SEM images of ZIF-67/PPy composites obtained from different addition amount of Co cation. When the Co cation was 1.5 mmol, few ZIF-67 polyhedra could be found. Increasing the amount to 2.5 mmol, it could be observed that ZIF-67 polyhedra with size of 300-500 nm were grown on the surface of PPy nanotubes, to form a grape-like structure, as shown in Fig.2c and d. Keeping increasing the amount to 3.5 mmol, the grape-like structure was maintained, but some ZIF-67 polyhedra appeared to integrate and agglomerate. In this case, 2.5 mmol could be the appropriate amount of Co cation.

![SEM images of ZIF-67/PPy obtained from different amount of Co cation](image)

Figure 2. SEM images of ZIF-67/PPy obtained from different amount of Co cation. (a, b)1.5 mmol, (c, d)2.5 mmol, (e, f)3.5 mmol.
3.3. Effect of addition of TEA

Triethylamine (TEA) was introduced into the solution B by mole ratio of 1:1 with 2-mIm, for further obtaining ZIF-67/PPy composites with high density and uniform distribution. Figure 3 showed the SEM images of ZIF-67/PPy composites obtained with TEA. It was obvious that the size of ZIF-67 polyhedra was decreased to as low as 10-20 nm after the addition of TEA. The addition of TEA as deprotonant can deprive the proton of heterocyclic N atoms of 2-methyl imidazole and fully exposed its lone electron pairs. The N atoms contacting with Co cation could rapidly coordinate to form a plenty of nucleation centers, which accelerated the nucleation process and relatively restricted the growth rate, thus effectively controlling the size of ZIF-67 polyhegra. Owing to the characteristic of small size, the high dense coating layer of nanocrystals could be achieved, which made the PPy nanotubes have a roughened surface and thicker diameter.

![Figure 3. SEM images of ZIF-67/PPy prepared with TEA](image)

3.4. Effect of addition amount of Co cation with TEA

The amount of substance of Co cation was adjusted to 0.1 mmol, 0.2 mmol, 0.3 mmol, 0.4 mmol, and 0.5 mmol, respectively, for studying the appropriate amount of Co cation with the addition of TEA. As Figure 4 depicted, the density of ZIF-67 nanocrystals on PPy nanotubes increased with the increase of addition amount of Co cation. When the Co cation was 0.3 mmol, a layer of well-distributed ZIF-67 nanocrystals as the shell was coated on the surface of tubular PPy as the core and template to form a core-shell structure. When the amount of substance of Co cation was more than 0.3 mmol, the ZIF-67 nanocrystals were incline to agglomerate to bulk structure. The amount of Co cation anchored onto the surface of PPy tubes was decided by the amount of N sites located outer wall of PPy. It could be concluded that 0.3 mmol Co cation was appropriate with the addition of TEA.
4. Conclusions

The controllable and core-shell structural ZIF-67/PPy composites were prepared by *in situ* self-assembled method with PPy nanotubes as supporter. The effects of the addition of TEA and the amount of substance of Co cation on the morphology of composites were investigated. With the addition of TEA and the amount of Co cation of 0.3 mmol, the ZIF-67/PPy composites with small size, high density and uniform distribution of ZIF-67 nanocrystals could be prepared. This strategy provides a controllable and promising method to synthesize conductive and uniform homogenously MOF-based precursor.

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