Facile Preparation and Morphological Characteristics of PPy-based Nano-sized Carbon Materials

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Introduction

In recent years, nano-carbon-materials of various types including tubes, particles, and fibers have drawn much attention due to their potential applications as such as electronic devices, flat panel displays, nano-switches, energy storage media, separation media, etc. [1-3]. As compared with other nano-carbon-materials such as nanotubes and nanofibers, relatively less attention has been paid to carbon nano-particles although some preparation methods have been introduced such as CVD, arc discharge, and ordinary laser-vaporization methods [4-6]. Those preparation methods are relatively well established and find their advantages in morphology controllability and high yield, but they also have drawbacks in that they need complicated equipment, higher furnace temperature and catalyst.

We report here a novel and facile preparation method for carbon nanoparticles by fabricating nano-sized polypyrrole (PPy) precursor. In the conventional polymer processing techniques, nano-sized polymer particles have been obtained typically from microemulsion polymerization at low temperature. However, this method itself limits its wide use since it needs excess amount of surfactant and low temperature [7]. We thus introduce a novel and facile method for the preparation of nano-sized polypyrrole particle, which characterizes itself in the controlled monomer-feeding rate and surfactant free preparation at room temperature. Carbon nano-particles were prepared by carbonizing nano-sized PPy particles under N_2 atmosphere, and morphological characteristics were studied as a function of polymerization conditions such as various types of oxidants, controlled monomer feeding rate, and kinds of dopants.

Experimental

***Materials*:** Pyrrole (Aldrich Chem. Co., 97%) was purified by distillation under reduced pressure to remove oligomeric species that may influence the synthesis and properties of resulting PPy. Purified pyrrole is a colorless transparent liquid with a molecular weight of 67.1 g/mol. Ferric chloride ($FeCl_3$, Aldrich Chem. Co.) was used as an oxidant as received.

***Synthesis of nano-sized PPy* (*n-PPy*):** To obtain nano-sized PPy (n-PPy) particle without using template and surfactant, the monomer-feeding rate was controlled by

loading on a carrier gas. The obtained product was subjected to convection oven drying for one day. To obtain unagglomerated Ppy particles, polyvinylalcohol (PVA) was used as a stabilizer [8] during preparation of n-PPy.

***Preparation of nano-sized carbon particles*:** Nano-sized PPy particles were carbonized at 800℃ for 5 hr under N_2 atmosphere, followed by cooling down to room temperature.

Results and Discussion

***Nano-sized PPy*:** Figure 1 shows the morphologies of PPy prepared by different polymerization methods such as bulk polymerization (Figure 1(a)) and the controlled monomer feeding rate method without PVA stabilizer (Figures 1(b)) and with stabilizer (Figure 1(c)), respectively. Figure 1 clearly shows that the bulk polymerized PPy particles have a typically known cauliflower-like morphology, and are very much agglomerated of micrometer size in diameter, however, with the control of monomer feeding rate, size reduces to nano-size although they are still agglomerated. It is noteworthy in Figure 1(c) that, with the combination of the use of a stabilizer and the controlled monomer-feeding rate, well-defined unagglomerated nano-PPy particles of ca. 100 nm are successfully prepared. Therefore, it is clear that the control of monomer feeding is a very effective method to control the particle size. It is speculated that, during polymerization, the competition between the rate of aggregation of pyrrole monomer to growing PPy and the rate of adsorption of the stabilizer on the growing polymer is balanced at the observed size in the controlled monomer feeding rate method.

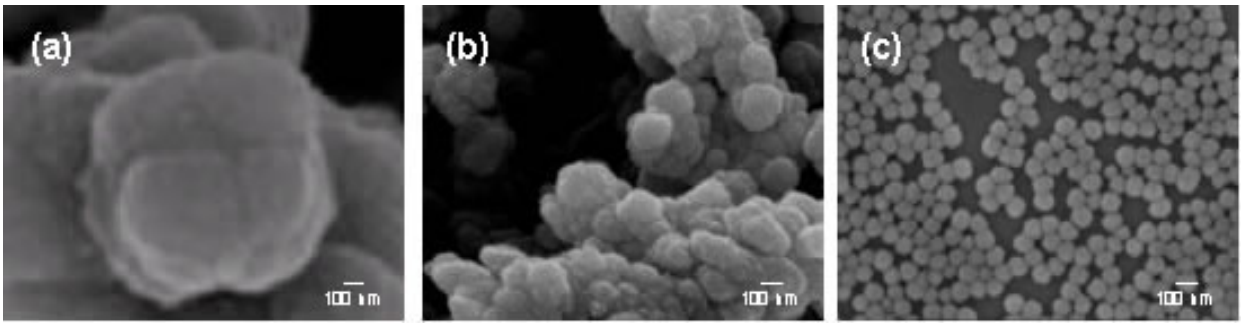

Figure 1. SEM micrographs of PPy particles by bulk polymerization method (a), and the controlled monomer feeding rate method without PVA stabilizer (b) and with stabilizer (c).

***Nano-sized carbon particles*:** Figure 2 shows the morphologies of nano-sized carbon particles prepared by carbonizing the nano-sized PPy precursor under N_2 atmosphere. In general, the size of nano-carbon particles is smaller than that of n-PPy particles due possibly to thermal shrinkage by carbonization. And, Figure 2(c) clearly shows that unagglomerated nano-carbon particles can be prepared from the unagglomerated nano polymer-precursos.

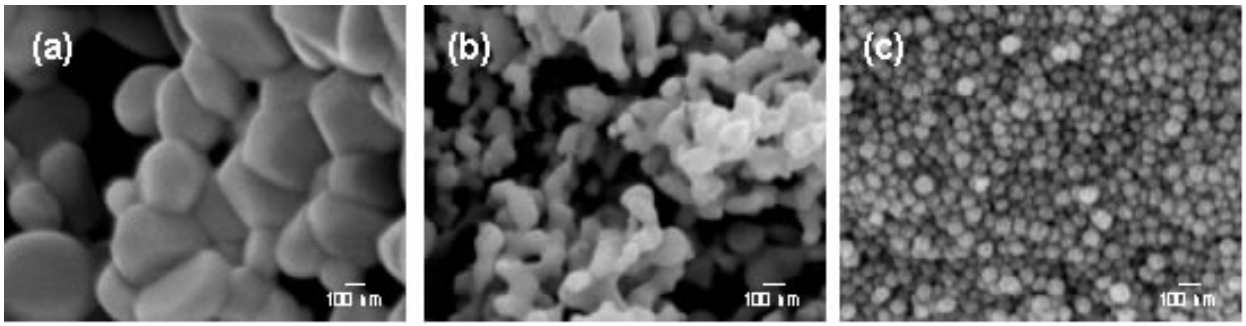

Figure 2. SEM micrographs of carbonized PPy particles by bulk polymerization method (a), and the controlled monomer feeding rate method without PVA stabilizer (b) and with stabilizer (c).

Conclusions

In this study, a novel and facile synthesis method of n-PPy particles and subsequently obtainable nanocarbon particles were suggested. It was found that the combination of the use of PVA stabilizer and the controlled monomer feeding rate during polymerization is very effective in obtaining unagglomerated nano-particles of the polymer precursor for nano carbon particles.

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