

PREPARATION OF NANOSHELL FROM POLYOXINE COBALT COMPLEX AND ITS ELECTROCATALYTIC ACTIVITY FOR AN OXYGEN REDUCTION REACTION

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Introduction

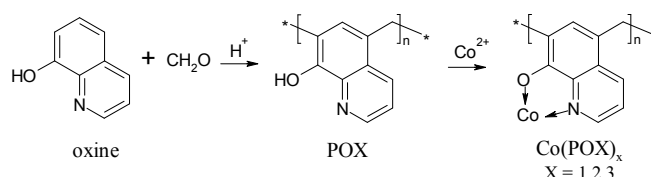
Nanoshell is a type of nanocarbon, which is prepared by carbonization of polymers in the presence of transition metal complexes. This carbon structure is hollow spherical shape with 20~100 nm by diameter composed of partially stacked carbon layers and it shows electrocatalytic activity for oxygen reduction reactions (ORR)^[1]. Its ORR activity depends on the diameter of nanoshell, small nanoshell with 20 nm shows high ORR activity^[2]. Therefore, the reduction in nanoshell size is an important issue for the improvement of ORR activity. In the conventional way of preparation of nanoshell, we employed metal complexes such as phthalocyanines, which were physically mixed to a polymer precursor. During the carbonization process, the aggregation of the introduced phthalocyanine took place; resulting in the formation of larger metal clusters, which acted as the catalysts for the formation of nanoshell. Immobilization of the metal species is an important idea to reduce the sizes of nanoshell. Polymeric ligands seemed to be suitable for our purpose of the reduction of the nanoshell size. The objective of this study is to observe the effectiveness of polymeric metal complexes, i.e. polyoxine cobalt complex.

Experimental

Polyoxine is synthesized by condensation of oxine and formaldehyde in acid condition (scheme 1). The complexation was performed in a the N,N-dimethylformamide (DMF) solutions of polyoxine and CoCl₂, where the ligand/metal ratios were varied to provide 1, 2 and 3 to observe the influences of the metal content on the geometrical features of the formed nanoshells. After removing the solvent by a rotary evaporator, the product was purified by extraction with ethanol for 12 h using a Soxhlet extractor. The metal chelating polymers are labeled Co(POX)_x (x=1,2 and 3). The prepared complexes were carbonized at 1000°C for 1 h in a nitrogen stream, with a heating rate of 10°C/min. The carbonized samples were pulverized using agate mortar and pestle. The sample was then acid-washed with 12 mol dm⁻³ hydrochloric acid for 2 h three times in order to remove the effect of the cobalt species on the catalytic activities of the carbons. The carbons thus obtained are labeled as Co(POX)_x-HT. (x=1,2 and 3). A conventional nanoshell was also prepared in the same manner as described elsewhere^[3] for the purpose of comparison of the effects of the precursors. The nanoshell

prepared in the conventional preparation is denoted as CoPc/PF-HT.

The ORR activities of the obtained carbons were evaluated by rotating disk electrode voltammetry at room temperature, where an oxygen saturated 0.5 M H₂SO₄ solution was used as the electrolyte. The voltammograms were recorded by sweeping the potential from 0.8 to -0.2 V vs. Ag/AgCl at 0.5 mVs⁻¹, while the electrode was rotated at a fixed speed of 1500 rpm. Transmission electron microscopic (TEM) observation was carried out for the ground sample placed on a copper grid coated with an amorphous carbon film. The transmission electron microscope was operated at an acceleration voltage of 200 kV.



Scheme 1 Preparation of POX and introduction of cobalt to the polymer.

Results and Discussion

TEM images of each prepared sample are shown in Fig. 1. The formation of the nanoshells were confirmed for all of the carbons derived from the Co(POX)_x precursors; however the size and the uniformity of the formed nanoshells in these carbons were found to be different depending on the ligand/metal ratios. The nanoshell from the precursor with

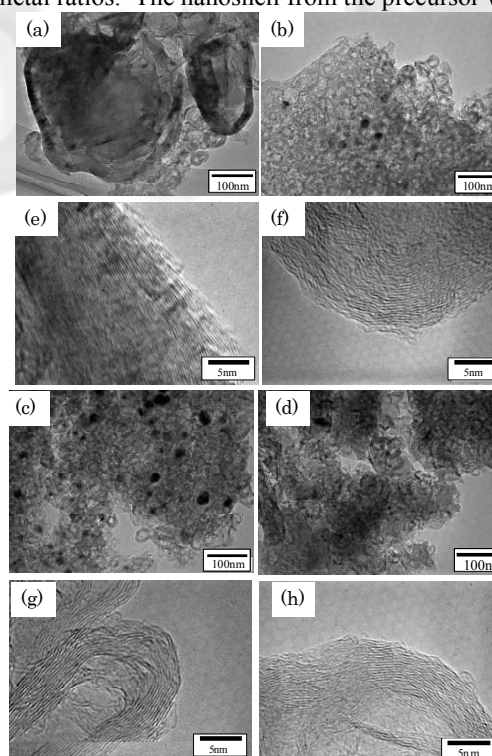


Fig. 1 TEM images of (a) Co(POX)-HT, (b) Co(POX)₂-HT, (c) Co(POX)₃-HT and (d) CoPc/PF-HT. Plates (e)-(h) are the magnified images of (a)-(d), respectively.

the largest metal content, Co(POX), was uniformly developed with the size of the nanoshell ranging 20–300 nm; the magnified TEM image revealed the well-organized stacking of the graphitic sheets of the larger nanoshells. The sizes of the nanoshells from the precursors with smaller cobalt contents, Co(POX)₂ and Co(POX)₃ were smaller and the distribution was quite uniform. The surfaces of these nanoshells were revealed to be composed of graphitic layers with many defects and edges by high resolution TEM observations. According to our previous study, such defects were responsible for the ORR activity of the nanoshells.

The size distributions were obtained by measuring the size of the nanoshells. They are presented in Fig. 2. As mentioned above, Co(POX)-HT showed wider range distribution than other samples. Decrease in the cobalt content from Co(POX)₂ to Co(POX) resulted in the increase in the uniformity of the distributions; i.e. the effect is obvious particularly in the decreases in the larger size components. It is interesting to point out that the conventional nanoshell, CoPc/PF-HT had a distribution with higher frequencies for the larger components, even the content of cobalt was considerably smaller than that of the Co(POX)_x derived nanoshells. This is one of the effect of immobilization of metal species by coordination as we expected to observe.

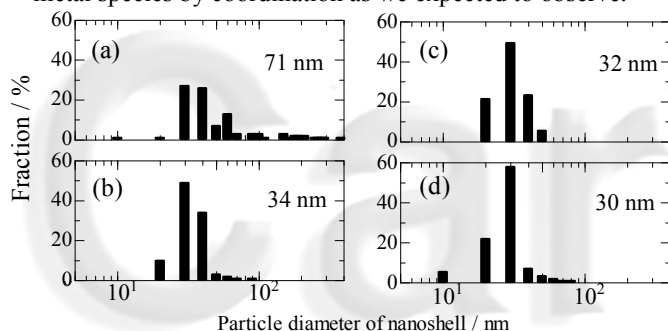


Fig. 2 Fraction of particle diameter of nanoshell.

(a) Co(POX)-HT, (b) Co(POX)₂-HT, (c) Co(POX)₃-HT and (d) CoPc/PF-HT

Fig. 3 shows the ORR voltammograms of the samples prepared in the present study, of which the current density was expressed in terms of BET surface area basis in order to compare the intrinsic activity of the nanoshells. The ORR activities of the nanoshells from the three Co(POX)_x complexes dependent on the ligand/metal ratios; Co(POX)₂-HT and Co(POX)₃-HT showed the highest activities among the nanoshells prepared in the present study. The nanoshell formed in Co(POX)-HT was the lowest among the nanoshells including conventional nanoshell, CoPc/PF-HT.

The current density at 0.7 V vs. NHE was taken as an indicator of the ORR activity. The parameter was plotted against the averaged sizes of the nanoshells shown in Fig. 4. An excellent correlation was obtained between these two parameters. An interesting point was found for CoPc/PF-HT; the ORR activity of the nanoshell was lower than the Co(POX)_x-derived nanoshells, even the average sizes of these three nanoshells were almost the same. There are two possible

explanations for the lower activity of the CoPc/PF-HT; one is due to the presence of the amorphous carbons in the material and another is due to the differences in the nitrogen contents. More quantitative studies on these materials are now conducted in our laboratory.

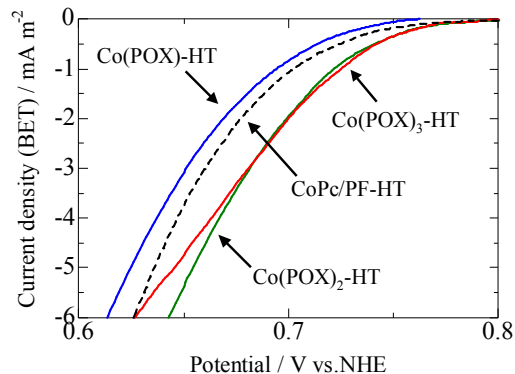


Fig. 3 O₂-reduction voltammograms of the samples normalized by BET specific surface area.

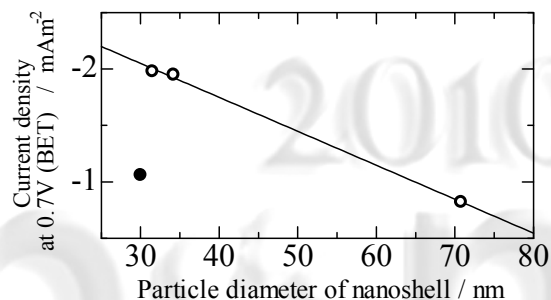


Fig. 4 The relationship of nanoshell diameter and Current density at 0.7 V (BET).

Conclusions

Polymeric metal complex i.e. polyoxine cobalt complex was used to obtain small nanoshell. The size and the uniformity of nanoshells were depended on the composition of the polyoxine-cobalt complex. The nanoshells from the polyoxine cobalt complex with the smaller ligand/metal ratios resulted in the formation of smaller nanoshells with higher uniformity. The ORR activity of the nanoshells was found to depend on the average size of the nanoshell; however it is necessary to consider other factors such as the amorphous contents and the nitrogen contents.

References

- [1] Ozaki J, Nozawa J, Yamada K, Uchiyama Y, Yoshimoto Y, Furuichi A, Yokoyama T, Oya A, Brown LJ, Cashion JD. Structures, Physicochemical Properties and Oxygen Reduction Activities of Carbons derived from Ferrocene-Poly(furfuryl alcohol) mixtures. *J. Appl. Electrochem* 2006;36:239-247.
- [2] Ozaki J, Kanematsu Y, Kannari N, Koshigoe Y, Kishimoto T. Influence of the nanoshell size on their oxygen reduction activity. *Carbon2009 Extended Abstract 2009*;C3-6.
- [3] Ozaki J, Tanifuji S, Furuichi A, Yabutsuka K. Enhancement of oxygen reduction activity of nanoshell carbons by introducing nitrogen atoms from metal phthalocyanines. *Electrochim. Acta* 2010; 55:1864-1871