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In situ Free-Surfactant Synthesis and ORR-Electrochemistry of Carbon-Supported Co_3S_4 and $CoSe_2$ Nanoparticles

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In recent years, the polymer electrolyte fuel cells (PEFCs) have been regarded as systems that have a lot of potential applications in transportation, generation of power, and portable electronic devices such as mobile cell and notebooks, resulting from their high energy-conversion efficiency, low temperature of operation, and environmental benefits.[1] Until now, the best and most frequently used catalysts for the oxygen reduction reaction (ORR) have been Pt-based materials, an expensive metal that is not abundant. Therefore, partial or complete replacement of Pt metal is of interest and much progress has been made so far.[2] Some Pt-free catalysts have been obtained and have shown promising activities such as carbonized catalase,[3] Co- or Fe-based catalysts,[4] tungsten carbides,[5] and transition-metal chalcogenides developed by Alonso-Vante et al.[6]

Thirty two years ago, Co_3S_4 as one of the $Me^{(a)}Me_2^{(b)}X_4$ ($Me^{(a)}$ = Mn, Fe, Co, Ni, Cu, or Zn; $Me^{(b)}$ = Ti, V, Cr, Fe, Co, or Ni; X = O, S, Se, or Te) spinels synthesized at a high temperature between 300 and 650 °C was reported to have the highest electrocatalytic activity for ORR in 1 M H_2SO_4, with an open circuit potential (OCP) of ca. 0.8 V vs a hydrogen electrode in the same solution.[7] More recently, the reversible potential of ca. 0.74 and 0.5 V vs RHE for ORR were also predicted for Co_9S_8 and Co_9Se_8.[8] On the other hand, a new synthesis method of monodispersive cobalt nanoparticle has recently been developed based on the thermal decomposition of cobalt carbonyl in organic solvents, using surfactants such as oleic acid and trioctylphosphane oxide (TOPO) to prevent the particle aggregation.[9] Lately, linnaeite Co_3S_4 nanocrystals have been synthesized by a direct reaction of monodispersive cobalt nanoparticles with sulfur powder under mild conditions (below 200 °C).[10] However, the ORR electrocatalytic activities of these nanocrystals have not been investigated yet. Furthermore, the surfactants are difficult to completely remove from the particles after synthesis, which influences the electrochemical and magnetic properties of these nanoparticles.[11]

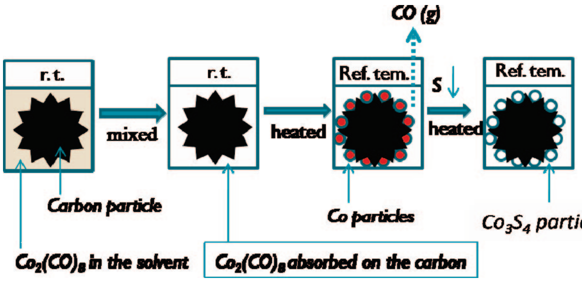

Figure 1. Scheme of the in situ synthesis method of Co_3S_4 nanoparticles supported on Vulcan XC-72 carbon without any surfactant, based on decomposition of cobalt carbonyl $Co_2(CO)_8$.

Vulcan XC-72 carbon is usually used as a supporting substrate for electrocatalysts and as a dispersing agent during synthesis of bimetallics. However, to the best of our knowledge, it is the first time carbon is being used not only as supporting substrate but also as dispersing agent to prepare cobalt chalcogenide nanoparticles, instead of the surfactants. The reaction scheme is shown in Figure 1. Carbon first absorbs cobalt carbonyl ($Co_2(CO)_8$) on the surface, and cobalt carbonyl then decomposes in situ on the carbon by heating to form cobalt particles, and finally, sulfur (or selenium) reacts with cobalt particles to produce Co_3S_4 and $CoSe_2$ particles supported on the carbon. Additionally, microwave heating has many advantages compared with conventional heating, e.g., short heating time, easy heat control, and saving energy as reported.[12]

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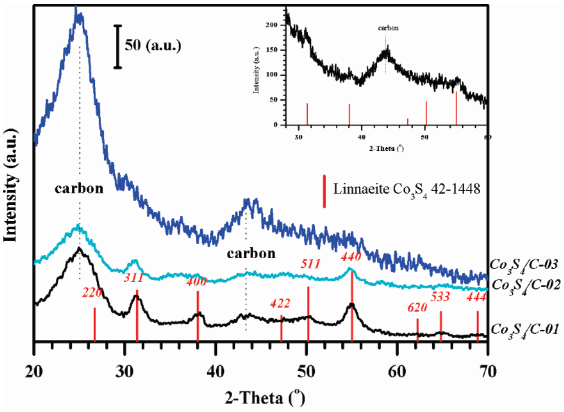
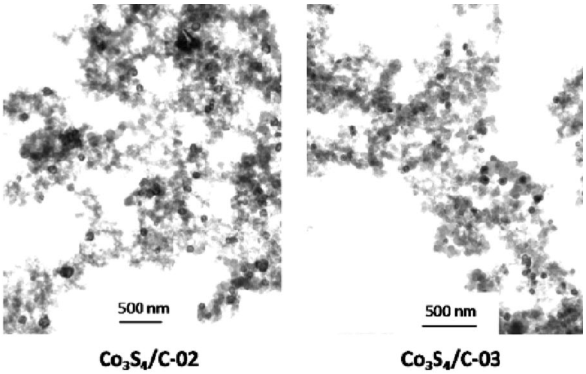


Figure 2. Powder X-ray diffraction patterns at room temperature using Cu Kα radiation for three samples of 20 wt % Co_3S_4/C obtained in three routes, i.e., Co_3S_4/C-01, Co_3S_4/C-02, and Co_3S_4/C-03. The inset shows the powder XRD of Co_3S_4/C-03 after annealing at 250 °C under nitrogen for 2 h with a step length of 0.015° (2θ) in 5 s.

In the present work, three 20 wt % Co_3S_4/C materials as a probe were synthesized in three routes (see the Supporting Information): Co_3S_4/C-01 was obtained by decomposition of $Co_2(CO)_8$ in the mixture solution containing the surfactants such as oleic acid and TOPO at the refluxing temperature followed by the reaction between cobalt particles and sulfur and then deposited on the carbon, as described in ref 10; Co_3S_4/C-02 was prepared by in situ synthesis method using a conventional heating, i.e., in situ decomposition of $Co_2(CO)_8$ absorbed on the carbon at the refluxing temperature followed by the in situ reaction between cobalt particles and sulfur. Typically, 0.27 g of $Co_2(CO)_8$ (0.79 mmol) and 0.64 g of carbon (XC-72) were dispersed in 15 mL of *p*-xylene under vigorous stirring and a nitrogen atmosphere at room temperature for 30 min. The mixture suspension was then heated to the refluxing temperature (ca. 142 °C), and cooled to room temperature. Later, 0.068 g of sulfur (2.12 mmol) in 6 mL of *p*-xylene were added to the above suspension containing cobalt particles. The resulting suspension was mixed at room temperature for 30 min and heated again to the refluxing temperature. Subsequently, the final suspension was cooled to room temperature and washed with anhydrous ethanol. Finally, the product was collected on a Millipore filter membrane (diameter 0.22 μm, pore size) and dried in a vaccum at room temperature. Co_3S_4/C-03 was synthesized by the microwave-assisted method in a microwave reactor (Discover LabMate from CEM Corporation) by a process similar to that of Co_3S_4/C-02. In the microwave reactor, the heating process and the cooling process can be accelerated by microwave with a preset power at 200 W in 3 min from 25 to 142 °C and fluxing pressurized air in 2 min from 142 to 50 °C, respectively, favoring the formation of monodispersive particles and the control of particle size.

Figure 2 shows the powder XRD patterns of the three samples. Co_3S_4/C-01 and 02 display the typical crystalline characteristics such as 311, 440 Bragg reflection lines of linnaeite Co_3S_4, according to the ICDD-PDF2-2004 card 42–1448[13] marked at the bottom, whereas the Bragg reflection peaks for Co_3S_4/C-03 are very weak. The annealing treatment at 250 °C favors the crystalline improvement of Co_3S_4/C-03, as shown in the inset.



Co_3S_4/C-02 Co_3S_4/C-03

Figure 3. Transmission electron micrograph (TEM) images of two 20 wt % Co_3S_4/C samples: Co_3S_4/C-02 and Co_3S_4/C-03.

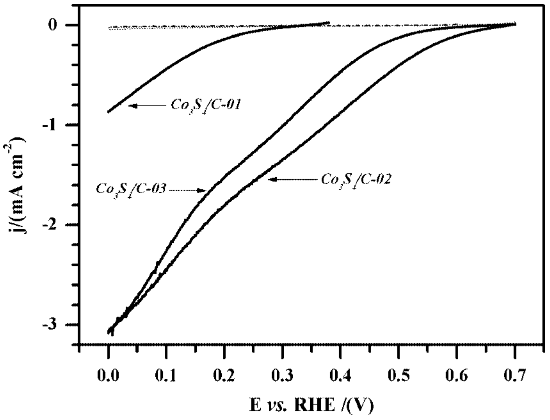


Figure 4. Linear potential scan curves of 20 wt % Co_3S_4/C-01, 02, and 03 on rotating glassy carbon electrode (1600 rpm) in oxygen-saturated 0.5 M H_2SO_4 at room temperature. Sweep rate, 5 mV s^{-1}; catalyst loading on the electrode surface, 11 μg cm^{-2}. The dashed lines present the linear potential scan curves recorded under nitrogen.

Figure 3 presents TEM images of Co_3S_4/C-02 and Co_3S_4/C-03 showing good dispersion. However, Co_3S_4/C-01 particles are not clearly distinguished, probably resulting from the surfactant coating (see the Supporting Information). The average particle size can be determined: ca. 64 nm for Co_3S_4/C-01, 86 nm for Co_3S_4/C-02, and 55 nm for Co_3S_4/C-03. These results indicate that both of the in situ synthesis methods are effective in preventing the particle aggregation. Furthermore, the microwave-assisted method can synthesize smaller particles resulting from the heating and cooling process in a short time in the microwave reactor.

Figure 4 shows the electrocatalytic activities of the three samples for ORR in 0.5 M H_2SO_4 recorded at 1600 rpm. No mass-transfer effect was observed. The samples were annealed at 250 °C for 2 h under a high-purity nitrogen atmosphere before the electrochemical measurement. Co_3S_4/C-02 and 03 without surfactant show higher activity toward ORR with an OCP of between 0.66 and 0.68 V vs RHE and higher current densities than Co_3S_4-01 with the surfactants. The OCP values are comparable to the predicted value 0.74 V for Co_9S_8.[8a] One of the possible reasons is that the surfactants used in the synthesis process block the active sites as described in ref 11b. Noteworthy, the in situ powder XRD

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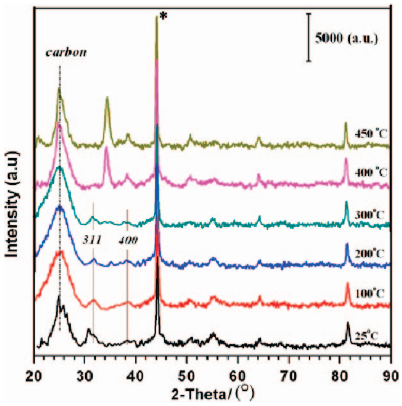
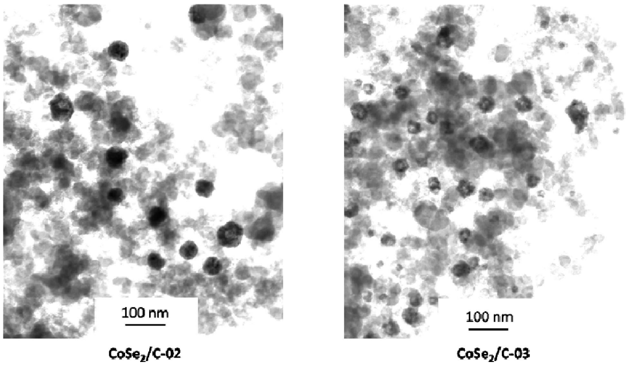


Figure 5. In situ high-temperature powder X-ray diffraction patterns of Co_3S_4/C-01 in the temperature range from 25 to 450 °C with a rate of 5 °C min^{-1} under an air atmosphere. Peak marked with an asterisk (*) belongs to the substrate of Kanthal.



$CoSe_2$/C-02 $CoSe_2$/C-03

Figure 6. TEM images of 20 wt % $CoSe_2$/C samples obtained by in situ synthesis methods: conventional heating for $CoSe_2$/C-02 and microwave heating for $CoSe_2$/C-03.

results in Figure 5, at temperatures higher than 300 °C, show that Co_3S_4 nanoparticles are not stable under air environment. Thus the removal method of surfactants reported in ref 11b cannot be applied for Co_3S_4 particles by calcination above 400 °C under an air atmosphere. These results indicate that other two routes without the surfactants are effective alternative methods to synthesize the similar electrocatalysts supported on the carbon.

Figure 6 shows TEM images of 20 wt % $CoSe_2$/C (the phase was verified by powder XRD, as shown in the Supporting Information) obtained by in situ synthesis methods: conventional heating for $CoSe_2$/C-02 and microwave heating for $CoSe_2$/C-03, respectively. From TEM images, a good dispersion can be observed in both cases. Again, microwave heating favors better particle dispersion and smaller particle size than conventional heating: average particle size ca. 52 nm for $CoSe_2$/C-02 and ca. 36 nm for $CoSe_2$/C-03.

Figure 7 displays the electrocatalytic activities of 20 wt % $CoSe_2$/C-02 and $CoSe_2$/C-03 nanoparticles. Both systems show the similar OCP values: 0.72 V for $CoSe_2$/C-02 and 0.69 V for $CoSe_2$/C-03, which are higher than the reported one for Co_9Se_8 (ca. 0.5 V).[8b] The Tafel curve of $CoSe_2$/C-02 shows a slope of 125 mV $decade^{-1}$ (see the straight line). This slope is not clearly defined for $CoSe_2$/C-03, which shows a higher catalytic current. This difference may result from the different particle size and nanocrystallinity as observed in TEM images and powder XRD patterns, respectively.

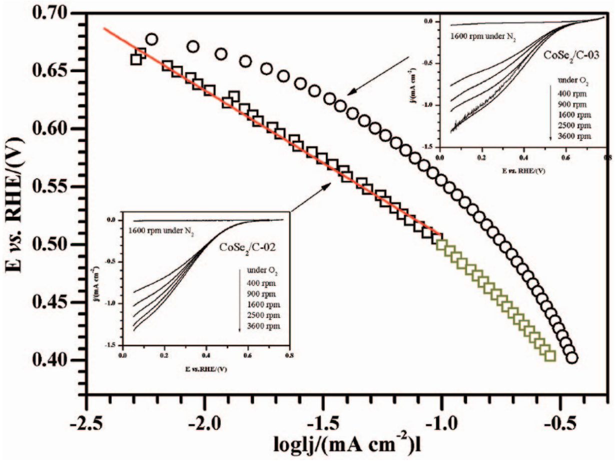


Figure 7. Tafel plot after the mass-transfer correction and linear potential scan curves (inset) of 20 wt % $CoSe_2$/C-02 and $CoSe_2$/C-03 on rotating glassy carbon electrode in nitrogen and oxygen saturated 0.5 M H_2SO_4 at room temperature. Sweep rate, 5 mV s^{-1}; catalyst loading on the electrode surface, 11 μg cm^{-2}.

In conclusion, Co_3S_4 and $CoSe_2$ nanoparticles supported on carbon have been successfully prepared by in situ synthesis method under mild conditions without any surfactant preventing particle aggregation. These promising materials as nonprecious metal electrocatalysts have shown the electrocatalytic activities toward ORR in 0.5 M H_2SO_4 with the onset potential at ca. 0.7 V vs RHE, though it is still lower than that of Ru_xSe_y type electrocatalysts.[6e] To further improve electrocatalytic activities, we are making attempts at optimizing synthesis conditions to obtain a smaller particle size and better particle dispersion as well as an optimum of the particle's surface chemistry.

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Supporting Information Available: Chemicals, 20 wt % Co_3S_4/C and $CoSe_2$/C synthesis details, characterization techniques such as powder X-ray diffraction (XRD), in situ high-temperature powder X-ray diffraction, transmission electron micrograph (TEM), and rotating disk electrode (RDE) measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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