

Electrodeposition of Polypyrrole Nanowires within Vertically Oriented Mesoporous Silica Template

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Abstract : Polypyrrole (Ppy) nanowire has been electrochemically synthesized via vertically oriented mesoporous silica template. The mesoporous template is also electrochemically deposited on indium tin oxide coated (ITO) glass from tetraethyl orthosilicate (TEOS) and cetyltrimethylammonium bromide (CTAB) surfactant. The highly ordered silica template is demonstrated to be 100~120nm thick with the pores of 4~5 nm diameter by scanning electron microscope (SEM) and transmission electron microscope (TEM). Ppy is formed to fill pores of the silica template from pyrrole solution by electrochemical oxidation. The Ppy in Ppy/silica/ITO composite was found to exhibit reversible electrochemical activity, as characterized by cyclic voltammetry (CV).

Keywords : Polypyrrole, Nanowire, Mesoporous silica, Electrochemical capacitor

1. Introduction

Vertically oriented porous materials are promising templates for fabrication of nanowires and nanotubes. Various metal and conducting polymer (CP) nanowires can be synthesized by simple deposition into the porous template. Especially, extensive research on the fabrication of nanowires using porous anodic aluminum oxide (AAO) template has long been conducted.^{1,2)} Recently, a novel method to prepare highly-ordered mesoporous silica thin film in which the direction of pores are normal to the substrate was reported by Walcarius group.^{3,4)} Novel synthesis and application is possible with the silica template due to its much smaller pores compared to AAO. Silica template with vertically aligned pores to the electrode surface has many advantages in terms of conductivity and modification of pores. Prussian blue⁵⁾ and polythiophene⁶⁾ depositions into the silica template have been recently reported.

This study demonstrates Ppy nanowires embedded in the vertically oriented mesoporous silica template. The silica film is prepared by electrochemically-assisted method

based on sol-gel process^{7,8)} from silica sol solution containing surfactant. In ethanol and water mixture solution, silica precursors and surfactants form mesostructures by self-assembly.⁹⁾ The mesostructures are mainly determined by the ratio of silica precursor and surfactant concentrations. Cylindrical mesostructure of silica-surfactant is formed by adjusting solution concentrations¹⁰⁾ and hydroxyl ions generated by cathodic potential catalyze sol-gel process.⁴⁾ Subsequently, Ppy is deposited into silica template by anodic oxidation from aqueous pyrrole solution.

2. Experimental

2.1. Chemicals and preparation

Tetraethylorthosilicate (TEOS, 99.0%), cetyltrimethylammonium bromide (CTAB, 99.0%), sodium nitrate (99.0%), potassium ferricyanide ($K_3Fe(CN)_6$, 99+%), and pyrrole (99%) were purchased from Aldrich(Seoul, Korea). Hydrochloric acid (min 35%, Junsei), absolute ethanol (Merck) and ultrapure water (> 18 M, Millipore system) were used. Indium tin oxide (ITO, 0.7 mm, 50 Ω) glass was purchased from JMI Korea.

The starting sol solutions were prepared from 0.1 M $NaNO_3$ aqueous solution. To 20 ml of this solution,

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1.32~3 mmol of TEOS, 20 ml ethanol, and CTAB were added to adjust the mole ratio of CTAB/TEOS to 0.32. Before using, the sol solutions were stirred moderately and aged for 150 mins. Electrochemical experiments were conducted by the three electrode system using SCE as reference electrode, and platinum wire as counter electrode. Working electrode was immobilized and the surface area was limited by O-ring in Teflon cell. Cathodic potential was applied for growing of silica films and sol solution was immediately removed and washed by water after electrochemical treatment for inhibition of any further unexpected deposition of silica. After silica deposition, the electrodes were dried in 130°C for overnight for condensation and hardening the silica skeletons. The surfactants were removed by 0.1 M HCl ethanol solution for 5 min under mild stirring. Subsequently, washing by water and blowing by nitrogen steps were followed. Potentiostatic and galvanostatic method for deposition is tested in varying deposition time. 0.1 M pyrrole, 0.2 M KCl aqueous solution is used for Ppy deposition. Ppy is synthesized on silica-ITO composite electrode by galvanostatic oxidation.

2.2. Characterization

Cross-sectional SEM was employed to estimate the thickness of silica film and surface morphology is demonstrated by tilted SEM.

Silica film is mechanically scratched from ITO glass electrode and placed on TEM grid by water dispersion.

Ion accessibility through silica film is tested by cyclic voltammetric analysis using 0.1 mM ferricyanide as redox probe. Electrolyte effect to ion accessibility is tested in various 0.01~0.1 M of KCl supporting electrolyte. Reduction and oxidation of Ppy nanowires embedded in silica template is characterized by CV in 0.2 M KCl solution.

3. Results and Discussion

3.1. Characterization of mesoporous silica template

Ordered mesoporous silica film was prepared on ITO glass electrode from aqueous TEOS solution containing CTAB by electrochemical method. The thickness of this silica film was determined as 100~120 nm from cross-sectional SEM image (Fig. 1(a)). Aggregation-free silica surface was observed on ITO glass (Fig. 1(b)). TEM image supports the formation of well-ordered mesopores (dia. 4~5 nm) in the silica template (Fig. 1(c)).

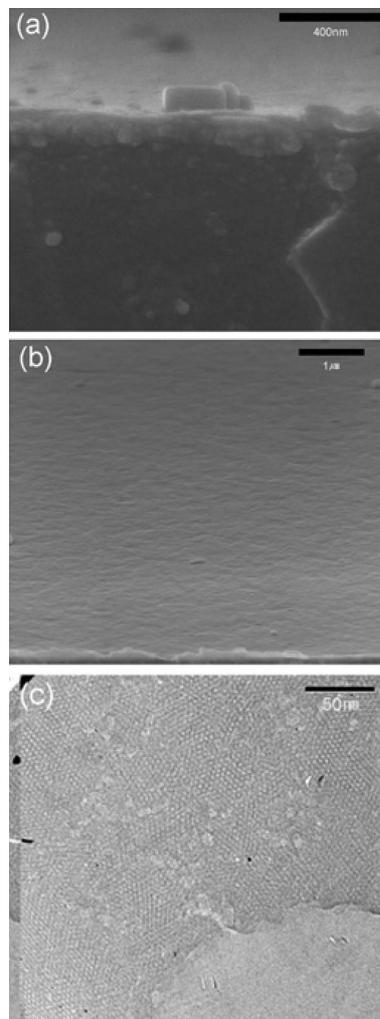


Fig. 1. (a) Cross-sectional image, (b) surface morphology obtained by tilted SEM and (c) TEM image of silica film.

Cyclic voltammetry (CV) of ferricyanide redox couple was performed to examine ion accessibility to the surface of substrate through the silica template (Fig. 2(a)). Before surfactant removal, a redox signal of ferricyanide anion is not observed in its original redox potential range before surfactant (CTAB) removal but the current appears after subsequent surfactant removal. This indicates that ferricyanide ions are accessible to the ITO surface only after surfactant removal. The decreased redox current compared to result on bare ITO electrode implies restricted mass transport of ferricyanide anions by silica template. The restriction is ascribed to the repulsive electrostatic

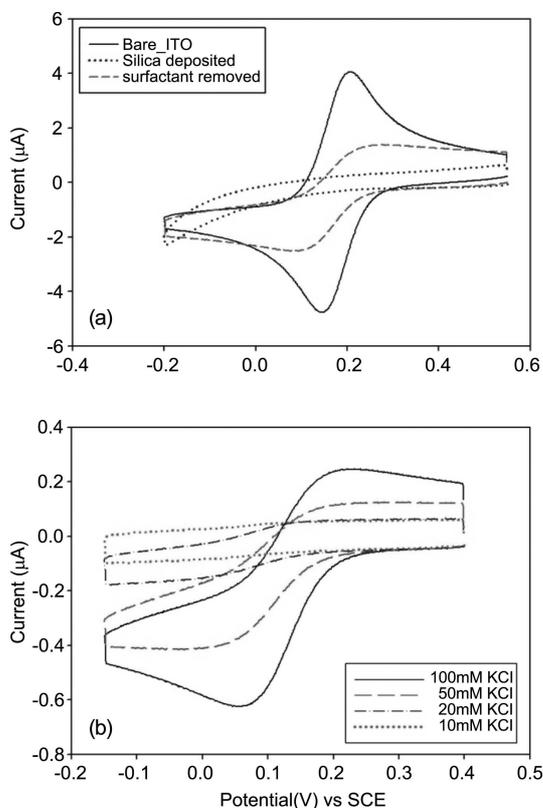


Fig. 2. Cyclic voltammogram of $\text{Fe}(\text{CN})_6^{3-/4-}$ redox couple (a) in 0.1 M KCl solution on silica/ITO composite electrode before/after surfactant removal and on bare ITO electrode. (b) 0.01-0.1 M KCl solution on silica-ITO composite electrode. Scan rate : 50 mV/s. Surface area of electrode is 0.28 cm^2 .

interactions between negatively-charge silica pore walls and ferricyanide anions.^{4,5)} The redox current becomes smaller with decreasing supporting electrolyte concentration (Fig. 2(b)), which reflects the increased unfavorable interaction at lower ionic strength. In brief, all these characteristics unequivocally prove the formation of the vertically oriented silica template.^{4,5)}

3.2. Deposition of Ppy into silica template

Ppy deposition on silica-ITO composite electrode from pyrrole monomer solution is demonstrated by CV and compared with the result on bare ITO electrode (Fig. 3(a)). The onset potential of Ppy deposition on silica template is slightly decreased compared with bare ITO, while overall current is much smaller.

Fig. 3(b) shows the voltage profile observed in galva-

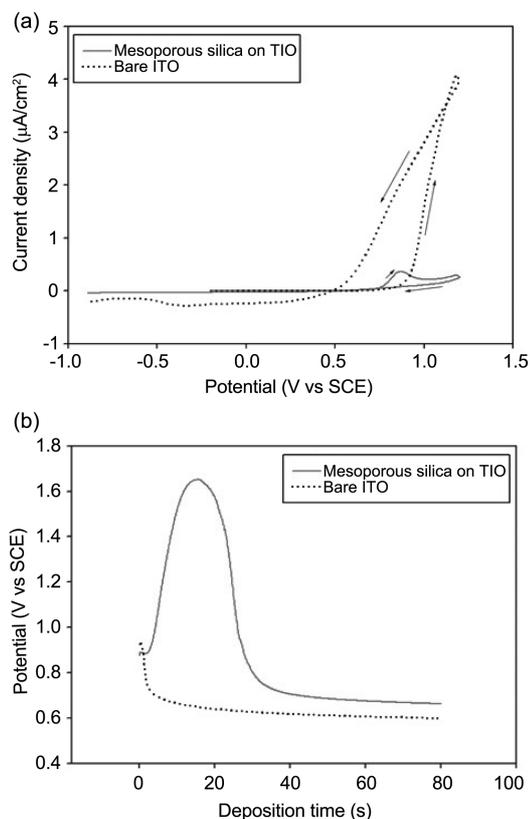


Fig. 3. (a) Cyclic voltammogram at scan rate 0.1 V/s and (b) Potential-time curve on galvanostatic deposition at the current density, 57 A/cm^2 on silica/ITO composite electrode. 0.1 M pyrrole, 0.2 M KCl solution was used.

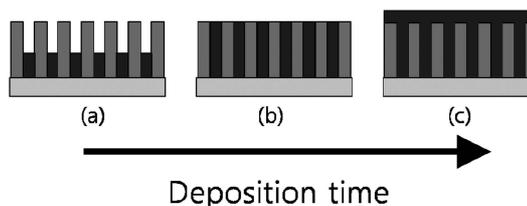


Fig. 4. Hypothesis of progress of Ppy growth.

nostatic Ppy deposition. Ppy polymerization is initiated at lower potential on the silica template compared to bare ITO electrode. The potential required to maintain constant current increases as the deposition progress. After passing through the maximum, the voltage decreases to flatten around 0.7 V. The voltage profile in Fig. 3(b) can be related with the degree of deposition (Fig. 4). It seems that higher potential is required to grow Ppy nanowires through the mesopores, because mass transfer for Ppy

growth is restricted compared with bare ITO (Fig. 4(a)). After the pores are filled with Ppy nanowires completely (Fig. 4(b)), further Ppy growth takes place at larger area, requiring less overpotential (Fig. 4(c)) than before. Similar features are also observed in growth of templated gold nanowires.¹¹⁾

3.3. Redox behavior of Ppy nanowires embedded in silica template

Redox behavior of Ppy nanowires in vertically aligned silica template on ITO electrode is assessed by CV. The amount of Ppy deposited is controlled by the total charge consumed for the electropolymerization.¹²⁾ Ppy has been galvanostatically deposited until the potential-time curve passes the maximum. About 2.15 mC was consumed to deposition process. The same amount of charge was used on bare ITO to prepare a counterpart. Fig. 5(a) is cyclic voltammogram of Ppy nanowires embedded in silica/ITO electrode and compared with the silica/ITO electrode without Ppy. Reversible reduction and oxidation current observed in the potential range of -0.2 V~ 0 V. It is interesting to note that Ppy nanowires exhibits redox activity as embedded in silica template on electrode without template removal. In the case of Ppy deposited on bare ITO (Fig. 5(b)), the redox peaks are not clearly

observed, due to the increased non-faradaic charging current. The redox behavior of Ppy nanowires after removal of silica template (i.e., by HF etching) and the origin of the different redox behavior deserve further study.

4. Conclusion

In this study, Ppy nanowires embedded in vertically aligned mesoporous silica template have been prepared by electrochemical method on ITO electrode. The composite electrode was demonstrated by scanning electron microscope and electrochemical experiment. Ppy nanowires in the composite electrode were found to exhibit reversible electroactivity.

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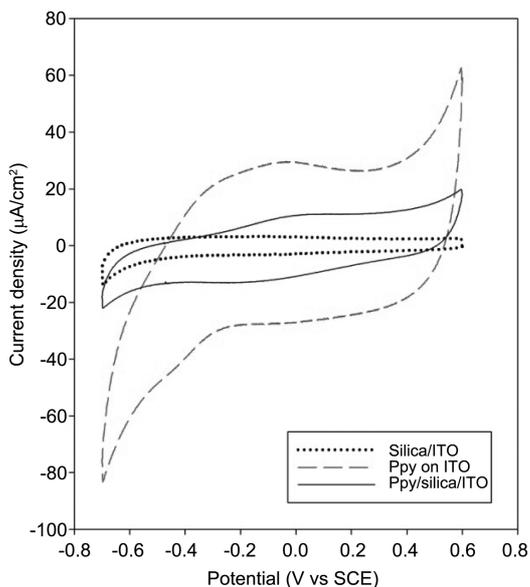


Fig. 5. Cyclic voltammogram of Ppy/silica/ITO composite electrode and Ppy/ITO in 0.2 M KCl solution. Scan rate : 0.1 V/s.

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