



NANO | MICRO small

Phase-Transition Nanowires

Direct identification of proteins, important but non-amplifiable biomolecules, is critical in advancing modern biomedicine technologies.

J. Joo, D. J. Ahn, and co-workers explore the phase-transition phenomenon of conjugated polymer nanowires in response to the presence of protein particles on page 1154. Even a single polythiophene nanowire having capture aptamers functionalized on its surface responds to a specific interaction with target proteins. Such a unique phase-transition evokes enhancement of photoluminescence and generation of a local resonance Raman signal simultaneously, dramatically corresponding to protein concentration.

9/2016

WILEY-VCH

Protein Recognition by Phase Transition of Aptamer-Linked Polythiophene Single Nanowire

J. Joo, D. J. Ahn, and co-workers

Protein Recognition by Phase Transition of Aptamer-Linked Polythiophene Single Nanowire

Chunzhi Cui, Dong Hyuk Park, Hyun Choi, Jinsoo Joo,* and Dong June Ahn*

Conjugated polymers have made a profound impact and provided smart sensing systems with superior performance for biological application. These applications exploit the advantage of enhanced compatibility of conjugated polymers with biological materials.^[1–5] As a typical conjugated polymer, cationic polythiophene has been assessed as active systems for biological sensing.^[2,4] Most sensing events of conjugated polymers are easily quantified from optical signal changes, such as absorption,^[6] fluorescence,^[7–11] or electrical signal responses.^[12] These signal changes generally depend on conformational changes or the doping level of conjugated polymers.^[13,14]

There are also some other sensing methods upon surface-enhanced Raman spectroscopy effect^[15–18] which use Raman tags for indirect observation. In addition, for direct observation of the sensing probe (conjugated polymer) associated with bioevents, applying the resonance Raman scattering (RRS) effect^[19,20] is an operative option. By selecting the excitation laser energy, the RRS change of π -conjugated polymers induced by a bioevent can be directly observed. In recent years, many of the bioevents have been observed by the confocal fluorescence or Raman microscopy,^[21–23] and collecting confocal spectroscopic data with respect to a single nanoprobe becomes more important.^[11,14,17,24]

In the previous report of our group, DNA sensing using doped poly (3-methylthiophene) (P3MT) single nanowire, in which the dopant moiety successfully mediated surface functionalization of oligonucleotide sequence, was performed by nanoscale photoluminescence (PL) observation in solid state.^[11] In this study, the dopant moiety was a successful mediator of surface functionalization of oligonucleotide sequence. Herein, for sensing another important but unamplifiable biomolecules, i.e. protein, we utilized phase-transition property of a single P3MT nanowire having aptamers functionalized on its surface. Our intention is to explore the phase-transition characteristics corresponding to specific interaction with target proteins. Doped light-emitting P3MT nanowires were electrically prepared by using tetrabutylammonium trifluoromethane sulfonic acid (TBACF₃SO₃) as a dopant based on an anodic alumina oxide (Al₂O₃) nanoporous template.^[25] The thrombin aptamer (*T*-aptamer) easily attached to the P3MT nanowire surface through electrostatic interaction (i.e., ionic binding) between sulfuric trioxide (SO₃[−]) from the TBACF₃SO₃ dopant and the terminal amine (NH₃⁺) modified aptamer.

Figure 1a shows the normalized UV/vis absorption spectra of the P3MT, P3MT/*T*-aptamer, and *T*-protein treated P3MT/*T*-aptamer nanowires, respectively. For the P3MT nanowires, a broad bipolaron peak was observed at ≈ 800 nm, implying a doped state, and the π - π^* transition peak was observed at ≈ 385 nm.^[25] The P3MT nanowires functionalized with *T*-aptamer exhibited a marked decrease in the intensity of the doping-induced bipolaron peak. This suggests that the interaction between the SO₃[−] group of the TBACF₃SO₃ dopant and NH₃⁺ group of the *T*-aptamer reduced the interaction between the cationic P3MT main chains and the negative counter ions. After interaction with *T*-protein, the π - π^* transition peak was noticeably redshifted from ≈ 385 to ≈ 396 nm and new π - π^* transition peaks were observed at ≈ 550 and ≈ 610 nm, respectively. It has been reported that the P3MT polymer chain adopts two helical configurations, i.e., a coil-like and a rod-like configuration. The coil-like configuration of the P3MT nanowire gives rise to an absorption peak at ≈ 385 nm, nonplanar with less π -conjugated and region-random like characteristics. However, the rod-like conformation gives rise to absorption peaks at ≈ 550 and ≈ 610 nm, and is more planar with, more π -conjugated, and region-regular like characteristics.^[26] Hence, the data indicate formation of relatively well-ordered configuration upon interaction of the P3MT/*T*-aptamer nanowires with *T*-protein. Figure 1b shows

Dr. C. Cui, Dr. H. Choi,^[*] Prof. D. J. Ahn
Department of Chemical and Biological Engineering
Korea University
Seoul 136–701, Korea
E-mail: ahn@korea.ac.kr

Prof. D. H. Park
Department of Applied Organic Materials Engineering
Inha University
Incheon 402–751, Korea

Prof. J. Joo
Department of Physics
Korea University
Seoul 136–713, Korea
E-mail: jjoo@korea.ac.kr

Prof. D. J. Ahn
KU-KIST Graduate School of Converging Science and Technology
Korea University
Seoul 136–701, Korea

^[*]Present address: Central Technology R&D Institute, Hyundai Oilbank Co., Ltd., Seongnam-si, Gyeonggi-do 463–400, Korea

DOI: 10.1002/sml.201501908

