Sensors and Actuators B 218 (2015) 31–36

Contents lists available at ScienceDirect

Sensors and Actuators B: Chemical

journal homepage: www.elsevier.com/locate/snb

Short communication

Scattering analysis of single polyaniline nanoparticles for acidic environmental sensing

Yoochan Hong[a,b], Seungyeon Hwang[a,c], Dae Sung Yoon[d], Jaemoon Yang[a,e,*]

[a] Department of Radiology, College of Medicine, Yonsei University, Seoul 120-752, Republic of Korea
[b] Department of Biomedical Engineering, Yonsei University, Wonju, Gangwondo 220-710, Republic of Korea
[c] Nanomedical National Core Research Center, Yonsei University, Seoul 120-752, Republic of Korea
[d] Department of Biomedical Engineering, Korea University, Seoul 136-703, Republic of Korea
[e] YUHS-KRIBB Medical Convergence Research Institute, Seoul 120-752, Republic of Korea

ARTICLE INFO

Article history:
Received 6 January 2015
Received in revised form 15 April 2015
Accepted 20 April 2015
Available online 6 May 2015

Keywords:
Nanoscattering
Single nanoparticle scattering spectrum
Polyaniline nanoparticle
Acidic environment

ABSTRACT

Herein, we demonstrate an acidic environmental sensing technique based on polyaniline (PAni) nanoparticles and a nanoscattering spectrum imaging analysis (NSSIA) system. PAni nanoparticles (PNs) were formulated by a homogeneous coating process using Tween® 80 as a surfactant. Subsequently, PNs were immobilized to an aminated glass substrate to sense environmental pH conditions for single PNs, using the NSSIA system. In contrast to dark-field scattering imaging of the PN, the NSSIA system enabled us to obtain scattering spectra for a single PN to specifically identify the environmental pH conditions. Furthermore, the immobilized PN on the substrate exhibited excellent reversibility for the acquisition of the scattering spectra after repeated change of environmental pH.

1. Introduction

Nano-bio sensing technologies using single nanoparticles have attracted considerable attention to increase the sensitivity and analytical sensing [1,2]. Recently, nano-bio sensors based on the characterization of a single nanoparticle were continuously reported [3,4]. Because only a few nanoparticles needed to be monitored at a time, the required sample volume was significantly lower rather than the conventional ensemble method for multiple nanoparticles [5]. Furthermore, the absolute detection limit (number of analyzed molecules per single nanoparticle) can be dramatically reduced [6].

Numerous studies for nano-bio sensing based on a scattering light from single nanoparticles have been conducted using plasmonic metal nanoparticles [7–10]. When the metal nanoparticles interact with specific wavelength of incident light, collective oscillations of conduction electrons is occurred in the surface of metal nanoparticle, called as localized surface plasmon resonance (LSPR) effect [11]. The peaks of LSPR related spectra are sensitive to the dielectric medium on the surface of the metal nanoparticles that can be used to recognize biomolecules [12]. However, the metal nanoparticles are hard to intrinsically sense the surrounding environments without surface ligands.

On the other hand, conjugated polyaniline (PAni) nanoparticles as a sensing material have been extensively emerged because of their ease of synthesis, low cost per monomer, tunable opto-electric properties, and better chemical stability compared to other conjugated polymers [13]. Thus, various reports have dealt with the synthesis, characterization, and applications of PAni and its composites for a nano-bio sensing [14,15]. In particular, the electronic band gap for PAni can be controlled by doping/dedoping states [16]. The difference between doping and dedoping states affect changes of optical spectra of PAni in visible range [17]. These doping and dedoping states of PAni can be adjusted by various dopants, such as strong acids, Lewis acids, transition metals, and alkali ions [18]. However, previously reports about characterizations or applications using PAni as a sensing material have demonstrated by ensemble analysis for multiple PAni nanostructures [19–21]. To the best our knowledge, up to date, researches for light scattering of single PAni nanoparticles (PN) were deficient.

In this study, PAni nanoparticles (PNs) using Tween® 80 were preferentially fabricated by a solvent shifting method to construct stable nano-substrates [17]. PNs were then immobilized onto aminated glass slides for scattering sensing and imaging. Herein, nanoscattering spectrum and imaging analyzer (NSSIA) system has been developed to monitor the light scattering of single nanoparticles and to achieve a reasonable signal-to-noise ratio. Because

* Corresponding author at: Department of Radiology, College of Medicine, Yonsei University, Seoul 120-752, Republic of Korea. Tel.: +82 2 2228 0845.
E-mail address: 177hum@yuhs.ac (J. Yang).

http://dx.doi.org/10.1016/j.snb.2015.04.098
0925-4005/

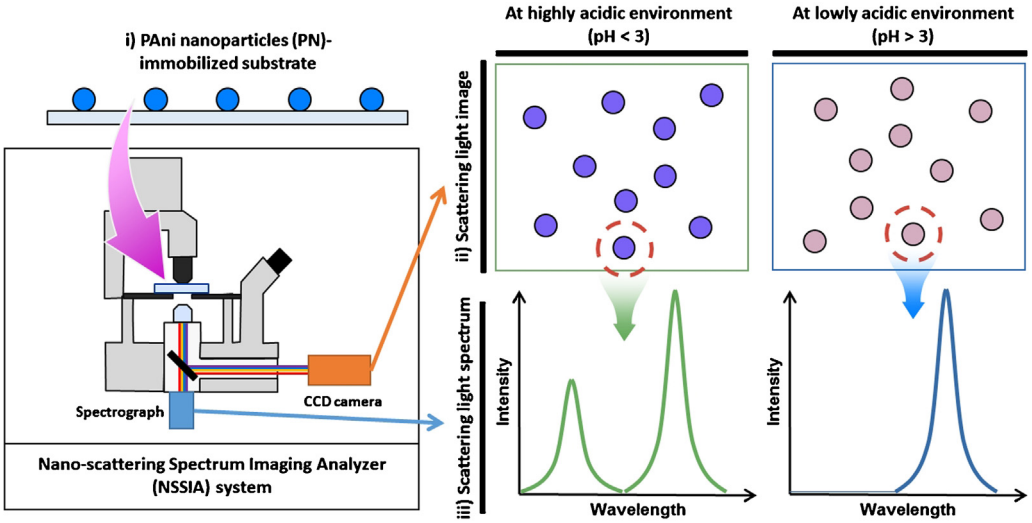

Fig. 1. Schematic illustration of a method of acidity sensing by detection of light scattering from a single polyaniline nanoparticle (PN). (i) The preparation of PN-immobilized substrate, (ii) imaging scattered light from the PN, and (iii) the acquisition of light scattering spectra from a single PN using the NSSIA system.

conventional absorbance spectroscopic analysis for nanoparticles does not provide a practical means of accomplishing sensitive sensing due to low sensitivity and poor signal-to-noise ratio [6]. The instrumental approach based on NSSIA system involves using highly magnified microscopy coupled with oblique irradiation of light toward the individual nanoparticle [22]. The scattered light from the single nanoparticle can be collected to an objective lens and be analyzed by a spectrograph. Thus, the PN-immobilized substrate was exposed to various pH conditions, and scattered light from a single PN was detected and analyzed using the NSSIA system for the acquisition of scattering spectra and images (Fig. 1). Furthermore, the optical reversibility for immobilized PN under changes in chemical states, by varying the surrounding acidic environments, was evaluated using NSSIA system.

2. Materials and methods

2.1. Synthesis of PAni

PAni was synthesized by a chemical oxidation polymerization reaction as previously described [18]. Typically, aniline monomer (0.2 moles) was added to 300 mL of 1 M hydrogen chloride (HCl), in an aqueous solution. Successively, the polymerization process was carried out by a dropwise addition of ammonium persulfate (0.05 moles) solution prepared in 200 mL of 1 M HCl, in aqueous solution, as an oxidant, for 6 h at 4 °C. The precipitated polymer salt was recovered from the reaction vessel by a filtration and dispersed in 500 mL of 1 M sodium hydroxide solution. Then, the deprotonated emeraldine base (EB) PAni was filtrated and dispersed in 500 mL of acetone. Finally, a fine EB PAni powder was obtained after filtration and was dried in an oven for 48 h.

2.2. Preparation of PNs

The PNs were prepared by a solvent shifting method [17]. Briefly, 5 mg of EB PAni powder was dissolved in 4 mL of N-methyl-2-pyrrolidinone. The prepared solution was added to 30 mL of deionized water (DW) containing 100 mg of Tween® 80. The mixture was vigorously stirred at room temperature for 4 h. After the reaction, PNs were dialyzed for 24 h (Mw, 1000 Da dialysis cut-off), and then centrifuged using a centrifugal filter (Mw, 3000 Da, Merck Millipore Korea, Seoul, Republic of Korea) at 3000 rpm for 3 h. PNs were then dispersed into 5 mL of DW. The absorbance spectra of PNs were measured using a UV-Vis spectrometer (Lambda 25; Perkin Elmer Korea, Seoul, Republic of Korea) to confirm the optical properties of the PNs.

2.3. Preparation of PN-immobilized substrate

PN-immobilized substrate was fabricated as follows. Cover slides (12 mmϕ) were cleaned by piranha solution (3:1 H_2SO_4/30% H_2O_2) for one hour. After the piranha cleaning, the cover slides were thoroughly rinsed three times with DW and dried. To coat the cover slides with amino groups, the cover slides were immersed in 5 mL of DW containing 100 μL of aminopropyltrimethoxysilane solution for 24 h. After the reaction, the cover slides were rinsed with excess DW and ethanol, and dried. Subsequently, the amino group-coated cover slides were immersed in PN solution (1 mg/mL) for 24 h, rinsed with DW, and dried.

2.4. Nano scattering spectrum imaging analysis (NSSIA) system

All single nanoparticle light scattering spectroscopic measurements and imaging were performed using an inverted microscope (Axio Observer A1; Carl Zeiss Korea, Seoul, Republic of Korea) equipped with an imaging spectrograph (Acton SP2500; Princeton Instruments, New Jersey) and a charge-coupled device (CCD) detector (PIXIS400B; Princeton Instruments, New Jersey). A color CCD camera (DCU224C; Thorlabs, New Jersey) was also attached to the front port of the microscope to facilitate identification and alignment of a single PN. A dark field condenser [numerical aperture (NA) = 1.2–1.4] was used to illuminate the PN and a variable aperture 100× objective (NA = 0.6–1.5) was used to collect the light scattering signal from a single PN.

The method for scattering spectroscopic measurements and imaging using NSSIA system are as follows. Briefly, the spectrograph grating was placed in zero order and the spectrograph entrance slit was opened to the maximum setting to project a wide-field image onto the CCD detector. Next, single PN was placed in the center of the field and the entrance slit was closed to 20 μm. Then, the spectrograph grating was rotated to disperse the first-order diffracted light onto the CCD detector. To ensure that only the scattered light from a single PN was analyzed, the region of interest was selected using the CCD control software. An adjacent empty region of the CCD detector with the same dimensions was also collected to perform background subtraction. Integration times varied,