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Ultra-sensitive direct detection of silver ions via Kelvin probe force microscopy

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ABSTRACT

Nanotoxicity is receiving great importance due to its potential impact on human health and environment and due to rapid development in the field of nanoscale research and industry. Herein, we report the Kelvin probe force microscope (KPPM)-based nanotoxicity material detection using surface potential difference. In general, it is difficult to measure the size of ion (Ag^+) using a conventional atomic force microscope (AFM) because of the limited resolution. In this study, we have demonstrated that KPFM is capable of ultra-sensitive detection of silver ion with silver specific DNA by a single droplet. Furthermore, the measured surface potentials for Ag+ and DNA binding enable the detection performance for a practical sample that is general drinking water. Remarkably, the KPFM based silver ion detection enables an insight into the coordination chemistry, which plays an important role in early detection of toxicity. This implies that KPFM based detection system opens a new avenue for water testing sensor.

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1. Introduction

Over the past two decades, scientific research and industrial innovation on the subject of nanomaterials have seen radical development, which has led to considerable scientific and public concern about the potential influence of nanotoxic materials on human health and the living environment (Krug and Wick, 2011). Nanotoxic materials characterized by small sizes could have unpredictable reactivity due to their extensive surface area, which can lead to serious health and environmental risks (Buzea et al., 2007). Silver (Ag) is a representative nanotoxic material that has been widely employed in modern industries such as electronics, photography, batteries, brazing, and mirrors (Chun et al., 2010; Greenwood and Earnshow, 1997; Liu and Yu, 2011; Siddhartha et al., 2007; Vanhaverbeke et al., 2002). Silver, however, is also one of the most hazardous species of metal pollutants in the environment and contaminates ambient air, water, soil, and even food (Dean, 2000; Wood et al., 2004). Annually, approximately 2500 t of silver pollutant is released into the environment through industrial wastes and emissions, with an additional 150 t and 80 t released into wastewater sludge and surface water, respectively (Ratte, 1999). In the microbiological world, the silver ion (Ag^+) is capable of inhibiting the activities of many microorganisms, including bacteria, viruses, algae, and fungi (Bhardwaj et al., 2006). In addition, Ag^+ is able to produce dose-dependent cytopathogenic effects on distinct cell species, including human tissue mast cells, endothelial cells, keratinocytes, and human gingival fibroblasts, by binding with various metabolites and inactivating sulfhydryl enzymes (Hidalgo and Domínguez, 1998; Poon and Burd, 2004; Schedle et al., 1995). Moreover, the entry of Ag^+ into the human body could result in internal organ edema, and even death. Considering all these potential problems and hazards, the development of a technique capable of highly sensitive and selective detection of Ag^+ is of great importance.

Some metal ions are able to selectively bind to native or synthetic DNA duplexes and form thermally stable metal-mediated base pairs (Clever et al., 2007; Ono et al., 2008; Zimmermann et al., 2002). Based on this binding mechanism, the interaction between metal ions and DNA base pairs has attracted great attention owing to its potential application in metal ion sensing (Clever et al., 2007; Zhang et al., 2011). Latterly the cytosine–cytosine (C–C) mismatches have a specific interaction with Ag^+ which is a significant viewpoint of Ag^+ sensors (Feng et al., 2011; Gong and Li, 2011; Huy et al., 2011; Ono et al., 2008; Park et al., 2013; Wen et al., 2010; Zhao et al., 2010). Ono et al. developed a fluorescent sensor to detect Ag^+ using C–Ag^+–C coordination chemistry with a limit of detection (LOD) 8 nmol (10 nM, 800 mL) (Ono et al., 2008). Based on this study, Zhao et al. reported a single wall carbon nanotube (SWNT)-based fluorescence spectroscopy method to detect Ag^+ within concentrations of 0.55 nmol (1 nM, 5.5 mL) (Zhao et al., 2010). Similarly, Wen et al.

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developed a graphene oxide based sensor for detecting Ag^+ within 5.5 nmol (10 nM, 5.5 mL) using a fluorophore-labeled C-rich DNA as a recognition unit and graphene oxide as a quencher (Wen et al., 2010). More recently, ultraviolet–visible absorption spectra were used for Ag^+ detection with a 3 pmol (5 nM, 0.6 mL) resolution based on functionalized gold (Au) nanoparticles and thiolated C-rich DNA (Feng et al., 2011; Huy et al., 2011). In addition, in our previous work, we reported a C-rich DNA immobilized oscillator, which was able to detect Ag^+ by using resonant frequency shift within 0.5 pmol (1 nM, 0.5 mL) (Park et al., 2013). Despite the success of these approaches in the laboratory, drawbacks and limitations, such as high cost, complex synthesis of fluorophore materials, and unsatisfactory LOD, exist in their practical application for Ag^+ detection. The use of fluorescence dyes that are attached to DNAs and nanometer-sized detectors (nanoparticles, carbon nanotubes, and graphene) is the major reason for the high cost and requirement for complex synthesis and fabrication. Although Gong et al. reported a sensitive detection of Ag^+ within 2.5 fmol (10 fM, 250 mL) using C-rich double-strand DNA and electrochemical impedance spectroscopy (Gong and Li, 2011), foreign substance absorption has been a major obstacle for its applicability (Grieshaber et al., 2008).

To overcome the problems experienced by the detecting techniques, we proposed the use of a novel approach for ultra-sensitive direct detection of Ag^+ via scanning probe microscopy (SPM), in particular Kelvin probe force microscopy (KPFM), using a single droplet of the analyte. The fundamental principles of KPFM technique originate from the research work carried out by Kelvin (1898), and the technique is widely used to analyze a variety of molecular species such as protein arrays (Cheran et al., 2004), immunochemical molecules (Cheran et al., 2005), biomolecular monolayers (Sinensky and Belcher, 2007; Zhou et al., 2003), and single proteins (Leung et al., 2009). The mechanism action of KPFM involves the measurement of local contact potential difference between the probe tip and sample by imaging the sample surface potential with high spatial resolution (Barth et al., 2011; Melitz et al., 2011). The KPFM technique has already been demonstrated as an influential equipment for the measurement of electrostatic forces and distribution of surface potential with nanoscale resolution (Liscio et al., 2010). Moreover, our previous study has shown the performance of KPFM in probing surface potential difference between ligand and adenosine triphosphate (ATP) or ligand and drug at single-molecule level (Park et al., 2011), indicating its durability and promise in the detection of binding between proteins and small molecules based on the binding-induced surface charge. Herein, we proposed the utilization of KPFM for the label-free and direct detection of Ag^+ and DNA binding at molecular resolution. The KPFM-based sensing technique was used for the ultra-sensitive detection of Ag^+ at a concentration of 2 fmol by applying a single droplet of solution which was 1000 times higher in sensitivity compared with general silver ion sensors. Moreover, additional analysis of Ag^+ in regular drinking water was performed to evaluate its performance in practical Ag^+ detection.

2. Experimental

2.1. Sample preparation

In this experiment, a 10-nM silver specific nucleotide with sequence of 5′–CCC CCC CCC CCC CCC CCC CCC CCC CCC CCC-3′ (Integrated DNA technology, CA, USA) (Park et al., 2013) was dissolved in an aqueous Tris–EDTA buffer solution (pH 8, Sterile Solution 10 mM Tris–HCl, and 1 mM EDTA, Bio Basic Inc.). Buffer solution (2 μL) containing silver specific nucleotide was then added to triple distilled water (Millipore, Bedford, MA, pH 7.6) of the same volume. Ag^+ ions were generated by dissolving silver nitrate ($AgNO_3$, Sigma-Aldrich) in the prepared solution for 2 h (Feng et al., 2011; Huy et al., 2011; Park et al., 2013; Wen et al., 2010). For the tapping mode-AFM and KPFM-based imaging, a 2 μL droplet of the buffer solution containing nucleotide or nucleotide with Ag^+ was placed onto a silicon substrate, which was washed by ethyl alcohol and triple distilled water, and dried for 9 h prior to its usage. Even though 1 h drying time was enough to dry the sample, 9 h drying time was able to reduce the error signal which was related to the humidity in sample state. From this dropping and drying procedure, the DNAs and DNA with silver ions were adsorbed on the substrate using the van der Waals' force (Leung et al., 2009). In addition, the surface of the silicon substrate suspended with DNA or DNA with Ag^+ was gently rinsed with distilled water in order to remove ions that could possibly affect the surface potential charge of sample (Leung et al., 2009), and subjected to a final drying process before analysis.

2.2. Tapping-mode AFM and analysis

AFM tapping-mode measurements were performed using an Innova microscope (Veeco Corp., Santa Barbara, CA, USA) with a Nanodrive controller (Veeco, USA) in air at ambient pressure and temperature, where a ~20 nm radius SCM-PIT cantilever tip (Veeco, USA) was used with exhibited resonance of ~75 kHz. To obtain precise and reproducible images of the sample at each state, a closed-loop scanner was used in the experiments. All the images were produced with 1 μm × 1 μm image size at 0.65 Hz scanning, leveled in two dimensions and processed using SPM Lab Analysis software V7.00 (Veeco, USA). The height profiles and height analysis were obtained using Nanoscope analysis software V1.20 (Bruker Corp., Santa Barbara, CA, USA).

2.3. KPFM imaging

In general, KPFM analysis can be categorized into two groups according to the operational modes: the lift mode and dual-frequency mode that consists of amplitude modulation (AM) and frequency modulation (FM) modes (Melitz et al., 2011). The lift mode is suitable for the measurement of a small potential variation (< 100 mV) (Park et al., 2011; Sinensky and Belcher, 2007). In this study, the lift mode was used to investigate the binding of Ag^+ and nucleotides, where the tip bias potential oscillated at the same resonance frequency as that of the cantilever (~75 kHz) used for imaging. In order to obtain reliable KPFM analytical data, a three-step coarse tuning procedure was performed. The first step involved the production of a clear image of the nucleotides using normal tapping-mode AFM with the same cantilever. Secondly, with the attained tapping mode image, the *y*-axis direction was then fixed and only the *x*-axis direction was analyzed with the same height profile as that of the sample. After the uniform *x*-axis profiles were obtained, the lock-in phase was finally identified and adjusted to its maximum contrast, which enabled optimum conditions for driving the potential feedback. The KPFM parameters, including proportional and integral corner frequency and overall gain, were set properly for image acquirement. For fine-tuning, we adjusted the KPFM control feedback parameters through KPFM error profiles with an error range of $\sim \pm 5$ mV. For the accurate and clear surface potential measurement, the representative optimizing factors were selected which were scan speed and scan height. For the scan height, the tip was then held 5 nm above the sample surface, and applied with a 4 V alternating current (AC). Also, we used the optimized scan speed (0.65 Hz). This scan height and scan speed were identified to be the optimal distance for probing small biomolecules by minimizing the interference between the tip and sample as discussed in

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