High-sensitive, direct and label-free detection technique of nanotoxic material using QCM

Chanho Park[*], Kuewhan Jang[**], Sangmyung Lee[***], Juneseok You[****], Jinsung Park[*****] and Sungsoo Na[******]

[*]Department of Mechanical Engineering, Korea University,
Seoul 136-701, Republic of Korea, chanhoo91@naver.com
[**]Department of Mechanical Engineering, Korea University,
Seoul 136-701, Republic of Korea, qguy@korea.ac.kr
[***] Department of Mechanical Engineering, Korea University,
Seoul 136-701, Republic of Korea, bjfbhbi@gmail.com
[****] Department of Mechanical Engineering, Korea University,
Seoul 136-701, Republic of Korea, protrossko1@korea.ac.kr
[*****]Department of Control and Instrumentation Engineering, Korea University,
Sejong 339-700, Republic of Korea
[******] Department of Mechanical Engineering, Korea University,
Seoul 136-701, Republic of Korea, nass@korea.ac.kr

ABSTRACT

For the several decades, various nanomaterials are broadly used in industrial fields, research areas and commercialized products. Among many nanomaterials, silver ion, carbon nanotube, ZnO, and mercury ion etc are of the widely used nanomaterial in real life. However, high toxicity of those materials has been reported and the detection method is required for human health and environment. In present study, high-sensitive, label-free detection methods of nanotoxic materials are described.

We have developed a sensitive and selective quart crystal microbalance (QCM) based sensor for detection of nanotoxic materials by using frequency shift. In this study, we propose the sensitive in situ detection of nanotoxic materials by using QCM functionalized with a specific DNA for a target material. It also allows the detection of target material rapidly in real time. In contrast to the conventional methods, this method is label-free and sensitive, capable of direct rapid detection and real-time monitoring. The results suggest that QCM-based detection opens a new avenue for the development of a practical water-testing sensor.

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Keywords: nanomaterial, toxicity, label-free detection, quart crystal microbalance, resonance frequency

1 INTRODUCTION

In recent years, there has been a rapid growth of nanomaterials usage from scientific interest to commercial products. Commercial products such as sun-creams, tennis rackets, solid lubricants, detergents, etc, are using nanomaterials due to unique properties of nanomaterials [1]. Among nanomaterials, single-walled carbon nanotube (SWNT), zinc oxide nanowire (ZnO NW) and silver ion (Ag^+) are the most widely used nanomaterials due to the extraordinary properties of those materials such as SWNT properties of high aspect ratio, light weight with elastic modulus of ~1.4 TPA, conductivity higher than copper, ZnO NW properties of piezoelectric and semiconductor, and Ag^+ properties of sterilization [2-4].

While SWNT, ZnO NW and Ag^+ are widely used for the commercial products, human exposure to those materials has not been concerned. Effluent from manufacturing, consumer utilization and after disposal of those nanomaterials will increase the release to the water system, and this will eventually increase human exposure to nanomaterials [5]. Moreover, recent studies have investigated the toxicity of effect of those nanomaterials [4, 6, 7]. Interstitial inflammation in the lungs was frequently observed in the high dose injection of SWNT and the decrease in cell viability of A549 and H1299 lung epithelial cell line was also observed [8]. Moreover, oxidative potential of SWNT was observed that can stimulate ROS production [3]. In the case of ZnO NW, ZnO NW started the degradation process to an ionic state of zinc ion, because of a week acid liquid state [7]. Then zinc ion leads to cytoxic phenomenon in the cell which is harmful mechanism and critical harmful concentration is about 10μg/ml of ZnO NW in weak acid

 TechConnect Briefs 2015, TechConnect.org, ISBN 978-1-4987-4729-5

solution.4 Ag^+ has greatly toxicity to living organisms by inactivating the sulfhydryl enzymes [9].

In order to protect human health from nanotoxic materials, detection of nanotoxic materials in water systems have to be concerned [1]. If we are able to monitor the concentration of nanomaterials, we can determine how harmful the concentration of nanomaterials will be acting on human health. One of approaches that can detect nanomaterial is the measurement of natural frequency of resonator sensor. There exist many resonator works for detection of biomaterials, chemical molecules, such as DNA, RNA, proteins due to the high-sensitivity and label-free method by the measurement of natural frequency [10]. Moreover, natural frequency is function of mass change and the detection is directly achieved [11].

In this paper, we have developed sensing methodology of nanotoxic materials such as SWNT, ZnO NW and Ag^+ using measurement of natural frequency of resonators. The sensing methodology is based on the shift of natural frequency upon binding of nanomaterials absorption on the DNA immobilized resonators in which the DNA sequences were specified for each case. Similarly, nanotoxic materials were also modified in order to adsorb and increase the detection performance. In case of SWNT, two different DNA sequences were used to conjugate SWNTs together for the mass amplification and the conjugate SWNTS were designed to adsorb on the DNA functionalized resonators. Similarly, ZnO NWs were wrapped with graphene and designed to adsorb on the DNA immobilized resonator. For Ag^+, Ag^+ was designed to adsorb on the poly cytosine bases DNA on the resonator through specific intercalation. By measuring the nature frequency of resonators, we were able to detect 10 ng/ml of SWNT, 100 ng/ml of ZnO NW and 1 nM of Ag^+.

2 THEORY

The natural frequency of resonator can be described by classical elastic continuum model:

$$\omega_0 = \left(\frac{\alpha}{l}\right)^2 \sqrt{\frac{EI}{\rho A}} \tag{1}$$

where α is the eigenvalue by the positive root of $1+\cos(\alpha)\cosh(\alpha)=0$, l, E ,I, ρ and A is the length, Young's modulus, cross-sectional moment of inertia, mass density and cross-sectional area of resonator. Furthermore, the natural frequency shift can be simplified by mass or stiffness change as below:

$$\Delta\omega = \frac{1}{2}\omega_0\left(\frac{\Delta k}{k} - \frac{\Delta m}{m}\right) \tag{2}$$

where ω_0 is the natural frequency, Δk, k, Δm and m is the stiffness change, stiffness, mass change and mass of resonator. From the equation, we can see that the natural frequency shift is related to stiffness and mass change. In general, the mass effect is the dominant effect and the stiffness effect can be ignored. This implies that the natural frequency shift is directly related to the mass change which caused by the adsorption of nanomaterial in our system.

Since the natural frequency of resonators were not constant, normalized natural frequency shift was used:

$$\omega_n = \frac{\omega_b - \omega_a}{\omega_b} \times 100 \tag{3}$$

where ω_b and ω_a is the natural frequency of resonator before detection and after detection.

3 RESULT

The detection was performed by the interaction of nanotoxic material with the resonator. As nanotoxic material bind on the resonator, the mass of resonator increased and the natural frequency decreased. By analyzing the natural frequency shift, we were able to detect nanotoxic material.

4. CONCLUSION

In summary, we developed detection methodology of SWNT, ZnO NW and Ag^+ by using natural frequency of resonator. The sensing mechanism is based on the measurement of the natural frequency shift arisen from the detection of the target nanotoxic materials on specified DNA immobilized resonator. The natural frequency shift was well responded to the each concentration of nanomaterial. In detail, we were able to detect SWNT, ZnO NW and silver ion with the detection limit of 10 ng/ml of SWNT, 100 ng/ml of ZnO NW and 1 nM of silver ion, respectively. Moreover, our sensing methodology is label-free and sensitive, showing the potential of natural frequency based sensing methodology as the nanotoxic material screening tool.

Acknowledgment

This study was supported by the National Research Foundation of Korea (NRF) under grant numbers of NRF-2012-0000785, NRF-2012-0006646, NRF-2014R1A2A1A11052389 and NRF-2013R1A1A1058102 funded by the Ministry of Science, ICT & Future Planning.

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