2010 Symposium on Security Detection and Information Processing

Novel nanoparticle detection method using electrochemical device based on anodic aluminum oxide nanopore membrane

Fanli Meng[a,§], Yan Chen[a,c,§], Jinyun Liu[a], Zhen Jin[a], Yufeng Sun[a,b,*], Jinhuai Liu[a,*]

[a]Research Center for Biomimetic Functional Materials and Sensing Devices, Institute of Intelligent Machines, Chinese Academy of Sciences, Hefei, 230031, China
[b]Department of Mechanical and Automotive Engineering, Anhui Polytechnic University, Wuhu, 241000, China

[c]Yantai Institute of Coastal Zone Research, Chinese Academy of Sciences, Yantai, 264003, China

Abstract

Some investigations suggest that nanoparticles are potentially the most dangerous because they can also penetrate deeper into lung tissue than other large particles. However, some researchers declare that the research on security of environmental nanoparticles should be on the basis of the standardization of investigation system. Therefore, it is significant to detect nanoparticles for both environmental evaluation and further treatment. In this paper, a method for iron oxide nanoparticle detection was investigated by a novel electrochemical device based on AAO nanopore membrane and preliminary results was taken out which may create novel avenues and applications for nanoparticle detection.

Keywords: nanoparticle; anodic aluminum oxide; nanopore; electrochemical; iron oxide

1. Introduction

Nanotechnology is the study of the controlling of matter on an atomic and molecular scale. Generally nanotechnology deal with structures sized between 1 to 100 nanometers in at least one dimension, and involves developing materials or devices within that size. Nanotechnology may be able to create many new materials and devices with a vast range of applications, such as in medicine, electronics, biomaterials and energy production. On the other hand, nanotechnology raises many of the same issues as with any introduction of new technology, including concerns about the toxicity and environmental impact of nanomaterials [1-2]. Lots of investigations indicated that many materials in nanoscale level are harmful to human body [3-5]. Nel et al. suggested that nanoparticles are potentially the most dangerous because they can also penetrate deeper into lung tissue than other large particles. They are the major component in vehicle emissions, which is the largest source of air pollution in

––––––––––

§ These two authors contributed equally to this work.
* Corresponding author. Tel.: +86-551-5591142; fax: +86-551-5592402.
E-mail address: jhliu@iim.ac.cn (J. Liu); sunyufeng118@126.com (Y. Sun).

urban areas, and they have the largest surface area and highest content of potentially toxic hydrocarbons among all particle pollutants [6-7]. Wu et al. indicated that nanoparticles induce skin aging through oxidative stress in hairless mice [8]. However, some researchers deal with this issue cautiously. They suggested that the assessment of effect of carbon nanotube on the cells, organ, or whole organism should be firstly standardized [9]. Therefore, it is significant to detect nanoparticles for both environmental evaluation and further treatment. For this reason, Chinese researchers held the 314th section of Xiang Shan Science Conferences for special topic discussion in 2007.

Currently, most of the measurements of nanoparticles are based on optical principle [10-11] or electrical mobility method [12-14]. Those equipment are all expensive. Novel technology based on nanopore membrane has been widely investigated [15]. Nanoparticles are in the same level in size with nanopores which may thereby act as filters to separate them. Takashi et al. developed a single carbon nanotube-based Coulter nanoparticle counter which may measure the characteristics of individual particles and provide the average and polydispersity distribution of nanoparticle properties [16]. That carbon nanotube-based Coulter nanoparticle counter provides a novel avenue for nanoparticle detection that nanopore membrane could be well used. Lee et al. used track-etched polycarbonate nanopore membranes to fabricate a scanning electrochemical microscope for detecting nanoparticles [17]. Their results indicate that the nanopore membrane-based scanning electrochemical microscope may achieve size- and charge-selective particle detection by a electrochemical capture and release process. However, the fabricating process of track-etched polycarbonate nanopore membrane is complicated and not suitable for mass production. Anodic aluminum oxide (AAO) membrane possesses regular, uniform and diameter controllable cylindrical nanopores and suitable for mass production [18-19]. Besides, AAO possesses higher mechanical strength than polymer-based membrane. Toh et al. used to make AAO as a filter to separate nanoparticles [20]. In this paper, a method for iron oxide nanoparticle detection was investigated by a novel electrochemical device based on AAO nanopore membrane and preliminary results was taken out which may create novel avenues and applications for nanoparticle detection.

2. Experimental

2.1 Preparation of AAO membrane

A two-step anodization process was adopted for the preparation of AAO membranes [21]. Briefly, highly pure aluminum (99.999%) sheets were annealed at 500 °C in N_2 for 4 h in order to obtain homogeneous pores in the template. Before anodization, the sheets were cleaned and electropolished to remove the surface layer. A first anodization was carried out under a constant anodization potential of 40 V in an oxalic acid at 10 °C for 6 h. The as-prepared AAO film was removed by dipping them into a mixture of phosphoric acid (6% wt) and chromic acid (1.8% wt) at 60 °C for 6 h. A second anodization was carried out under the same condition for 12 h. Finally the underlying aluminum layer was dissolved by saturated $SnCl_4$ solution. The barrier layer at the bottom of the AAO membrane was removed by placing the sample in 6% H_3PO_4 until the barrier layer was dissolved. After washing and drying, the AAO template with nanopores was obtained.

2.2 Preparation of iron oxide nanoparticles

Iron oxide nanoparticles were prepared as follows [22]: firstly, a required amount of $Fe(NO_3)_3 \cdot 9H_2O$ was dissolved in distilled water and sonicated for 15 min. Hydrazine monohydrate was then added dropwise to the ferric nitrate solution under sonication. At the end of the reaction, a black precipitate was obtained. The precipitate was centrifuged, washed with distilled water and ethanol in sequence. The filtrate was dried at 70 °C for 5 h in air.

2.3 Set-up of the electrochemical device

The electrochemical device consisted of two chambers divided by an insulating block, in the middle of which a piece of AAO membrane was placed as shown in Fig. 1. Ag/AgCl electrodes immersed in an electrolyte (0.1 M KCl in phosphate buffered saline) in each chamber were used to drive an ionic current through the channel of AAO membrane. If particles having a size on the order of the channel diameter were present in the electrolyte, then they may be driven into the channel or block other ions pass through, which would thereby cause changes of the electrochemical current. The output of the device was a plot of electrochemical current versus time. Under favorable conditions, these current could be correlated to the size and mobility of nanoparticle.

3. Results and Discussion

3.1 Characterization of nanopore membrane and iron oxide nanoparticles

Fig. 2a shows the top view of the surface of as-prapared AAO membrane. The SEM image presents that the AAO membrane possesses highly ordered nanopores of about 80 nm in mean diameter which forms naturely the channel for ions passing through. The AAO membrane is generally several to tens of micrometers in thickness. Fig. 2b shows the SEM image of the across section of the as-prepared AAO membrane. The thickness of the as-prepared AAO membrane is about 85 nm, which is very long for nanoparticles to pass through. So, it will consume many time of the particles to pass through the AAO membrane in the electrochemical device.
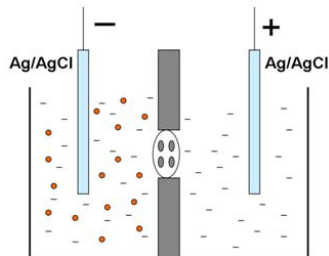

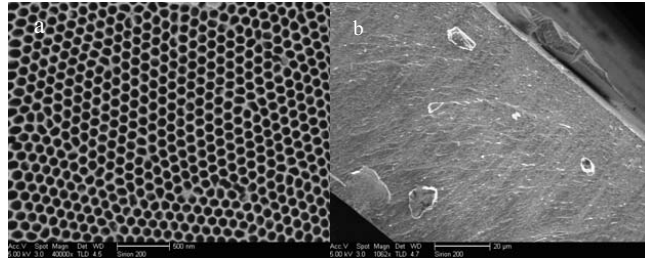**Fig. 1.** Set-up of the electrochemical Device.

Fig. 2. (a) SEM image of top view of the AAO membrane. (b) SEM image of the across section of the AAO membrane.

The as-prepared Fe_2O_3 particles were dispersed into ethanol by ultrasonic cleaner and dropped onto a silicon wafer to be observed. The SEM image is shown in Fig. 3, in which the size of the Fe_2O_3 particles is uniform and the mean diameter is about 40 nm. The size of the particles is close to that of the AAO membrane. So, both of them are suitable for the investigation.

3.2 Operating Principle

There are two operating principle to calculate the concentration and distribution of target nanoparticle. One reacts under the condition that the filter membrane has only a single nanopore [16]. The other reacts under the condition that there are lots of nanopores in the filter membrane [23]. The AAO membrane-based electrochemical device in this paper operates under the latter condition. According, the magnitude of the conductance change is given by:

Fig. 3. SEM image of the as-prepared iron oxide nanoparticles.

$$\triangle G = \frac{2\pi r^3 \sigma}{L^2} \qquad (1)$$

where r is the particle radius, σ is the solution conductivity, and L is the length of the pore. This equation is strictly applicable in cases where the diameter ratio of nanoparticles to nanopores is approximately 2-60%. Usually, Fe_2O_3 nanoparticles show negative charge in aqueous solution [24]. So, they should be put into the side of negative electrode.

3.3 Electrochemical measurement of iron oxide nanoparticles

Nanoparticles in indoor or outdoor environment have great potential to harm human beings. Especially, metal components (metal ions, or metal oxide synergism, particularly involving transition metals Fe and Ni) are often associated with chronic, toxic, or related effects which may be enhanced by mixing of soil components and subsequent wind events, or atmospheric reaction phenomena involving photooxidation or other photothermal effects [25]. Metal oxides (e.g. Fe_2O_3, TiO_2) are the regular contamination of nanoparticle. The famous London event was mostly caused by atmospheric Fe_2O_3 particles which oxidized SO_2 to SO_3, and then to form H_2SO_4, and the condensate in the dust to form the mist being a killer of the incident. Petroleum combustion may generate abundant Fe_2O_3 nanoparticles. So, it is important to detect Fe_2O_3 nanoparticles. Capillary zone electrophoresis as a method to separate nanoparticles with different shapes and sizes was used to detect them. Vanifatova et al. investigated the
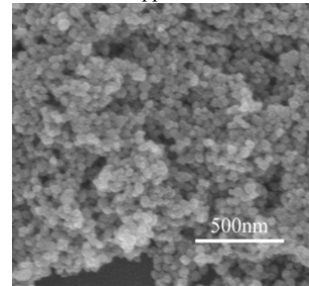
electrophoretic behavior of iron oxide nanoparticles in aqueous solutions and well detected two kinds of Fe_2O_3 particles (smooth and with spikes) [14].

In our investigations, the iron oxide nanoparticles were detected by the electrochemical device based on AAO nanopore membrane. As in Fig. 4a, the results shows that the electrochemical device based on AAO nanopore membrane actually does work and the Fe_2O_3 nanoparticles are detected by the electrochemical signals. When the measurement begins, the currents rapidly increase and soon decrease. That is because the electrolytes rapidly penetrate the AAO membrane at beginning and the iron oxide nanoparticles will gradually permeate through the pores of the AAO membrane to block the electrolytes pass through. When the particles of coming into filter are equivalent to that of going out, the in/out balance arises and then the currents keep steady. No sharp peaks occur in the balance sections of the curves, which may be because the amount of the pores is large and the current changes present statistical phenomena. Fig. 4b shows the plots of ΔI *vs* concentration resulting from the data points of Fig. 4a at 50 s. From that figure, it can be seen that the balance current linearly changes with concentration. According to formula (1), ΔG is proportional to σ and the slope is $\dfrac{2\pi\,r^3}{L^2}$ when the particles are uniform. Ohm's Law can be given as follows:

$$I = U \bullet g \tag{2}$$

where U is the measurement. Since the measurement voltage is a constant in this experiment, ΔI is proportional σ and the slope is $\dfrac{2\pi\,r^3}{L^2}U$. So, the diameter of the nanoparticles can be calculated by the slope of the fitting line in Fig. 4b.
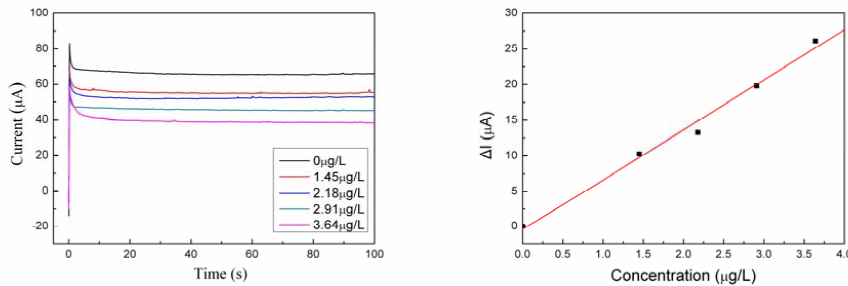

Fig. 4. (a) The curves of the measurements of iron oxide nanoparticles with different concentrations by the electrochemical device based on AAO nanopore membrane operating at 0.5V voltage. (b) The plots of ΔI vs concentration resulting from the data points of (a) at 50 s.

3.4 Influence of measurement voltage

There are a few factors could be optimized in the whole system. The measurement voltage is one of the few factors, which is also the most important factor. The investigation results present that the measurement voltage directly affect the signals. Fig. 5 shows the curves operating at different measurement voltages, which suggests that the measurement current increases with increasing the measurement voltage and the noise also increases. The noise maybe generates by the nanoparticles pass through the AAO membrane. When the measurement voltage increases, the driving force increase and the nanoparticles become more active that may enlarge the noise.

3.5 Measurement of polystyrene nanoparticles

In order to further illuminate the applicability of the electrochemical device based on AAO nanopore membrane. Polystyrene nanoparticles were measured as target sample. The polystyrene nanoparticles about 200 nm in diameter were purchased from Duke Scientific Corporation. The measurement results are shown in Fig. 6. The measurement current also changes when polystyrene nanoparticles are joined, but the magnitudes of change are less and the noise are large than that of measuring iron oxide nanoparticles. The main reason is that the size of the particle is bigger than that of the nanopores. The polystyrene nanoparticles can not pass through the AAO membrane and therefore the main function of them is to block the electrolytes pass through.
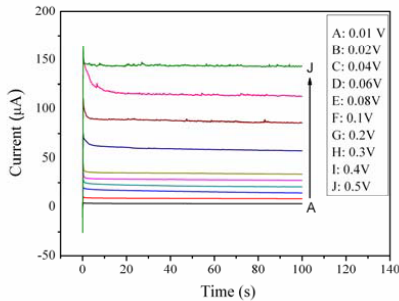
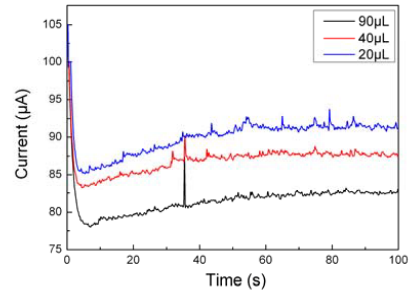**Fig. 5.** Measurement curves operating at different voltages.

Fig. 6. The curves of the measurements of 2.18 μg/L polystyrene nanoparticles with different sampling volumes by the electrochemical device based on AAO nanopore membrane operating at 0.5V voltage.

4. Conclusion

A novel method for iron oxide nanoparticle detection was investigated by the electrochemical device based on AAO nanopore membrane which may create novel avenues and applications for nanoparticle detection. The preliminary results present that the balance current linearly decreases with concentration increasing and the diameter of the nanoparticles can be calculated from the measurement curves. The device also can detect big diameter of polystyrene nanoparticles. However, the full potential of such electrochemical device based on AAO nanopore membrane has yet to be demonstrated in more targets and operating conditions, such as different sizes of nanoparticle and membrane nanopore, different electrolytes, and so on. The preliminary results make the AAO membrane-based electrochemical device attractive for the purpose of nanoparticle detection.

Acknowledgements

References

[1].	Brumfiel, G., Nanotechnology: A little knowledge ... *Nature,* 2003. **424**(6946): 246-248.
[2].	Xia, T., N. Li, and A.E. Nel, Potential Health Impact of Nanoparticles. *Annual Review of Public Health*, 2009. **30**:137-150.
[3].	Khaydarov, R.R., et al., Silver Nanoparticles Environmental and Human Health Impacts. *Nanomaterials: Risks and Benefits*, 2009,**472**:287-297.
[4].	Geiser, M., et al., Ultrafine particles cross cellular membranes by nonphagocytic mechanisms in lungs and in cultured cells. *Environmental Health Perspectives*, 2005. **113**(11):1555-1560.
[5].	Oberdorster, G., et al., Translocation of inhaled ultrafine particles to the brain. *Inhalation Toxicology*, 2004. **16**(6-7):437-445.
[6].	Nel, A., Air pollution-related illness: Effects of particles. *Science,* 2005. **308**(5723): 804-806.
[7].	Nel, A., et al., Toxic potential of materials at the nanolevel. *Science,* 2006. **311**(5761): 622-627.
[8].	Wu, J.H., et al., Toxicity and penetration of TiO_2 nanoparticles in hairless mice and porcine skin after subchronic dermal exposure. *Toxicology Letters,* 2009. **191**(1):1-8.
[9].	Ren, H.X., et al., Toxicity of single-walled carbon nanotube: How we were wrong? *Materials Today*, 2010. **13**(1-2): 6-8.

[10]. Bootz, A., et al., Comparison of scanning electron microscopy, dynamic light scattering and analytical ultracentrifugation for the sizing of poly(butyl cyanoacrylate) nanoparticles. *European Journal of Pharmaceutics and Biopharmaceutics,* 2004. **57**(2): 369-375.

[11]. Murdock, R.C., et al., Characterization of nanomaterial dispersion in solution prior to In vitro exposure using dynamic light scattering technique. *Toxicological Sciences*, 2008. **101**(2): 239-253.

[12]. Wang, S.C. and R.C. Flagan, Scanning Electrical Mobility Spectrometer. *Aerosol Science and Technology,* 1990. **13**(2): 230-240.

[13]. Winklmayr, W., et al., A New Electromobility Spectrometer for the Measurement of Aerosol Size Distributions in the Size Range from 1 to 1000 Nm. *Journal of Aerosol Science,* 1991. **22**(3): 289-296.

[14]. Vanifatova, N.G., et al., Investigation of iron oxide nanoparticles by capillary zone electrophoresis. *Talanta,* 2005. **66**(3): 605-610.

[15]. Dekker, C., Solid-state nanopores. *Nature Nanotechnology,* 2007. **2**(4):209-215.

[16]. Ito, T., et al., A carbon nanotube-based Coulter nanoparticle counter. *Accounts of Chemical Research,* 2004. **37**(12): 937-945.

[17]. Lee, S., et al., Electrophoretic capture and detection of nanoparticles at the opening of a membrane pore using scanning electrochemical microscopy. *Analytical Chemistry,* 2004. **76**(20): 6108-6115.

[18]. Lee, K., Y. Tang, and M. Ouyang, Self-Ordered, Controlled Structure Nanoporous Membranes Using Constant Current Anodization. *Nano Letters,* 2008. **8**(12): 4624-4629.

[19]. Lei, Y., W.P. Cai, and G. Wilde, Highly ordered nanostructures with tunable size, shape and properties: A new way to surface nano-patterning using ultra-thin alumina masks. *Progress in Materials Science*, 2007. **52**(4):465-539.

[20]. Toh, C.S., et al., Fabrication of free-standing nanoscale alumina membranes with controllable pore aspect ratios. *Nano Letters*, 2004. **4**(5): 767-770.

[21]. Chen, X., et al., Preparation of well-aligned CNT arrays catalyzed with porous anodic aluminum oxide template. *Chinese Journal of Chemical Physics,* 2006. **19**(1): 79-83.

[22]. Ray, I., et al., Room temperature synthesis of gamma-Fe_2O_3 by sonochemical route and its response towards butane. *Sensors and Actuators B-Chemical,* 2008. **130**(2): 882-888.

[23]. Schmidt, J., Stochastic sensors. *Journal of Materials Chemistry,* 2005. **15**(8): 831-840.

[24]. Mustafa, S., S. Tasleem, and A. Naeem, Surface charge properties of Fe_2O_3 in aqueous and alcoholic mixed solvents. *Journal of Colloid and Interface Science,* 2004. **275**(2): 523-529.

[25]. Murr, L.E. and K.M. Garza, Natural and anthropogenic environmental nanoparticulates: Their microstructural characterization and respiratory health implications. *Atmospheric Environment,* 2009. **43**(17): 2683-2692.