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Short communication

# Membrane-based electrochemical device for monitoring nanowires in aqueous samples

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ABSTRACT

We report a membrane-based electrochemical detection of nanowires in aqueous sample. A gold-coated membrane is used both as a membrane filter and a working electrode. Using filtration method, it is possible to concentrate silver and zinc oxide nanowires on the gold working electrode on top of the membrane and the nanowires on the electrode can be differentiated and quantified by differential pulse voltammetry. Moreover, the new method shows better reproducibility in comparison with conventional immersion method, without modification of electrode surface according to the nanomaterial to be detected.



A variety of metal and metal oxide nanowires (NWs), such as Ag and ZnO, have recently been exploited for consumer goods and industrial products due to their unique physical, chemical, optical, and electrical properties [1–4]. Consequently, there is more chance of environmental exposure to NWs due to manufacturing, use, or disposal of NWs-containing products, and therefore the toxicity of NWs in aquatic system is becoming a cause of great concern [5–9]. Scanlan et al. found that the median lethal concentrations ($LC_{50}$) of different-sized Ag NWs on Daphnia magna ranges from 0.2339 to 0.4210 $\mu g\,mL^{-1}$ [6]. Müller et al. found that the ZnO NWs are toxic to human monocyte macrophages with $LC_{50}$ value of 14.5 $\mu g\,mL^{-1}$ [7]. Nelson et al. demonstrated that silica NWs are highly and selectively toxic and teratogenic to zebrafish embryos [9]. Accordingly, reliable and suitable analytical techniques are required to quantify NWs. In environmental monitoring, reliable detection and quantification of the nanomaterials is very challenging due to low concentration of nanomaterials and coexistence of ionic and colloidal forms of the same elements. Some analytical techniques, such as resonator, inductively coupled plasma mass spectrometry and atomic absorption spectroscopy, have been proposed to quantify the nanomaterials in aqueous samples [10–13]. However, these techniques need time-consuming chemical pretreatments and require expensive hardware which are difficult to miniaturize into portable detection devices for simple and rapid analysis.

Recently, an electrochemical technique was proposed for the characterization of nanomaterials where an electrode is immersed into the suspension of nanomaterials for the adsorption of nanomaterials onto the electrode surface and adsorbed nanomaterials are differentiated and quantified by linear sweep voltammetry [14–17]. This immersion method is not very effective for electrolyte solutions containing small amounts of nanomaterials which is often very time-consuming and irreproducible [18]. Therefore, the working electrode has to be modified to improve the adsorption of nanomaterials on the electrode. Moreover, the adsorption affinity of nanomaterials to the working electrode depends on the electrode material used [19].

Most of the analytical techniques are unable to quantify highly soluble nanomaterials in aqueous solution, because it is difficult to separate the signal for the nanomaterials from that for dissolved ions with the same elements. In that case, dissolved ions should be separated from the nanomaterials before analysis. Filtration could be a simple solution for the separation.

In this work, we propose a membrane filtration technique with electrochemical detection method for on-site detection of nanowires in aqueous solution. A gold-coated membrane is used both as a membrane filter and a working electrode. Ag NWs and ZnO NWs are concentrated on the gold working electrode on top of the membrane by filtration and the nanowires on the electrode

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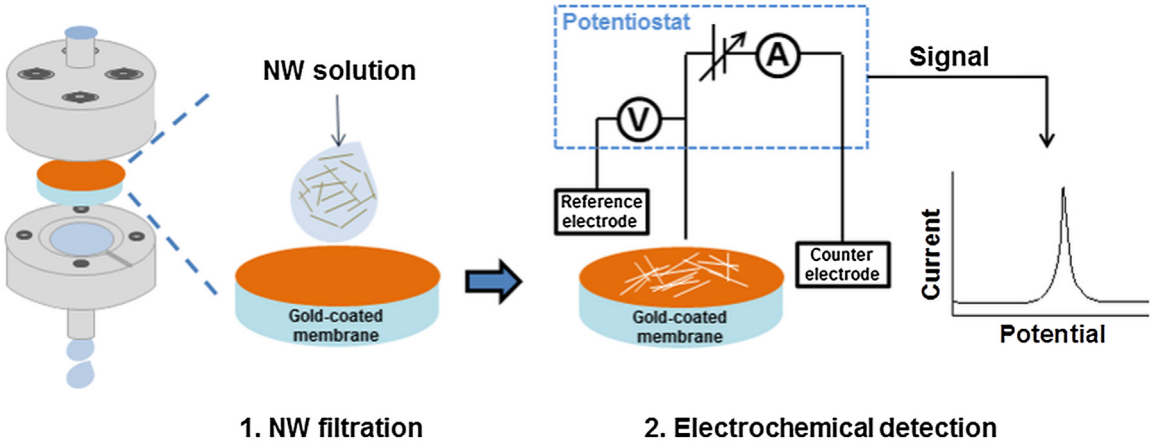


**Fig. 1.** Schematic experimental setup for the membrane filtration and electrochemical measurement.

are differentiated and quantified by differential pulse voltammetry (DPV) in one device. We also do experiments on the electrochemical detection of Ag NWs and ZnO NWs with conventional immersion method to confirm competitiveness of the newly proposed method.

Fig. 1 shows the experimental setup for the membrane filtration and electrochemical measurements. First, a membrane was prepared by coating the surface of polycarbonate membranes (0.05 μm pore size) with 50 nm layer of gold via direct current magnetron sputtering (SNTEK RSP-5004). The membrane was placed into a homemade syringe filter holder and the electrical contact to the gold surface of the membrane was made using a gold wire, which was clamped in the filter holder. The diameter of the membrane area in contact with the feed solution was 10 mm, as defined by the inner diameter of the O-ring. Prior to filtration, deionized water was added into the filter holder to remove air bubbles in the membrane pores. Then, the dispersion of nanowires, which was pre-sonicated to disperse the nanowires homogeneously, was injected into the holder at a flow rate of 0.2 mL $min^{-1}$ with a syringe pump. The UV–vis absorption spectra and photographs of the feed solutions containing Ag NWs (D = 25–35 nm, L = 10–20 μm) and ZnO NWs (D = 100 nm, L = 8 μm), as well as the filtrate solutions are shown in Fig. 2. For the feed solution of Ag NWs (Fig. 2A (a)), absorption peak at the wavelength of 369 nm corresponding to transverse plasmon mode of Ag NWs, and the shoulder peak around 355 nm attributed to the plasmon resonance of long Ag NWs can be clearly observed [20]. The UV–vis absorption spectrum of ZnO NWs in the feed solution shows a sharp absorption peak at 369 nm which is known as the intrinsic exciton binding energy of ZnO (Fig. 2 B (a)) [21]. When the feed solution pass through the membrane, the yellowish color of Ag NW solution and the white color of ZnO NW solution disappear, respectively. More specifically, for both of the filtrate solutions of Ag NWs and ZnO NWs, the absorption peaks of Ag NWs and ZnO NWS are rarely observed in the UV–vis spectra. The results indicate that filtration of the nanowire solution through the gold-coated membrane allows the nanowires filtered out from the solution and concentrated on the membrane due to the high aspect ratio of nanowires. For nanomaterials easily dissolved in aqueous solution, such as ZnO, the signal corresponding to the dissolved ions may overlap that from the nanomaterials with the same elements making quantification of the nanomaterials challenging in many analytical techniques (eg. inductively coupled plasma mass spectrometry) [13]. The filtration method is able to exclude the dissolved metal ions in the sample from the electrochemical analysis making quantification of nanowires more reliable.

In order to investigate the electrochemical behavior of the gold-coated membrane electrode, the redox process between ferricyanide ($Fe(CN)_6^{3-}$) and ferrocyanide ($Fe(CN)_6^{4-}$) in an aqueous solution is served as a standard reaction. Electrochemical measurements were carried out with a CHI 660E analyzer connected in a three-electrode arrangement, to a refillable miniature Ag/AgCl (3 M NaCl) reference electrode (eDAQ, Australia), a Pt auxiliary elec-

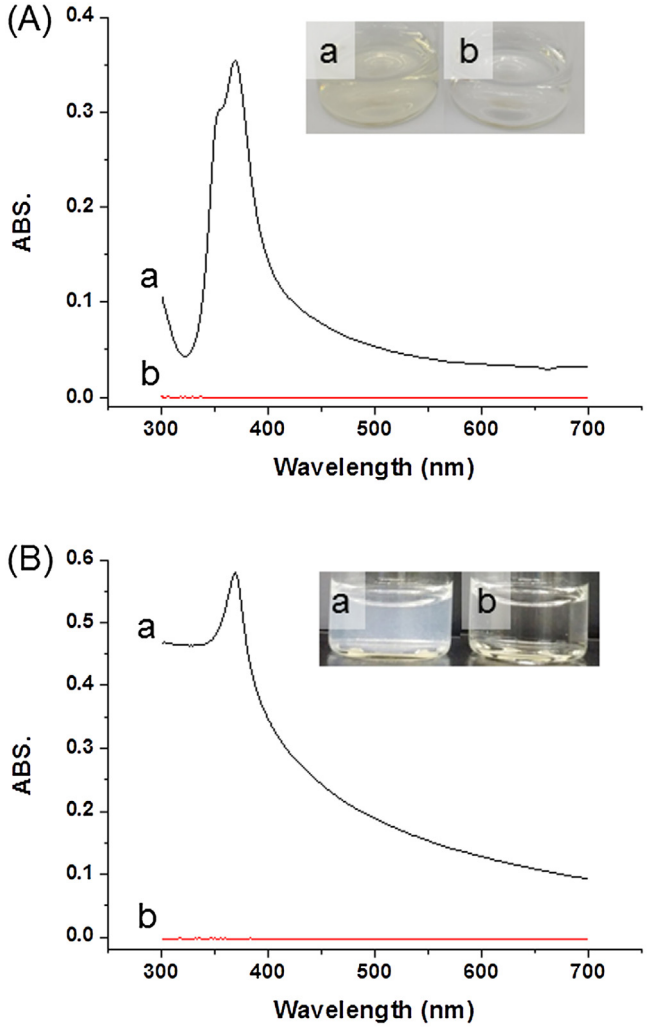


**Fig. 2.** UV-Vis absorption spectra of (A) Ag NWs and (B) ZnO NWs dispersions: (a) feed solution and (b) filtrate. Inset: Digital photograph of Ag NWs and ZnO NWs dispersion (a) before and (b) after filtration, respectively.