The effect of colloids on nanofluidic power generation

Y. Wang [a], H. Wang [a, *], C.Q. Wan [b]

[a] Department of Physics, Capital Normal University, Beijing Key Laboratory of Metamaterials and Devices, Key Laboratory of Terahertz Optoelectronics, Ministry of Education, and Beijing Advanced Innovation Center for Imaging Technology, Beijing, 100048, PR China
[b] Department of Chemistry, Capital Normal University, Beijing, 100048, PR China

ARTICLE INFO

ABSTRACT

We discussed the influences of colloidal particles on ion transport in nanofluidic power generation system, which is an unavoidable issue for actual membrane-based power generation systems. By introducing negatively charged colloidal particles (~100 nm) with different concentrations, power generation by reverse electrodialysis in a porous anodic alumina membrane was analyzed. The power was enhanced in a colloid concentration of $(2.6–4.2) \times 10^{-5}$ g/ml. The maximum power was acquired when the colloid ($\sim 3.05 \times 10^{-5}$ g/ml) was on the same side as the salt solution (1 M KCl). Modifying the surface of the porous anodic alumina membrane by using an ultra-thin metal layer (10 nm of platinum) achieved almost the same maximum power, but the colloid concentration range of the power enhancement broadened. The electrokinetic interplay between colloidal particles and nanofluidics is complex. The appearance of colloidal particles in water bodies does not always result in a reduction in power generation, and their effects can be effectively regulated by engineering parameters.

© 2018 Elsevier Ltd. All rights reserved.

1. Introduction

Reverse electrodialysis (RED) has been one of the major techniques used to harvest electrical power from osmotic energy by using ion exchange membranes [1–5]. Benefiting from the pronounced ion selectivity induced by the overlap of the electrical double layer (EDL) [6–9], nanofluidic nanopores and channels function like ion exchange membranes [10–14]. Recently, RED relying on membrane-based nanofluidics has attracted great attention owing to its enhanced ion-separation efficiency [15–17] and application potential [18,19]. In 2013, Kim et al. showed that a power density of 0.84×10^{-3} W/m^2 can be harvested from the salinity gradient by RED using an anodic alumina membrane with a nominal pore diameter of 20 nm [20]. It is known that the ion selectivity is most pronounced if the Debye screening length is comparable to the smallest dimension of the nanochannel cross section [12]. Therefore, as the pore diameter of the membrane is reduced, the power output rises. A nanoporous polycarbonate track-etched membrane with a pore diameter ~15 nm yielded an energy density of ~0.058 W/m^2, as reported by Kwon et al. [21]. By 2014, an electric power output of 3.46 W/m^2 was reached by

attaching mesoporous carbon (pore size of ~7 nm) on one side of a macroporous alumina (pore size ~80 nm) membrane, as demonstrated Gao et al. [22]. Recently, Feng et al. exploited a single-layer MoS$_2$ membrane with a homogeneous pore size of 10 nm, and the optimistic estimated power density could reach 10^6 W/m^2 under parallelization at large scale [23].

In the application environment, colloidal particles can serve as transport vectors of diverse contaminants in surface water, such as seawater, lakes, rivers, and freshwater bodies [24–27]. The diameter of colloidal particles ranges from 1 to 100 nm and they have a large surface/volume ratio. Ion adsorption, ion dissolution, and surface ionization cause the surface of the colloidal particles to become charged. The structure, interaction, and distribution of counter-ions in a charge-stabilized colloidal suspension must have an effect on ion transport in the solution [28]. In discussions of ion selectivity in nanofluidic, the effect of counterions has not attracted sufficient attention. Even if the inside of a nanochannel is assumed to be free from the influence of the colloid, the charge distribution near the orifice of the nanopores inevitably suffers from counterions interaction, thereby disturbing ion enrichment or depletion near the orifice associated with the nanofluidic channels. What is the role of colloidal particles in membrane-based nanofluidic power generation when the actual water is exploited? This question is especially important for migrating laboratory prototypes to actual application scenarios. However, in this rapidly growing field, so far,

the effect of colloids on nanofluidic power generation have not been reported.

Here, we investigate power generation by RED in a porous anodic alumina membrane (PAAM). To highlight the role of the colloidal particles, a PAAM with a large pore size of ~30 nm is selected purposely; this has a poor power generation efficiency of ~0.62 nW under a 1 M potassium chloride (KCl) gradient. To mimic the colloidal particles in natural water bodies, we simply introduced an ink gel (with colloidal particle size of ~100 nm) to investigate the effect of the colloid on nanofluidic power generation. As the colloid concentration in the KCl solution reaches $\sim 3.05 \times 10^{-5}$ g/ml, the maximum output power (P_{max}) rises to ~2.6 nW, which is a factor of ~4 larger than that obtained in a PAAM without the colloid. The enhancement in P_{max} may encourage research on the relationship between colloids (i.e., their concentration, type, and size, etc.) and nanofluidic power generation. On the premise of maintaining power enhancement, we show that surface modification of a PAAM by an ultra-thin (10-nm) platinum film significantly restrains the power fluctuation caused by the variation of colloid concentration.

2. Materials and methods

PAAMs (1 cm in diameter) were prepared by two-step anodization in a 0.4 M oxalic acid solution under a potentiostatic condition at 283 K [29]. The surface morphology of the PAAMs was examined by using a Hitachi S4800 scanning electron microscope (SEM). Red ink (Hero, Shanghai Fine Stationery Co., Ltd.) was selected as an additive to mimic the charge-stabilized colloidal suspension in natural water bodies. The absorption spectra of colloidal solutions were tested by using an ultraviolet visible (UV–VIS) spectroscope (UV–2401PC) within the 400- to 800-nm range with a resolution of 0.5 nm. Electrical properties of colloidal particles in solution were determined by electrophoresis experiments. 99.5% KCl (Analytical Reagent) was provided by Tianjin Fuchen Chemical Reagents Factory. The RED setup consisted of a (4.4-μm) PAAM mounted between two halves of a custom-made electrochemical cell. The current–voltage (I–V) curves were recorded with a current/voltage source (Keithley 2636A) using a pair of Ag/AgCl electrodes. The platinum coating was deposited on the PAAMs by dc magnetron sputtering (JPG600A) with 0.3 Pa Ar gas. The base pressure was <8 × 10⁻⁷ Torr [30–32].

With the help of a salt bridge experiment, the effect of the colloid on the surface potential of the electrodes was examined carefully. The results indicated that the electrode surface potential is unchanged after introducing the red ink colloid. To avoid the effect of a broad particle size distribution on the measurement of ionic electrical transport, we first used PAAMs with an average pore diameter of ~35 nm (prepared under a constant voltage of 40 V) to filter the colloid solution (where the ratio of pure water to red ink was 200/3), by which colloidal particles and impurities with large size were removed. Colloids with different concentrations were acquired by controlling the filtration time. The filtered solutions were examined by using a UV–VIS spectroscope. The concentrations of the colloid solutions were determined by a comparison between their weight (obtained by using by an ME204 electronic balance) and their absorption spectra. PAAM with an average pore diameter of ~30 nm (prepared under a constant voltage of 30 V) were used for RED.

When only a PAAM was present, 125 mL of 1 M KCl solution and pure water were placed into the electrochemical cell on both sides of the PAAM. After the solution was left to stand for 5 min, 50 ml of 1 M KCl solution and pure water were injected into the two electrochemical cells, respectively. Then the I–V properties were recorded. To study ion transport under a stable colloidal particle

distribution, KCl was only introduced after the colloidal solution in the electrochemical cell was left to rest for 6 h. The measurement of I–V curves was performed under a 1 M KCl gradient.

3. Results and discussion

Colloids widely exist in natural water bodies, such as sea water and fresh water. A colloidal particle in solution forms a charged core–shell structure through the interactions between solution molecular and colloidal particles. The EDL forming on the surface of the colloidal particle dominates the particle electrokinetics in solution. When the same type of colloidal particles aggregate, size-constraint liquid channels form along the inter-space between the particles. If the colloidal particles self-aggregate near the orifice of nanopores, as illustrated in Fig. 1(a), the ion enrichment or depletion near the orifice is disturbed. This provides a new method to regulate ion transport and is consistent with the fact that colloidal particles widely exist in water bodies. As shown in Fig. 1(b), an electrochemical cell is divided into two parts by a 4.4-μm-thick PAAM and the red colloidal particles are well restricted to one side of the electrochemical cell. Even after several hours, the UV–VIS absorption of the colloidal particles on the pure water side still remains zero (black curve) compared to the absorption peak of the colloid (red curve), as evidenced in Fig. 1(c), which indicates that the diffusion of colloidal particles is effectively prevented or that the colloid diffusion through nanopores is negligible. In this sense, a PAAM is a semipermeable membrane of colloidal particles that only allows the free transport of ions and small molecules. Therefore, as the colloidal particles diffuse under the concentration gradient, self-aggregation occurs near the PAAM nanopores.

First, let us analyze the I–V curves of two typical cases: a PAAM without a colloid (case 1) and a PAAM with a colloid (case 2). As shown in Fig. 1(d), the grey solid line is obtained in case 1 and the red solid line represents case 2. In case 2, the colloid concentration is set as 3.048×10^{-5} g/ml. The open-circuit voltage (V_{OC}) and short-circuit current (I_{SC}) are read from the intercepts on the
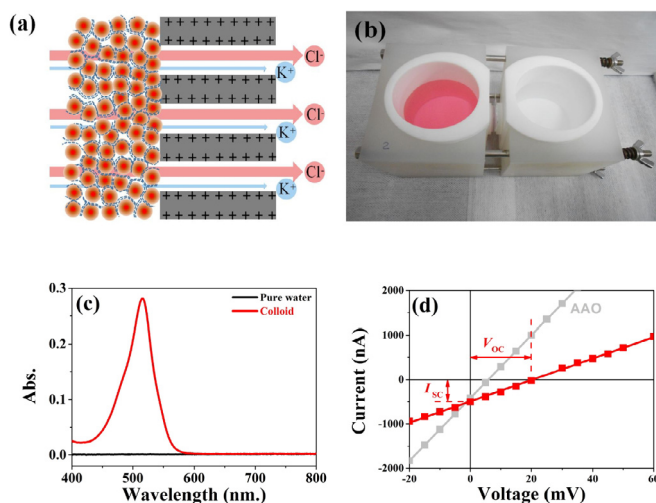

Fig. 1. Experiment for energy harvesting from reverse electrodialysis by mimicking the natural water environment. (a) Schematic of composite structure composed of colloidal particles and nanopore arrays. (b) Photograph of the experimental setup: on the left is a colloid, and on the right is pure water. (c) The UV–VIS absorption spectrum of the solution on both sides of the PAAM after 6 h. (d) Current–voltage characteristics for the PAAM without a colloid (grey data points and line) and for the PAAM with colloidal particles (red data points and line) under the same salinity gradient (1 M KCl). The contribution from the redox reaction on the electrodes is subtracted from the measured total current. I_{SC} and V_{OC} are the short-circuit current and open-circuit voltage, respectively.