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Unidirectional Transport of Small Ions by Melamine Foam Ratchets

Nobuaki Yonekura* and Ryo Shiroma
Faculty of Sciences, University of the Ryukyus, 1 Senbaru, Nishihara-cho, Okinawa 903-0213

(Received May 30, 2011; CL-110455; E-mail: yonekura@sci.u-ryukyu.ac.jp)

We report the unidirectional transport of ionic dyes by new soft matter ratchets, which are made of melamine foam with non-centrosymmetric triangular shapes and driven by an AC electric field. The time evolution of the distributions of the ions in the ratchet has been analyzed to reveal that the ratchets can transport the ions preferentially in one direction with an asymmetric transport ratio of more than 7.

Recently soft matter devices that control ion transport using soft materials such as hydrogel have attracted attention. One typical soft matter device is hydrogel diode (or polyelectrolyte diode), which permits the current flow when positive and negative ions counter-flow in the hydrogel but inhibits it when the ions are H^+ and OH^- and react to produce water.[1] Very recently, several soft matter devices embedded in microfluidic systems, such as an AND gate,[2a] a FET (field effect transistor),[2b] ion bridges,[2c] or an ion filter,[2d] have been demonstrated. Since soft matter devices can utilize various kinds of ion species, soft materials, and their interactions, they should have potential for useful functions not achieved by semiconductor devices. However, mechanisms to control ion transport and soft materials which have been used for the soft devices reported so far have been quite limited. Ratchet is a mechanism to realize unidirectional transport of particles using non-centrosymmetric potential, structure, or interaction and symmetric driving forces which are not bias.[3] Although Brownian ratchets, which can extract a unidirectional motion from Brownian motion or diffusion of particles, have been studied extensively, experimentally demonstrated examples have been limited. To date, the unidirectional transport of lipids,[4] colloid particles,[5] DNAs,[6] and electrons[7] based on Brownian ratchet mechanism have been reported. However, the unidirectional transport of small ions using soft materials has not been demonstrated yet.

In the present study, the first approach to developing a novel soft matter device based on a Brownian ratchet mechanism, we demonstrate the unidirectional transport of ionic dyes in melamine foams with triangular shapes by applying an AC electric field. The melamine foams and the AC electric field provide the non-centrosymmetric structure and the symmetric driving force essential for the ratchet mechanism. The distributions of the ions in the melamine foam were successfully visualized and their time evolutions were analyzed. Since the melamine foam is a porous soft material which can include water and be shaped easily, it is expected to become a superior building block for ion-transport control devices as well as the hydrogels. To our knowledge, however, even ion transport in it has not been studied.

As shown in Figure 1 (A1), a melamine foam (melamine–formaldehyde–sodium bisulfate, commercially available, thickness of 4 mm) was formed into a triangular shape with two rectangular parts at the apex (hereafter right channel, labeled by "R" in the figure) and at the bottom of the apex (left channel, labeled by "L"). A solution of Orange G, a divalent anionic dye, (50 mM, 4 µL) was spotted onto the center of the foam including TB (Tris-Borate) buffer solution. The ionic dyes were electrophoresed by a low-frequency AC electric field applied between two Pt electrodes (0.4 mm in diameter, labeled by "E" in the figure) inserted into the proximity of the edges of the channels. The images of the dye distribution in the foam were taken with a digital camera and analyzed. From the electrophoretic mobility of $1.6 \times 10^{-4}\,cm^2\,V^{-1}\,s^{-1}$ measured and the Einstein relation, the diffusion coefficient of Orange G in the melamine foam involving the buffer solution was estimated to be $2.0 \times 10^{-6}\,cm^2\,s^{-1}$, which is of comparable order with that in a solution, $4.3 \times 10^{-6}\,cm^2\,s^{-1}$.[8]

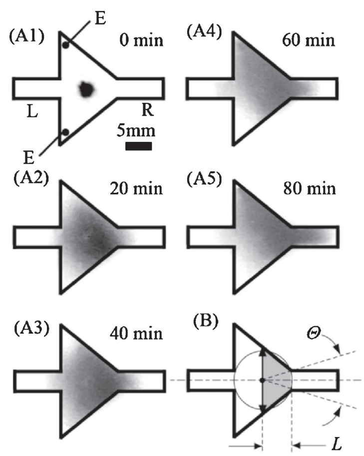

Figure 1. (A1)–(A5) Distribution of the ionic dyes (the darker area) in a triangular melamine foam ratchet driven by an AC electric field between Pt electrodes of which the positions are labeled by "E." "R" and "L" refers to the right and left channels (the rectangular parts jointed with the apex and bottom of the triangular part), respectively. (B) Diagram to explain the dye's distribution (for detail, see text) and the definition of θ and L in the eq 1.

Figures 1 (A1)–(A5) show the time evolution of the distribution of the ionic dyes in the melamine ratchet driven by an AC electric field (sine wave form; 4×10^{-3} Hz; 80 $V_{p\text{-}p}$). Obviously, as time passes, the ionic dyes are transported preferentially into the right channel, labeled by "R" in Figure 1 (A1). The distribution of the ionic dyes observed at 0–40 min can be explained using Figure 1 (B) as follows. The length of the double-headed arrow depicted in the figure corresponds to the vertical movable range of the ionic dyes driven by the AC electric field. For the right part of the triangular foam (the shaded part), the ionic dyes are concentrated at the upper and lower boundaries, since the interval between the boundaries is narrower than the vertical movable range. In contrast, the ionic dyes in the left part are not concentrated at the boundaries but dispersed in a larger area. Since the diffusion of

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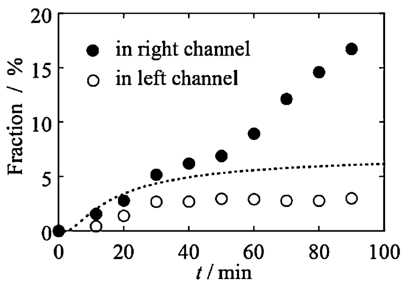

Figure 2. Time evolution of the fractions of the ionic dyes in the channels of right (closed circle) and left (open circle). The dashed curve is the simulated fraction in the channel when the dyes diffuse 2D symmetrically.

the ionic dyes in the horizontal direction is free, the concentration difference between the right and left parts can drive unidirectional transport.

Figure 2 shows the time evolution of the fractions of the ionic dyes transported into the right and left channels. The fraction in the right channel continues to increase with some variations. Unlike the right channel, the fraction in the left channel remains at lower values of ca. 3% after 30 min. Evidently, the present melamine foam ratchet achieves the unidirectional transport of the ionic dyes. The asymmetric transport ratio, which is defined as the ratio of the right fraction to the left, is more than 7 after 90 min. The dashed curve shown in the figure is the calculated fraction of the ionic dyes in the case that they diffuse 2D symmetrically and move directly into the channel, $F_{sym}(t)$, which is calculated by the following approximate equation,

$$F_{sym}(t) = \int_0^{\theta} \int_L^{\infty} [P(r,t) \times I(r)] r \mathrm{d}t \mathrm{d}\theta \qquad (1)$$

where the convolved $P(r,t)$ and $I(r)$ is the normalized radial probability distribution of the diffusing ionic dyes with the diffusion coeffient of $2.0 \times 10^{-6}\,cm^2\,s^{-1}$, the normalized initial distribution assumed to be Gaussian, and θ and L are the angle and a distance shown in Figure 1 (B). In the limit that $t \to \infty$, $F_{sym}(t)$ approaches 7.2% $(=\theta/2\pi)$. Obviously, the observed fraction curves are different from the simulated curve that represents symmetric diffusion. This results from a nonsymmetric diffusion brought about by the ratchet. After 60 min, the transport to the right channel increases remarkably. This relates to the distribution of the ions changing to the up-down asymmetric, as shown in Figures 1 (A4) and (A5). The asymmetric distribution could be more favorable to introduce the ions into the narrow channel than the almost symmetric distribution before 60 min. The fact that the distributions bias toward the upside might be determined by the initial moving direction of the ions driven by the AC field, which is toward the upside.

The unidirectional transport depends on the potential, frequency of the AC electric field, and the size of the ratchet. The unidirectionality becomes lower with the decrease of the potential or the frequency. At higher potential or frequencies, the ionic dye diffusion is difficult because of being trapped around the electrode or difficult driving. A ratchet with a larger (smaller) size needs higher (lower) potential.

Figure 3 (A1) shows another type of the ratchet with two source channels (labeled by "S" in the figure), which were arranged one above the other at the center of the triangular part. The ionic dyes were spotted onto the additional channels and driven by an AC electric field (sine wave form; 4×10^{-3} Hz; 80 $V_{p\text{-}p}$) applied at the Pt electrodes. Figures 3 (A1)–(A3) show the time evolution of the distribution of the ionic dyes in the ratchet with the source channels. In spite of the positions of the ionic dyes spotted and the electrodes being different from those of the original ratchet, the ratchet with the source channels can also transport the ionic dyes unidirectionally to the right channel in a similar manner to the original one. The asymmetric transport ratio after 83 min is more than 5. Assuming the AC driven diffusion of the ions introduced from the source channels into the ratchet is an AC current, the unidirectional transport by the ratchet could be compared to the rectification by a four-diode bridge circuit shown in Figure 3 (B). Unlike the other ion control devices, the present ratchets can transport both positive and negative ions to the same direction. Therefore, the present ratchets are expected to work as an ion concentrator or ion pump as well as an ion rectifier.

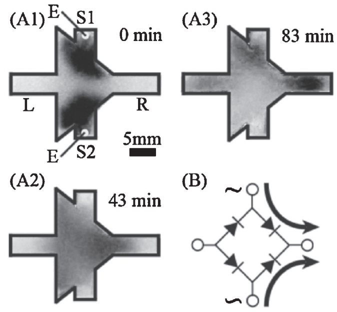

Figure 3. (A1)–(A3) Distribution of the ionic dyes (the darker area) in a triangular melamine foam ratchet with two source channels (labeled by "S"). The labels "E," "L," and "R" are used in the same manner as Figure 1 (A1). (B) Four-diode bridge rectifier. The tildes and the arrows indicate the inputs of AC and the outputs of DC, respectively.

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