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Photoelectrochemical ion concentration polarization: membraneless ion filtration based on light-driven electrochemical reactions†

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In this article we report a microelectrochemical system that is able to partially desalinate water. The underlying principles are similar to previous reports in which a local electric field resists passage of ions. However, in the present case, no membrane is required and, most interestingly, much of the power for desalination originates from light rather than electricity. This could greatly increase the power efficiency for desalination. The device is based on a TiO_2 photoanode coupled to a Pt cathode. Illumination of the photoanode drives faradaic reactions at the cathode that lead to an ion depletion zone. The resulting local electric field limits transport of charged species. *In situ* conductivity and fluorescence measurements demonstrate the effectiveness of the device.

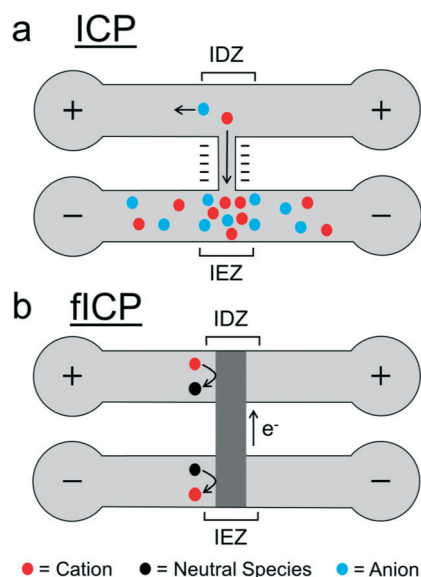
Introduction

Ion concentration polarization (ICP) is a general method for manipulating ions in solution.^{1–3} A typical approach for implementing ICP is shown in Scheme 1a.^{4–8} Here, two fluidic channels are separated by a negatively charged nanochannel or permselective membrane. When a driving voltage (V_D) is applied with the indicated polarity, cations are driven from the top channel, through the ion-selective channel or membrane, and into the bottom channel. Anions in the top channel then migrate toward the positive driving electrodes. This action results in formation of an ion depletion zone (IDZ) near the intersection of the top and ion-selective channels, and an ion enrichment zone (IEZ) near the intersection of the bottom and ion-selective channels. The loss of ionic charge carriers in the IDZ results in a co-located elevated local electric field.

Several years ago, we introduced an electrochemical version of ICP that we call faradaic ICP (fICP). As shown in Scheme 1b, the experimental configuration for fICP is similar to that used for normal ICP with the exception that the permselective nanochannel or membrane is replaced by a bi-

polar electrode (BPE).^{9–12} In this case, an electroactive cation in the top channel is electrochemically reduced to a neutral species, and in the bottom channel a neutral species is oxidized to form a cation. The net effect is that an IDZ forms near the cathode of the BPE in the top channel, and an IEZ forms near the BPE anode in the bottom channel.

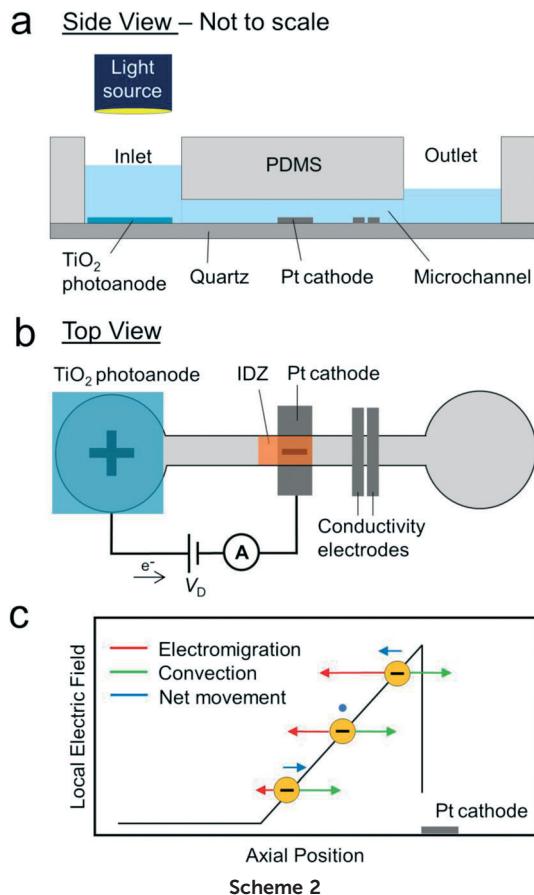
In the present article we introduce a new version of ICP called photoelectrochemical ICP, or pICP. This method is similar to fICP, but in this case the IDZ is generated primarily by light energy rather than by a power supply. The experimental arrangement for pICP is shown in Schemes 2a and b.



Scheme 1

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† Electronic supplementary information (ESI) available: X-ray diffraction of TiO_2 ; UV-vis spectrum of TiO_2 ; photograph of the macroscopic, two-electrode cell; intensity of incident UV-vis light; schematic diagram of the conductivity measurement electronics; conductivity of Tris buffer solutions; temperature effect on the conductivity signal; percentage change in solution conductivity measured using individual microelectrochemical devices; electrochemical neutralization of TrisH^+ ; explanation of Movie S1 showing microsphere accumulation due to pICP. See DOI: 10.1039/c7lc00455a



This is a typical two-electrode microelectrochemical cell configuration with a TiO_2 photoanode photolithographically defined at the bottom of the inlet reservoir of the device and a Pt microband cathode situated within the channel. The key point is that when the photoanode is illuminated, a corresponding faradaic electrochemical reaction is driven at the Pt cathode that results in formation of a local IDZ.

Regardless of whether the IDZ forms by ICP, fICP, or pICP, it has some characteristics in common. The most important of these is illustrated in Scheme 2c specifically for pICP, but it applies to the other methods as well. Here, the local IDZ results in a region of high electric field near the Pt cathode. When anions enter the IDZ they are accelerated by this higher field toward the photoanode by electromigration. If there is an opposing convective force, which in this case is pressure-driven flow (PDF) enabled by a difference in the height between the solutions in the two reservoirs (Scheme 2a), then anions feel the difference between the two forces. For example, anions in the weakest part of the local electric field gradient experience a net velocity from left to right, and those in the strongest part of the field move from right to left. The net effect is that anions are swept into a single location where their velocity sums to zero. In other words, anions are focused and concentrated at this one position within the microchannel. Techniques in which two forces oppose each other to drive ions to a single location

are generally known as electric field gradient focusing (EFGF) methods.^{13,14}

The most important uses of ICP and fICP are probably for partial desalination of water,^{15–17} molecular enrichment,^{4,18–22} and separation.^{12,23} For example, Han and coworkers reported ICP-based partial desalination of salt water in a microfluidic device featuring a Nafion permselective membrane as the active component (e.g., Scheme 1a).¹⁵ Sinton and coworkers reported a similar approach, but they used a three-dimensional fluidic system to improve efficiency.¹⁶ The unique properties of ICP have also been used to construct micromixers^{24,25} and ionic diodes.²⁶ Recently, ICP applications have even been adapted to paper fluidic devices^{27,28} for enrichment and detection of biomolecules.^{19,20,22,29}

In the present report, we describe the experimental approach for implementing pICP, and use *in situ* electric field measurements to confirm the presence of a light-generated IDZ. Finally, we demonstrate that the local electric field gradient associated with the IDZ acts as a membraneless filter that partially desalts water.

Experimental section

Chemicals and materials

The acidic and basic forms of Tris were obtained from Sigma-Aldrich (St. Louis, MO). A 100 mM Tris buffer solution was prepared by mixing approximately equal amounts of the two forms of Tris in deionized water (DI water, 18.0 MΩ cm, Milli-Q Gradient System, Millipore), and then titrating to pH 8.0. Different concentrations of these Tris buffer solutions (50.0 mM, 20.0 mM, 10.0 mM, and 1.0 mM) were prepared by diluting the 100 mM stock solution with DI water.

Quartz microscope slides were purchased from Technical Glass Products, Inc. (Painesville Twp., Ohio). H_2O_2 (30%), H_2SO_4 (98%), Cu wire, and acetone (HPLC grade) were obtained from Fisher Chemical. Adhesion promoter (Micro Prime HP Primer, Shin-Etsu MicroSi, Phoenix, AZ), positive tone photoresist (AZ 1518, AZ Electronic Materials, Somerville, NJ), and developer (AZ 400 K, AZ Electronic Materials) were used for photolithography. Ethanol was from PHARMCO-AAPER (Brookfield, CT) and Ag paste was from Electron Microscopy Sciences (Hatfield, PA). Carboxyl-functionalized polystyrene microspheres having a diameter of 0.99 μm and a density of 1.05 g cm⁻³ (PC04N, Bangs Laboratories, Inc., Fishers, IN) were used as tracers.

Device fabrication

The hybrid PDMS/quartz microfluidic device (hereafter, the ‘microelectrochemical cell’) was fabricated following a previously reported method.³⁰ Briefly, TiO_2 and Pt microband electrodes were patterned in separate steps on quartz slides using standard photolithographic techniques. Specifically, the slides were immersed in piranha solution (1:3 $\text{H}_2\text{O}_2/\text{H}_2\text{SO}_4$; *caution: piranha reacts violently with organic chemicals and it should be handled in a ventilated hood with extreme care*) for 15 min, followed by rinsing with DI water. Next, an

adhesion promoter and photoresist were spin-coated onto the dried slides. The photoresist was then exposed to UV light through a mask. Finally, the pattern was developed in the resist.

Next, 210 nm of Ti (Kurt J. Lesker Company, Jefferson Hills, PA) was deposited by electron-beam physical vapor deposition. Photoresist lift-off was performed by sonicating the substrate in acetone, leaving behind the desired electrode pattern on the quartz slides. The patterned Ti electrode was converted to TiO_2 by thermal oxidation under flowing air in a tube furnace (Model 55035, Lindberg, Riverside, MI).³¹ The temperature was ramped from 25 °C to 450 °C at a rate of 30 °C min⁻¹ and then held at 450 °C for 1.0 h. After oxidation, the substrates were cooled to 25 °C at a rate of 5.0 °C min⁻¹. The Pt (Kurt J. Lesker Company, Jefferson Hills, PA) electrodes (100 nm Pt plus 15 nm Ti adhesion layer) were patterned using the same procedure, but without thermal oxidation.

The PDMS microchannel (6.0 mm long, 100 μm wide, and 20 μm high) was fabricated by soft lithography using a Sylgard 184 silicone elastomer kit (Dow Corning Corporation, Midland, MI) and a SU-8 (MicroChem, Westborough, MA) mold patterned on a Si wafer. Inlet and outlet reservoirs (4.0 mm diameter) were punched into the PDMS, and then it was rinsed with ethanol and dried with flowing N_2 . The quartz slide and the PDMS channel were exposed to an O_2 plasma (Model PDC-32G, Harrick Scientific, Ossining, NY, 45 s, medium power setting), and then brought into contact. The assembled microelectrochemical cell was immediately placed in a 65 °C oven for 5.0 min to promote irreversible bonding between the PDMS and quartz. A single microelectrochemical cell can be used for many experiments as long as the microchannel does not become obstructed (e.g., the electrodes are quite stable).

Characterization of the TiO_2 electrode

To fully characterize the TiO_2 thin-film electrodes used in the microelectrochemical cells, it was necessary to prepare proxies having larger lateral dimensions. These larger films (210 nm- and 50 nm-thick) were processed identically to those used for the microelectrochemical cell experiments and then characterized by X-ray diffraction (XRD, Rigaku Ultima IV, Rigaku Americas Corp., The Woodlands, TX) and UV-vis spectroscopy (Cary 5000 UV-vis-NIR spectrometer, Agilent, Santa Clara, CA) as shown in Fig. S1 and S2 in the ESI,[†] respectively.

The photoelectrochemical properties of macroscopic TiO_2 thin films were examined using a macroscopic Teflon cell configured with the TiO_2 working electrode defined by a 4.0 mm-diameter O-ring at the bottom of the cell (Fig. S3[†]). The counter electrode was a Pt wire and the electrolyte solution was 100 mM Tris buffer (pH 8.0). A power supply (Model LLS9120, TDK-Lambda Americas, Inc., San Diego, CA) and an ammeter (Model 6517B electrometer, Keithley Instruments, Inc., Cleveland, OH) were connected in series between the TiO_2 and counter electrodes. The photocurrent was measured as a function of the applied bias and light intensity. The photocurrent arising from a Pt thin film working electrode

was also measured as a control. A 100 watt Hg arc lamp (Model OmniCure s1000, Lumen Dynamics, Ontario, Canada) configured with a 320–500 nm filter and a fiber optic were used to irradiate the electrodes. For photoelectrochemical measurements, the tip of the fiber was placed 2.5 cm away from the thin film electrodes. The intensity of the light at this distance was calculated to be $\sim 65 \text{ W cm}^{-2}$. Details of the measurement and a spectrum of the lamp emission are provided in Fig. S4.[†]

Electric field measurements

As previously described,^{32,33} the longitudinal electric field profile within the channel was monitored using a scanning digital multimeter (SDMM, Model 2700, Keithley Instruments, Inc., Cleveland, OH) equipped with a multiplexer module (Model 7701, Keithley). The multiplexer was connected to Pt microbands present near the Pt cathode in the microchannel. The SDMM was used to sequentially read the voltage difference between pairs of neighboring microbands. The acquisition time for each voltage measurement was ~ 0.10 s, and the voltage at each of the five positions within the microchannel was measured every 2.0 s. A total of five measurements was made at each position, so the total measurement time was 10 s.

Flow rate measurement

As shown in Scheme 2a, the rate of PDF was controlled by pipetting different volumes of buffer into the reservoirs at the ends of the microchannel. It is difficult to control the size of the reservoirs, however, and therefore we found the run-to-run variation in PDF to be significant. For some experiments this variation is not important, but for others it is. In those cases, polystyrene microspheres (0.01 w/v%) were added to buffer solution in the microchannel. Because the microspheres have a density similar to that of water, their flow velocity can be determined by visual observation and used as a proxy for the rate of PDF.

On-chip conductivity measurement

The apparatus used for *in situ* conductivity measurements is based on previously reported designs.^{17,34} Briefly, a pair of 20 μm -wide Pt microband electrodes separated by a 20 μm gap was patterned on the quartz base of the microelectrochemical device concurrent with photolithographic fabrication of the Pt cathode. A function generator (Model 182A, Wavetek, San Diego, CA) was connected to one of the microbands and used to apply a sinusoidal ac voltage (~ 100 kHz frequency, ± 0.30 V amplitude). The other microband electrode was connected to a prototype circuit board with an on-board, two-stage transimpedance amplifier. This circuit received and amplified the current resulting from the input voltage and converted it into a voltage signal. The output from the circuit board was connected to a multifunctional PC data acquisition board (Model NI PCI-6229, National Instruments, Austin, TX) through a connector block (Model SCB-68A, National Instruments). The input signal was digitally

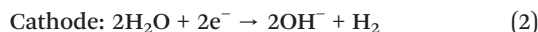
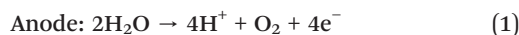
processed by the data acquisition board and provided the average peak-to-peak amplitude of the ac signal in LabVIEW software. Fig. S5† provides a detailed electrical diagram of the conductivity measurement system.

Results and discussion

pICP operation

As discussed in detail in the Experimental section, pICP was performed using the hybrid PDMS/quartz microelectrochemical device shown in Schemes 2a and b. To set up the experiment, the tip of a fiber optic connected to a Hg arc lamp was positioned 2.5 cm away from the TiO₂ electrode configured on the floor of the inlet reservoir. PDF was generated by introducing 40 μL and 34 μL of 100 mM Tris buffer into the inlet and outlet reservoirs, respectively, as shown in Scheme 2a. A power supply and ammeter were placed in series with the electrodes as shown in Scheme 2b.

When the power supply and light are activated, water is oxidized at the TiO₂ anode (eqn (1)) and reduced at the Pt cathode (eqn (2)). In a following reaction, electrogenerated OH[−] neutralizes TrisH⁺ present near the Pt cathode (eqn (3)).³⁵ The net result of these processes is that an IDZ forms near the Pt cathode (Scheme 2b, burnt orange rectangle). As discussed earlier, this results in a region of high solution resistance and a co-located local electric field gradient (Scheme 2c).



Current response of the TiO₂ photoanode

On the basis of our previous results relating to fICP,^{33,35} we know that the magnitude of the current has a dominant effect on the properties of the IDZ and hence the transport of ions. Accordingly, we characterized the photoelectrochemical properties of TiO₂ electrodes as a function of V_D and the light intensity at the photoanode. As a control, the same measurements were made for a photo-insensitive Pt electrode. As discussed in detail in the Experimental section, these preliminary electrochemical measurements were carried out using macroscopic electrodes, a macroscopic, two-electrode cell, and a solution containing 100 mM Tris buffer (pH 8.0), which is the same buffer used previously for fICP.^{32,33,36,37}

Fig. 1a is a plot of current density vs. time for a TiO₂ macroscopic electrode in the absence and presence of light. In this case, no V_D was applied, and the photocurrent density is ~0.20 mA cm^{−2}. This current originates from formation of a space-charge region, which promotes electron–hole separation.³⁸ On rutile TiO₂, this current arises from water oxidation (eqn (1)) at the TiO₂ electrode and water reduction (eqn (2)) at the Pt wire counter electrode.^{38,39}

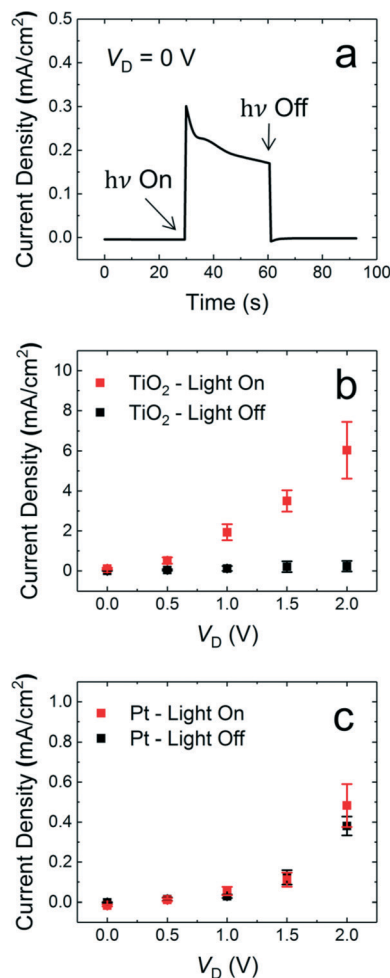


Fig. 1 Plots of photocurrent density as a function of time and driving voltage (V_D). All data were obtained using a macroscale, two-electrode Teflon cell containing 100 mM Tris buffer (pH 8.0). The counter electrode was a Pt wire. (a) Plot of photocurrent density vs. time obtained using a TiO₂ photoanode illuminated with a Hg arc lamp. $V_D = 0$ V. (b) Plot of photocurrent density vs. V_D in the presence and absence of light. The photoanode was a TiO₂ thin film. (c) Plot of current density vs. V_D in the presence and absence of light. For this control experiment, the working electrode was a Pt thin film. The current density has been normalized to the area of the thin film anodes. For (b) and (c) the current density was measured 30 s after applying V_D and, where relevant, light. The error bars represent the standard deviation from the mean for three measurements using independently fabricated Pt or TiO₂ thin films.

We next carried out measurements like those in Fig. 1a, but as a function of V_D (Fig. 1b). There are two key results that will become important when the microelectrochemical data are discussed. First, the current density increases monotonically in the presence of light, and, second, it is close to zero when the light is off over the range of V_D values examined.^{40,41} This occurs because the external bias, V_D , increases the electric field in the space-charge layer and hence the efficiency of electron–hole separation.⁴² Higher values of V_D result in higher efficiencies. The data in Fig. 1c were obtained by carrying out an experiment identical to that just described for Fig. 1b, except that the illuminated

anode was Pt rather than TiO_2 . In this case the current densities track each other regardless of illumination, but the magnitude for the light-on case is more than 10-fold lower than in Fig. 1b. Note that the current density is slightly higher on Pt than for TiO_2 when the light is off, but this is simply a consequence of the Pt anode being a good electrocatalyst for water oxidation.⁴³ The important conclusion from Fig. 1 is that the TiO_2 photoanode yields a substantial current under illumination at low values of V_D . This lowers the overall electrical energy required to drive a process like ICP-induced desalination.^{15–17}

Measurement of the local electric field

As discussed in the Introduction, fICP requires formation of a local electric field. Accordingly, we confirmed the presence of this field in the microelectrochemical cell (Scheme 2a) and measured its dependence on both illumination and V_D using an approach we have previously reported.^{32,33,44–46} Specifically, Pt microbands 1–6 (Fig. 2a) were configured in the vicinity of the Pt cathode (microband P), and a scanning digital multimeter (SDMM) was used to measure the voltage difference between pairs of neighboring microbands. The experiment was carried out as follows. First, the microfluidic device was filled with 100 mM Tris buffer (pH 8.0) and set up for pICP operation as discussed earlier. Second, the SDMM was attached to the numbered microbands to measure the local electric field. Third, V_D was applied to the

microelectrochemical device, and in some cases the TiO_2 electrode was illuminated.

Fig. 2b is a plot of the local electric field profile along the long axis of the microchannel and in the vicinity of the Pt cathode in the absence of light. Position 0 on the horizontal axis is the location of the Pt cathode, and the indicated distances are measured toward the photoanode. These distances represent the midpoint between pairs of adjacent microband electrodes. The important point is that in the absence of light, even at $V_D = 2.0$ V, a negligible local electric field gradient is observed. This result is consistent with the data in Fig. 1b, which shows that only a very small current passes between the photoanode and cathode in the absence of light.

Fig. 2c is analogous to Fig. 2b, but in this case the TiO_2 photoanode was illuminated. When $V_D = 0$ V, there is still no appreciable local electric field, because V_D alone is insufficient to create an IDZ. However, when $V_D = 0.50$ V, a slight increase in the local field is observed near the Pt cathode. At higher values of V_D , a more significant local electric field emerges. For example, when $V_D = 2.0$ V, the maximum field is $\sim 9 \text{ kV m}^{-1}$. These findings are consistent with the results in Fig. 1b, which shows a steady increase in current (and hence neutralization of buffer by OH^-) as V_D increases. Importantly, we have previously shown that a local electric field of $\sim 5.0 \text{ kV m}^{-1}$ is sufficient to deplete fluorescent ion tracers,⁴⁴ although the specific value for a particular experiment depends on the rate of convection.

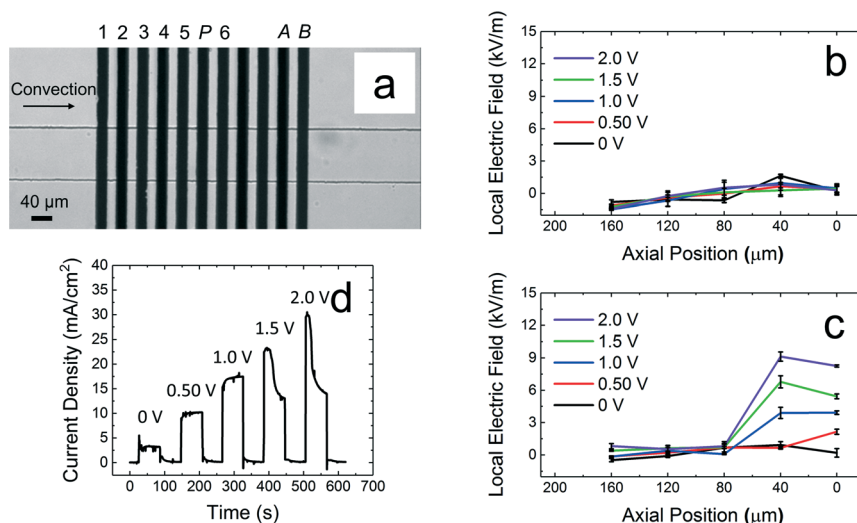


Fig. 2 (a) Optical micrograph of a microchannel in the vicinity of the Pt cathode. The numbered Pt microbands were used for electric field measurements. The Pt cathode is labeled P, and microbands A and B were used for conductivity measurements. All data were obtained using a pICP device containing 40 μL and 34 μL of 100 mM Tris buffer (pH 8.0) in the inlet and outlet reservoirs, respectively. The TiO_2 photoanode (not shown) was positioned at the bottom of inlet reservoir and was illuminated with an Hg arc lamp. V_D was applied between the Pt cathode and the TiO_2 photoanode. Each value of V_D was applied for 1.0 min with a 1.0 min interval (at open circuit) between measurements in the sequence: 0 V, 0.50 V, 1.0 V, 1.5 V, and 2.0 V. (b) Plot of average local electric field strength vs. position in the absence of light and as a function of V_D . (c) Plot of average local electric field strength vs. position in the presence of light and as a function of V_D . For (b) and (c), position 0 denotes the location of the Pt cathode, and the indicated distances are increasing in the direction of the photoanode. The value of the electric field strength at each position was measured five times during the final 10 s of the 1.0 min application of V_D (and where relevant, light). The error bars represent the standard deviation from the mean for the 5 measurements (in a single device). (d) Plot of photocurrent density measured concurrently with the data shown in (c). The total current has been normalized to the area of the Pt cathode.

Fig. 2d is a plot of the photocurrent density measured concurrently with the data shown in Fig. 2c. The values of V_D used for each measurement are provided in the figure. Each V_D was applied for 1.0 min with a 1.0 min time interval between measurements. The general trends of these photocurrents are similar to those found for macroelectrodes (Fig. 1b), but there is a decrease in current toward the end of the current transients for $V_D = 1.5$ V and 2.0 V. There are two possible explanations for the latter observation. First, an increase in solution resistance (R) in the IDZ increases the voltage drop in the solution between the photoanode and the cathode. This voltage drop is proportional to iR , where i is the current. The increase in the voltage dropped in the solution reduces the interfacial potential difference for each electrode and hence the current. A similar observation has been reported during fICP.³³ Second, the rate of water reduction (eqn (2)) at the cathode could decrease due to electro-generation of OH^- and the corresponding local pH change. This scenario is less likely, however, because the solution is buffered.

One final point should be mentioned. Although all the microelectrochemical devices exhibited electric field gradients for $V_D > 0.50$ V, there were substantial device-to-device variations in their size and shape. For example, at $V_D = 0.50$ V, the magnitude of the gradient near the cathode varied by as much as $\pm 50\%$ (standard deviation based on measurements from four independent devices). At present, the two most difficult variables to control reproducibly are the TiO_2 photocurrent response and the PDF rate. With regard to the latter, recall that PDF is generated by controlling the volume of solution in the two reservoirs. However, slight device-to-device variations in the dimensions of these reservoirs result in different solution heights and hence different flow rates. These variations between experiments do not detract from the main finding, which is that light can be used to electro-generate the IDZ. Note that in the next section, where quantitation is important, we carefully controlled the flow rates.

On-chip conductivity measurement

Consider the microelectrochemical device shown in Scheme 2b, and particularly the relationship between the IDZ and the conductivity measurement electrodes. In the previous section we confirmed the presence of the IDZ, and therefore we expect the associated electric field gradient will resist the passage of ions as shown in Scheme 2c. This means that ions will concentrate to the left of the IDZ, and consequently the conductivity of the solution downstream of the Pt cathode should be lower than that of the feed stream. We tested this hypothesis by measuring the downstream conductivity.

Fig. 3a is a calibration curve relating the conductivity signal obtained from solutions in the microelectrochemical cell (using the circuit shown in Fig. S5†) to the conductivities of the indicated Tris buffer solutions (measured using a commercial conductivity meter, Fig. S6†). These data were obtained in the absence of light and with $V_D = 0$ V.

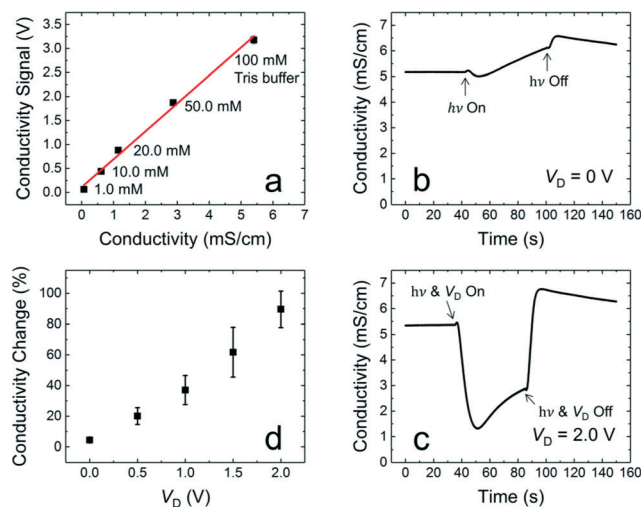


Fig. 3 (a) A calibration curve relating solution conductivity (measured using a commercial meter) to the signal obtained using the *in situ* conductivity measurement apparatus. For this experiment, 40 μL and 34 μL of Tris buffer were added to the inlet and outlet reservoirs so that the rate of PDF was comparable to the other experiments in this figure. The error bars (barely visible due to their small size) represent the standard deviation from the mean for three measurements obtained using a single device. $R^2 = 0.98$. (b) Plot of solution conductivity vs. time for $V_D = 0$ V. (c) Plot of solution conductivity vs. time for $V_D = 2.0$ V. For (b) and (c), the measured signals were converted into equivalent solution conductivities using the calibration curve in (a). In both cases, the light and V_D were turned on at 40 s and turned off at 100 s. (d) Plot of the percentage solution conductivity change (defined in the main text) vs. V_D . The error bars represent the standard deviation from the mean for triplicate measurements carried out using three independently fabricated devices. All conductivity data were measured using microbands A and B (Fig. 2a) positioned ~ 180 μm downstream from the Pt cathode. The rate of PDF was controlled by monitoring the motion of polystyrene microsphere tracers present in the 100 mM Tris buffer. In all cases the solution pH = 8.0.

Fig. 3b is a plot of solution conductivity of a 100 mM Tris buffer solution in the microelectrochemical cell as a function of time during pICP ($V_D = 0$ V). This plot was constructed by converting the conductivity signal (V), obtained from the conductivity measurement circuit, to solution conductivity (mS cm^{-1}) using the calibration curve in Fig. 3a. At $t = 0$, the conductivity of this solution was found to be 5.2 mS cm^{-1} , which can be compared to the nominal conductivity of 5.4 mS cm^{-1} measured using a commercial meter. The difference in magnitude between these two values is typical of the intrinsic error associated with the conductivity measurement.

At $t = 40$ s, the photoanode was illuminated, and a few seconds later the downstream conductivity decreased. Earlier we showed that no electric field gradient forms when $V_D = 0$ V (Fig. 2c), but a small current does pass (Fig. 2d). Therefore, the slight decrease in the solution conductivity in Fig. 3b must be due to a small amount of TrisH^+ being neutralized *via* eqn (2) and (3) and then transported to the conductivity electrodes by convection.

Following the initial decrease in conductivity, there is a gradual increase in the solution conductivity during the next

~60 s of the experiment. This is not due to an increase in ion concentration, however, but rather we believe it arises from an increase in solution conductivity due to heating of the solution by the Hg lamp. Specifically, the temperature increase results in a decrease in solution viscosity, a corresponding increase in ion mobility, and hence an increase in conductivity.⁴⁷ To confirm this hypothesis, we carried out an experiment identical to that represented in Fig. 3b, but in the absence of faradaic reactions (*i.e.*, at open circuit). The gradual change in solution conductivity in this case (Fig. S7†) is nearly identical to that shown in Fig. 3b. Finally, after 60 s of illumination at $V_D = 0$ V, the light was turned off which stops TrisH^+ neutralization (eqn (2) and (3)). Consequently, there is an immediate increase in the concentration of TrisH^+ followed by a slower decrease in the apparent concentration as the solution cools.

Fig. 3c is analogous to Fig. 3b, except now $V_D = 2.0$ V, which is sufficient to generate a significant IDZ. The characteristic gradual changes in the solution conductivity arising from heating and cooling are observed, but the most noticeable feature is the rapid (few seconds) and dramatic decrease in solution conductivity when both V_D and the lamp are switched on. We attribute this important observation to formation of an IDZ (as demonstrated by the data in Fig. 2c) and concomitant accumulation of ions upstream of the conductivity electrodes (Scheme 2b). After the light is turned off, the conductivity signal sharply increases, corresponding to collapse of the IDZ.

Fig. 3d is a plot showing the percentage solution conductivity change as a function of V_D . The data were obtained using three independently fabricated microelectrochemical devices for each value of V_D . The percentage solution conductivity change was calculated from data like those shown in Fig. 3b and c, and specifically from the differences between the initial and lowest measured solution conductivities. This difference was used, because it minimizes the effects of heating.

Unsurprisingly, there is a monotonic increase in the conductivity change as V_D increases. We conclude that a more depleted IDZ minimizes the amount of charge carriers reaching the conductivity measurement electrodes. The size of the error bars in these measurements is probably associated with slight differences in the photoelectrochemical properties of the TiO_2 thin films, which are independently prepared. When replicate experiments like those shown in Fig. 3d are carried out using a single device, the error bars are significantly smaller (Fig. S8†).

It is important to point out that as much as 50% of the change in solution conductivity represented by the data shown in Fig. 3d arises from the reactions represented in eqn (2) and (3) (*e.g.*, photoelectrochemically initiated neutralization of TrisH^+), rather than the local electric field (*e.g.*, pICP). In other words, part of the observed conductivity change arises from ICP, but part of it also arises from conversion of TrisH^+ to neutral Tris, which is swept over the conductivity electrodes. This point is discussed further in the ESI†

To confirm the salt rejection findings determined using conductivity measurements and represented in Fig. 3d, we also used fluorescent ion tracers to visualize pICP ion filtration. Fluorescent tracers have previously been used to visualize ion enrichment^{35,36,46} and ion separation^{23,45} in fICP, so it is a well-established methodology. In the present case, the tracers were negatively charged microspheres. The pICP experiment was carried out as discussed in the context of Fig. 3, except carboxyl-functionalized microspheres were added to the 100 mM Tris buffer.

When the TiO_2 photoanode is illuminated with $V_D = 0$ V, the microspheres move downstream due to PDF (Fig. 4a). However, when V_D is increased to 2.0 V, and with the light still on, the microspheres accumulate over the Pt cathode (white box in Fig. 4b). This is different from experiments involving ions, where accumulation occurs to the left of the cathode, and it is a consequence of the lower electrophoretic mobility of the microspheres compared to ions like Cl^- .⁴⁸ Specifically, the lower mobility of the microspheres results in their accumulation in a region of higher electric field, which is just above the Pt cathode where the solution resistivity is expected to be highest. Note, however, that we believe the actual electric field profile is more complicated than the schematic representation in Scheme 2c, and simulations will be required to develop a deeper understanding of its exact shape.

When V_D is returned to 0 V, the accumulated microspheres are released and flow downstream (Fig. 4c) due to convection and collapse of the IDZ. This behavior is qualitatively consistent with the conductivity measurements (*i.e.*, Fig. 3c). Movie S1 in the ESI† provides the complete video from which the frames in Fig. 4 were extracted.

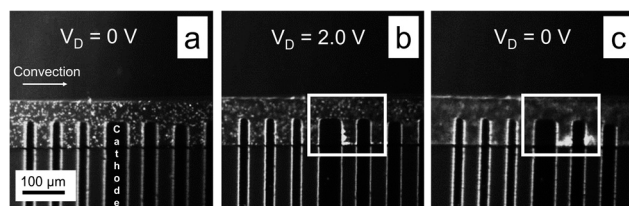


Fig. 4 Fluorescence micrographs showing accumulation of microspheres above the Pt cathode in the presence of an IDZ. For this experiment, 40 μL and 34 μL of 100 mM Tris buffer (pH 8.0) containing 0.027 w/v% carboxyl-functionalized microspheres were added to inlet and outlet reservoirs, respectively, to provide PDF. By measuring the velocity of the microspheres in the absence of an IDZ, the volumetric flow rate was determined to be 18.4 nL min^{-1} . During the experiment, the Hg arc lamp continuously illuminated the TiO_2 photoanode. The micrographs were obtained under the following conditions: (a) $V_D = 0$ V; (b) 13 s after the V_D was switched to 2.0 V; and (c) 1.0 s after the V_D was changed back to 0 V. Note that the images were obtained using an inverted microscope, so most of the fluorescent microspheres accumulated above the Pt cathode are not visible in frame b (white box). When the IDZ collapses (frame c), however, the released microspheres are clearly visible (white box). For this experiment, the 50 μm -wide Pt cathode extended only half-way into the microchannel to provide a visual representation of the effect of the IDZ (present only in the lower half of the channel). Movie S1 in the ESI† provides the complete video from which these frames were extracted.

Summary and conclusions

In this study, we showed that light energy can be used to manipulate the transport of ions, and we provided a framework for understanding the mechanism. Specifically, a photoanode drives formation of an IDZ, and hence a local electric field gradient, at a Pt cathode. This IDZ accumulates charged species, as shown in Movie S1,[†] in essence removing them from the downstream solution.

Looking to the future, the findings reported here represent an important step toward development of an energy efficient, membraneless ion separation system specifically for sea water desalination. We have previously used fICP for this purpose,¹⁷ thereby demonstrating the viability of the general methodology, but the use of photoelectrochemistry will minimize the amount of electrical energy per unit fresh water produced. Our approach for accomplishing this goal is to generate the IDZ by photooxidizing Cl^- , which of course is abundant in sea water. The key to successful implementation will be to find a suitable anode that selectively oxidizes Cl^- in the presence of water. Leading candidates are the types of dimensionally stable anodes widely used in chlor-alkali industry,^{49,50} which can be coupled to an appropriate photocathode. The results of these experiments will be reported in due course.

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