



Enhancement of nanofluidic ionic current via plasmon-mediated effect

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ABSTRACT

Localized surface plasmon resonance (LSPR) has been extensively used in various applications, but the comprehension of its role in plasmon-mediated photochemical and photothermal effects on ionic currents is still in its infancy. To improve the efficiency of optofluidic systems, it is imperative to investigate the ion transport behavior influenced by LSPR within electrolytes. In this study, we employ a 3D nanochannel network membrane (NCNM) integrated micro/nanofluidic device to elucidate the mechanisms underlying plasmon-mediated ionic current enhancement. By analyzing ionic currents generated by laser irradiation versus thermal heating, our results indicate that the photoelectrochemical effect, which increases the space charge density, plays a more significant role in ionic current enhancement than pure thermal effects. Furthermore, our investigation of various structural parameters shows that optimizing laser power absorption through the 3D NCNM is crucial for effective ionic current generation. This research represents a fundamental step in the understanding of plasmon-mediated ionic transport mechanisms and provides insights into efficient light-to-ionic transport conversion. These findings have potential for a wide range of applications, including photoinduced energy harvesting devices, ionic pumps and wavelength-selective nanochannels, such as fluidic rhodopsin systems.

1. Introduction

In recent years, the localized surface plasmon resonance (LSPR) using noble metal-based nanostructures have been widely used in various applications, including photocatalyst/solar cell-based energy harvesting and conversion [1,2], chemical and biological sensors [3], and enhanced spectroscopies such as Raman spectroscopy [4]. These significant applications are attributed to the unique properties of surface plasmons, which are collective oscillations of free electrons on the surface of a metal or at the boundary between a metal and a dielectric material when excited by incident light [5]. This oscillation, resulting from the interaction of free electrons in the metal with electromagnetic waves at the metal-dielectric boundary [6], leads to the formation of energetic charge carriers known as hot carriers [7]. The generation and injection of these charge carriers, and the subsequent increase in local temperature by the nonradiative decays of plasmons, induce photochemical effects, resulting in chemical reaction on the surface [8–10], and photothermal. These effects typically occur simultaneously in plasmon-mediated processes [11,12].

Recent studies have employed an electrochemical system based on

noble metal electrodes and modulation of incident light to characterize the plasmonic effect. The principle of this system involves adjusting the laser irradiation on the plasmonic structure and measuring the electric signals, which originate from electron transfer by direct laser irradiation and the heating of electrodes, respectively [13–15]. However, this system has difficulty in accounting for ionic composition change in the electrolyte and the resulting ionic transport within electrolytes. The electrochemical reactions induced by the plasmonic effect can influence the ionic composition at the liquid and solid interface (LSI), which results in the increase of the electric double layers (EDL) and subsequently affects the ionic transport around the nanostructured metal. Moreover, photothermal effect influences not only the electrochemical reaction, but also the ion diffusivity, further impacting transport characteristics. To analyze the changes in chemical property at the LSI owing to the plasmonic effect, the optical signal measurement via the change of refractive index was represented [16,17], but it is also hard to characterize the ion transport behavior induced by the plasmonic effect.

In this study, we present a novel nanofluidic platform to quantitatively characterize the ionic current enhancement induced by plasmonic effects through a 3D nanochannel network membrane (NCNM). The 3D

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plasmonic NCNM, formed by the evaporation-driven self-assembly of SiO_2 @Au core-shell nanoparticles enabling LSPR, provides nanochannel bundle, which allows for more collective and reliable measurement of the electrical signals generated by ion transport [18,19]. Through this, electrochemical changes induced by various stimuli applied to the membrane can be characterized and validated by measuring the ionic current. By comparing the ionic current generated by the plasmon with that by pure thermal stimuli at the same temperature range, the plasmon-mediated process can be quantitatively analyzed and the individual contribution to the net ionic transport can be decoupled. In addition, this study further analyzes the plasmonic effect by modulating the structural and photochemical conditions of the NCNM. Since understanding ionic currents enables the efficient application of micro-/nanofluidic systems, our results and methods offer significant potential for practical applications, including light-driven ionic current generation such as light-induced energy harvesting systems.

2. Experimental section

2.1. Fabrication of 3D NCNM-integrated micro-/nanofluidic device

The device was fabricated using the standard soft-lithography process. To fabricate a master mold, a Si wafer was spin-coated with negative photoresists SU-8 2002 and SU-8 2005 (Kayaku Advanced Materials, Inc., USA) and subsequently soft-baked to fabricate bridge channels with heights of 2 μm , 3.5 μm , and 5 μm . Then, photoresists were exposed to ultraviolet (UV) light using a mask aligner and the unexposed photoresists were removed by using the SU-8 developer, patterning bridge channels with the desired heights. Another photoresist SU-8 2050 (Kayaku Advanced Materials, Inc., USA) was spin-coated on the patterned mold to form 50 μm -height main channels. The patterning of main channels followed the same process used to fabricate bridge channels. The surface of the master mold was treated with trichloro (1H,1H,2H,2H-perfluorooctyl)silane (Sigma-Aldrich, USA). The poly (dimethylsiloxane) (PDMS; Sylgard 184, Dow Corning Korea Ltd., Korea) mortar with a mixing ratio of 10:1 with a curing agent (Sylgard 184 curing agent, Dow Corning Korea Ltd., Korea) was prepared, then placed in a vacuum jar for degassing for 30 min. The mortar was poured on a patterned, silane-treated mold and cured at 95 $^{\circ}\text{C}$ for 2 h, after which the cured PDMS was demolded. A microfluidic device was fabricated by bonding the PDMS with a slide glass that was treated with O_2 plasma (Cute-MP; Femto Science, Korea). The detailed fabrication process and photo of the device are shown in Figure S1.

SiO_2 @Au-based 3D NCNM was fabricated by the evaporation-assisted self-assembly of nanoparticles into the bridge channel. First, the suspension containing SiO_2 @Au core-shell nanoparticles of 150 nm diameter with carboxyl (-COOH) surface functionalization (GSXR150-5M, nanoComposix, USA) dispersed in 0.02 mM potassium carbonate was diluted with ethanol and then injected into the reservoir connected to main channels. The suspension was introduced into the bridge channel through capillary flow, but it did not pass through the interface of the bridge and the main channel on the other side owing to the surface tension-driven Laplace pressure. Specifically, the surface tension is higher in the bridge channel due to its smaller cross-sectional area compared to the main channel. As a result, the injected suspension does not cross the liquid-gas interface between the channels. Consequently, the solvent from the suspension was evaporated so the nanoparticles were drawn toward the interfaces. After the NCNM in the bridge channel was fully fabricated, the remaining suspension was completely removed from the main channels, and the device was dried for 2 days. The overall fabrication process and the optical image of NCNM are shown in Figure S2. All chemicals were purchased from Sigma-Aldrich unless otherwise specified.

2.2. Experimental setup for laser irradiation and thermal heating

The electrolytic solutions were prepared by dissolving potassium chloride (KCl) in distilled (DI) water. The electrolyte concentrations of 0.1, 1, and 10 mM were used. To measure and analyze the ionic current induced by the surface plasmon in the proposed nanofluidic device, a laser system was employed as shown in Figure S3. First, a 532 nm green laser system (CC30875, UNIONTECH, Korea) consisting of a laser power supply and a laser head was employed. A laser collimating lens was integrated through an optical fiber to ensure a spot size of 0.6 mm in diameter at a distance of 10 mm. The position of the collimating lens can be adjusted by the stages for precise alignment of the laser spot and the nanochannel. In addition, pipette tips containing electrolyte solutions were connected to each reservoir of the device. In a similar way, an 808 nm NIR laser system consisting of a diode mount (L808P500MM and LDM56/M, Thorlabs, Inc., USA) and a current controller (ITC4001, Thorlabs, Inc., USA) were employed. Laser intensity was adjusted using power meter interface (PM100USB, Thorlabs, Inc., USA).

A Peltier-based temperature control platform was utilized to modulate the temperature of the NCNM for measuring the ionic current induced by pure thermal stimulus. The platform comprises a copper (Cu) block and pin connected to the Peltier controller. The width of the Cu pin is 500 μm , which is identical to that of the bridge channel. The channel was aligned with the pin to accurately control the temperature of the NCNM (Figure S4).

2.3. Temperature measurement

The overall temperature of the NCNM induced by the plasmonic effect was determined by measuring the temperature of the NCNM under laser irradiation with certain structural and optical conditions, using thermal imaging IR camera (A325sc; FLIR Systems, Inc., USA). Figure S5 shows the overall temperature measurement results of the NCNM under various structural and optical conditions. The PDMS layer of the device was removed to directly access the NCNM. The temperature of the NCNM was measured for 2 min after laser irradiation. Note that the collimator was properly adjusted to avoid laser reflection, thereby excluding the excessive thermal effect on the area adjacent to the NCNM. Figure S4a shows the experimental setup using an IR camera, and the measured temperature of the copper (Cu) pin structure is shown in Figure S4b. Figure S4c illustrates the setup using a thermometer. For this setup, the NTC thermistor (GA10K3MCD1; TE Connectivity, USA) was placed between the glass substrate and the PDMS layer, emulating the NCNM-integrated nanofluidic device in a realistic manner. And then, the thermistor was carefully aligned with the Cu pin structure to accurately measure the target temperature. In the same manner, the temperature of the Cu pin structure was measured for 2 min after thermal heating. Figure S6 shows the operation cycles of the Peltier platform, with the measured temperature values shown in Figure S5.

2.4. Electric signal measurement

Sintered silver/silver chloride electrodes (Ag/AgCl; 541500; A-M Systems, LLC, USA) were used for the electric signal measurement. The electrodes were connected to a sourcemeter (Keithley 6487, Keithley 2635 A; Tektronix, Inc.) and dipped into the reservoirs of the device as illustrated in Fig. 1b. The potentiostatic method was employed to measure the current changes generated by plasmonic and pure thermal effects. The current values were determined by setting the applied voltage of the source meter to 1 V and measuring the resultant current. The current changes induced by each effect were separately measured by modulating the laser irradiation and thermal heating. External stimulations by using the laser system and the Peltier-based temperature control system were periodically turned on and off every 2 min for three cycles. The initial data measured over the first 5 min were discarded. Stimulations were consistently applied after 6 min and the data from 5 to

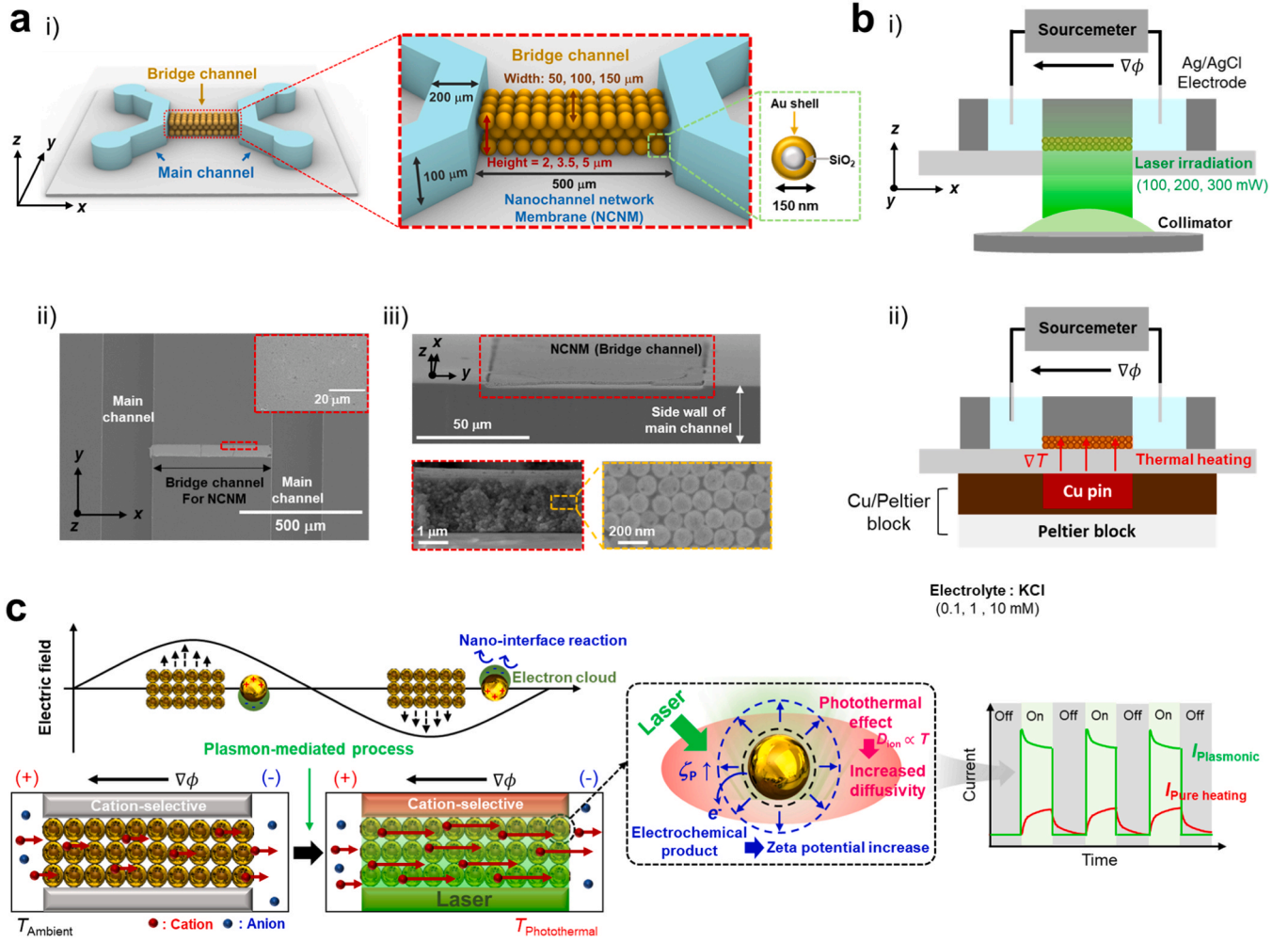


Fig. 1. Schematics and principle of the nanofluidic platform for quantitative analysis of plasmon-mediated process. (a) Fabrication of SiO₂@Au core-shell nanoparticle-based nanochannel networks and measurement system for plasmonic and pure thermal effect. SEM images show the cross-sectional view of the NCNM and its crystalline structure. (b) Operation method for laser irradiation and thermal heating for plasmonic and pure thermal effect, respectively. (c) Mechanism of ionic current generation and enhancement by plasmonic and pure thermal effect.

18 min were used to minimize experimental errors. The electrodes were immersed in the reservoirs for 10 min before measurements to further eliminate experimental errors.

2.5. Streaming current and potential measurements and calculation of zeta potential changes

The streaming current and potential were measured using the same experimental setup and NCNM-integrated devices except using a pressure pump to induce the fluid flow instead of applying voltages. The devices were connected to Ag/AgCl electrodes and the pressure pump through 1/16" perfluoroalkoxy tubes to completely pressurize the device. The pressure difference along the device was set to 65 kPa, which was basically applied between the two ends of the NCNM, and external stimulations of laser irradiation and thermal heating were applied as mentioned. The total current in the device in the absence of an applied voltage can be measured as the sum of conduction current (I_{Cond}) and streaming current (I_{PDF}) as follows [20]:

$$I_{\text{Total}} = I_{\text{Cond}} + I_{\text{PDF}} = \sigma \frac{\Delta\phi}{L} A - \frac{\varepsilon \zeta_w}{\eta} \frac{\Delta P}{L} A \quad (1)$$

where σ , ϕ , A , L , ε , ζ_w , η , and P are the molar conductivity of electrolyte, electric potential, cross-sectional area of the channel, length of the channel, permittivity, zeta potential of the wall, viscosity, and pressure,

respectively. The conduction current is equal in magnitude to the streaming current at steady state, which means I_{Total} is zero. The streaming potential (ϕ_{PDF}) can be calculated from Eq. (2) and the zeta potential can be calculated as follows:

$$I_{\text{Total}} = \sigma \frac{\Delta\phi}{L} A - \frac{\varepsilon \zeta_w}{\eta} \frac{\Delta P}{L} A = 0 \quad (2)$$

$$\phi_{\text{PDF}} = \Delta\phi = \frac{\varepsilon \zeta_w}{\eta \sigma} \Delta P \quad (3)$$

$$\zeta_w = \frac{\eta \sigma}{\varepsilon \Delta P} \phi_{\text{PDF}} \quad (4)$$

The change of the zeta potential can be calculated using the streaming potential change as derived in Eq. (4). In addition, the streaming potential change can be broken down as follows:

$$\Delta\zeta_w = \frac{\eta \sigma}{\varepsilon \Delta P} \Delta\phi_{\text{PDF}}, \quad \Delta\phi_{\text{PDF}} = \phi_{\text{PDF,On}} - \phi_{\text{PDF,Off}} \quad (5)$$

where $\phi_{\text{PDF,On}}$ and $\phi_{\text{PDF,Off}}$ are the streaming potential measured in the presence and absence of the external stimulations such as laser irradiation or thermal heating, respectively.

2.6. Characterization and data analysis

The inverted fluorescence microscope (IX71, Olympus Corporation, Japan) and scanning electron microscope (SEM; SU8220, Hitachi High-Tech Corporation, Japan) was used for the visualization of the device and NCNM. All images were processed using ImageJ (1.45 s; National Institutes of Health, USA). The zeta potentials (ζ_w) of SiO₂@Au nanoparticles for different electrolytic concentrations were measured using a Zetasizer Pro Blue (Malvern Panalytical Ltd., UK) (Table S1). All data were plotted using OriginPro 2020 software (ver. 9.7.0.185; OriginLab Corp., USA). Each experiment was repeated a minimum of three times to ensure reproducibility and consistency of the quantitative measurements.

2.7. Finite-difference time-domain simulation

Finite-difference time-domain (FDTD) simulations were carried out using software package Lumerical FDTD solutions for calculating the optical power absorption and electric fields in the NCNM. The structural model in FDTD (finite-difference time-domain) simulation was set as 2, 3.5, and 5 heights-FCC (faced-centered cubic) lattices consisting of the assembled Au nanospheres with 150 nm diameter as shown in schematics of Figure S7. The wavelength of the simulation was fixed to 532 nm, which is the same wavelength as the green laser used in the experiments. The light source adopted a total-field scattered-field (TFSF) source and was located at the same plane position from the bottom of FCC lattices for all cases. The boundary condition of x and y direction was set to periodic and z direction was set to a perfectly matched layer (PML) to calculate the absorption cross-section. The mesh size was set to be 2 nm $\times$ 2 nm $\times$ 2 nm.

The absorption per unit volume was calculated by the modified formula from the divergence of the Poynting vector for numerical stability and higher accuracy as follows [21]:

$$P_{abs} = -0.5\omega|\vec{E}|^2\text{Im}(\epsilon) \quad (6)$$

where ω , $\vec{E}$, and $\text{Im}(\epsilon)$ are the angular frequency, electric field, and imaginary part of the permittivity of Au, respectively. To calculate the absorption as a function of space and frequency, the required parameters are the electric field intensity and the imaginary part of the permittivity. Both quantities are easy to solve in FDTD simulations. In the FDTD simulations, each electric field component (E_x , E_y , E_z) can be calculated at different locations in the Yee cell grid. The total absorption is proportional to the electric field intensity, with higher absorption occurring when the electric field is concentrated. The simulated optical power absorption and electric field at the specific z -position described in Figure S7 are shown in Figures S8 and S9.

3. Results and discussion

3.1. Device concept and operation methods

Fig. 1 shows the schematic of the 3D NCNM-integrated micro-/nanofluidic device and the mechanism for the ionic current enhancement by the plasmon-mediated process and pure thermal effect. The structure of the device and SEM images of the fabricated NCNM is shown in Fig. 1a. The bridge channel which connects the two main channels is 500 μm long. The height and width of the bridge channel is changed between 2, 3.5, and 5 μm , and 50, 100, and 150 μm , respectively, for characterizing the effects of structural properties on plasmonic and pure thermal effect. The standard height and width of the NCNM are 2 μm and 150 μm , respectively. The corresponding SEM image shows that the NCNM was completely fabricated within the bridge channel. It can be observed from the cross-sectional view of the NCNM that the nanoparticles are arranged in face-centered cubic (FCC) structure, with pores acting as nanochannels. To measure each contribution from the

plasmonic and pure thermal effects, the proposed platform is applied to laser irradiation and Peltier-based temperature control as shown in Fig. 1b. Experimental setup for laser irradiation (532 and 808 nm wavelength) to measure the plasmonic effect on the devices is described in Figure S3. For measuring the pure thermal effect, the same temperature induced by the laser irradiation was applied to the platform using a Peltier-based temperature control device (TCD), which is precisely validated and calibrated by an IR camera and the TCD, as shown in Figures S4 and S5. Electric signals generated by both laser irradiation and thermal heating demonstrated high reproducibility (Figure S10), while the operation cycles of the Peltier platform validated stable temperature control under experimental conditions as shown in Figure S6.

Fig. 1c illustrates the mechanism for the ionic current enhancement by the plasmon-mediated process and pure thermal effect in the NCNM. Upon laser irradiation, surface plasmons are generated, initiating an electrochemical reaction on the surface of the NCNM [22]. This reaction produces electrochemical products, such as negatively ionized oxygen (O₂) [23,24], which increase the concentration of anions near the surface, thereby changing the ion distribution within the NCNM. This change, the increase of negative charge distribution, in turn increases the magnitude of effective ζ_w , and the cation transport through the NCNM increases to maintain electroneutrality, leading to an elevated ionic current. Simultaneously, the increase in the local surface temperature of the NCNM enhances not only the electrochemical reaction rate [25], but also ion diffusivity, thereby further increasing ionic transport.

It is essential to characterize the structural properties and EDL of the NCNM in relation to nanoscopic ion transport. The pore size (d_p) of the NCNM can be estimated to be about 15 % of the nanoparticle diameter used, which is approximately 22.5 nm [26]. Meanwhile, the Debye length (λ_D) ranges from approximately 3.07 to 30.7 nm at potassium chloride (KCl) concentrations of 0.1–10 mM. Comparing the values of d_p and $2\lambda_D$, the $2\lambda_D$ at the standard concentration of 1 mM KCl, which is 19.4 nm, is similar to d_p (i.e., $2\lambda_D/d_p \sim 0.86$). Hence, the NCNM exhibits cation selectivity owing to its negative ζ_w and comparable λ_D to d_p (i.e., $2\lambda_D/d_p \sim 1$) [18]. As the NCNM is fabricated using SiO₂@Au core-shell carboxylated nanoparticles, the total ionic current induced by the plasmonic effect can thus be measured as the sum of the current generated by selective cation transport, which is affected by the electrochemical reaction and local heating that induce the change of ionic charge density and increase of ion diffusivity. In other words, the ionic current resulting from the electrochemical reaction occurring on the NCNM surface, along with the subsequent change in ionic distribution and effective ζ_w , can be characterized by comparing the current generated solely by the pure thermal stimulus from the overall current induced by the plasmon-mediated process in the NCNM.

3.2. Validation for dominant effects and its mechanism of plasmon-mediated ionic current enhancement

Fig. 2a–d present the electric signal measurements, including changes in current, voltage, and effective ζ_w of the NCNM in response to the plasmonic and pure thermal control modes. The streaming current and voltage measurement were used to quantitatively characterize the ionic transport of the NCNM without applying an external electric field. The detailed methods and process for measuring electric signals and calculating effective ζ_w changes from the measured streaming potential values are described in Experimental Section. An increase in current and voltage indicates enhanced net ion transport and ion selectivity. Considering the cation selectivity of the NCNM and the absence of an external electric field, the changes in electric signals in Fig. 2a and b reflect the amount of selective cation transport and cation selectivity according to control modes, respectively. The changes induced by the plasmonic control mode are significantly higher than those induced by the pure thermal mode. Specifically, the average current change and voltage change in the plasmonic mode are approximately 0.7 times and 6.7 times larger than in the pure thermal mode, respectively.

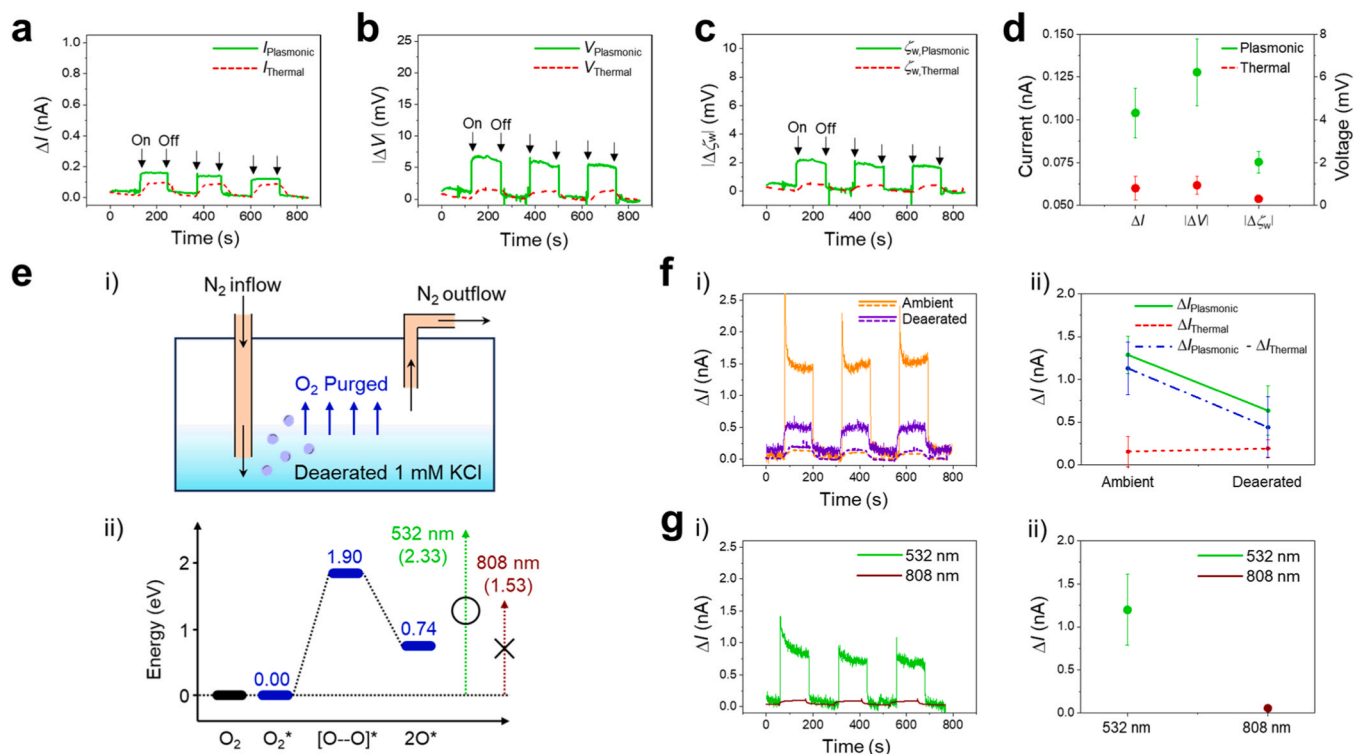


Fig. 2. Experimental validation for dominant effects and its mechanism of plasmon-mediated process. a)–d) Measurement results of current, voltage, and effective zeta potential (ζ_w) changes in plasmonic and pure thermal mode. e) N_2 deaeration process and energetic profile for the O_2 dissociation under 532 nm and 808 nm lasers. f) Current measurement results in plasmonic and pure thermal control mode on the nitrogen deaeration of the KCl electrolyte g) Current measurement results using lasers with wavelengths of 532 nm and 808 nm. Average values along with their error bars, were derived from data obtained from a minimum of three devices (# of devices = 3).

It is noteworthy that the voltage change in the plasmonic control mode is much higher compared to that in the pure thermal control mode, indicating a larger effective ζ_w change. The change in effective ζ_w calculated through voltage changes induced by the plasmonic and pure thermal effects are 2.03 mV and 0.30 mV, respectively, indicating that the effective ζ_w change from the plasmonic effect is about 6.7 times greater than that caused by the pure thermal effect (Fig. 2c). This suggests that the electrochemical change at the NCNM surface and the subsequent increase of effective ζ_w have a more dominant effect on the overall electric signal change than the ion diffusivity change. In addition, this indicates that the plasmon-mediated electrochemical reaction at the NCNM surface, along with the resulting effective ζ_w change, is the primary factor contributing to the increased ion selectivity of the membrane. In contrast, for the pure thermal control mode, the changes are relatively low. This is because the increase in ion transport flux by the elevated temperature is the dominant mechanism, whereas the change in ion selectivity caused by the altered λ_D at the elevated temperature is relatively marginal. These results demonstrate that plasmon-mediated process leads the improved cation-selective transport through electrochemical changes at the surface, eventually enhancing mass transport as illustrated in Fig. 1c.

To further investigate the influence of ζ_w , ionic current changes were measured using KCl electrolytes with different pH levels. Electrolytes at pH 3, 7, and 11 were prepared using hydrogen chloride and sodium hydroxide. The corresponding current changes are presented in Figure S11. As shown, decreasing the pH results in a reduced ionic current change, while increasing the pH enhances it. This is primarily attributed to the influence of pH on the ζ_w of the NCNM (Table S2) [27]. Although the electrolyte with pH 3 contains a higher concentration of hydrogen ions compared to the electrolyte with pH 7, the reduced ζ_w under acidic conditions likely contributes to the slight decrease in current. Similarly, the current change with the electrolyte at pH 11 is higher

than that at 7, owing to the increased ζ_w and hydroxide ions.

To further investigate the plasmon-mediated ionic current enhancement, additional experiments were conducted. Fig. 2e illustrates the concept diagram for N_2 -based deaeration of the electrolyte and energetic profile for the O_2 dissociation under 532 nm and 808 nm lasers [28]. Fig. 2f shows the current generated by plasmonic and pure thermal effects depending on nitrogen deaeration in the KCl electrolyte. According to previous studies on the kinetics at the surface of noble metals, dissolved oxygen in the electrolyte is activated by surface plasmons [11]. Through plasmon-mediated electron transfer induced by laser irradiation, species including oxygen anions (O_2^-) are generated from triplet oxygen ($^3\text{O}_2$) in the electrolyte [29,30]. Specifically, energetic electrons generated from the plasmonic structure are injected to the $2\pi^*$ antibonding orbital of oxygen molecules, which are adsorbed on the metal surface, resulting in electron-assisted O_2 dissociation and the formation of chemical species such as oxygen radicals [24,31–34]. Based on the plasmonic NCNM structure, the generated anionic species, such as O_2^- ions, affects to the overall anion distribution at the NCNM surface. The resulting change in the ion distribution increases the space charge density, which is reflected in the enhanced magnitude of the effective ζ_w of the NCNM.

The concentration of dissolved oxygen in the electrolyte decreases as deaeration is applied, which in turn suppresses the oxygen-related electrochemical reactions induced by surface plasmons [35]. To validate the reduction in dissolved oxygen concentration via N_2 deaeration, a direct comparison was conducted between the concentrations in ambient and deaerated electrolytes. N_2 deaeration was applied for 1 hour, and Figure S12 presents the measurement results obtained using a dissolved oxygen meter. The results showed that the concentration of dissolved oxygen in the deaerated electrolyte was 1.8 mg/L, compared to 6.6 mg/L in the ambient electrolyte, indicating that about 73 % of the dissolved oxygen was removed through deaeration.

Under laser irradiation, the current generated from the deaerated electrolyte decreased dramatically compared to that from the untreated electrolyte. When comparing the plasmonic and pure thermal effect-induced ionic currents under identical conditions, the plasmonic-based current decreases to the comparable level of the pure thermal-based current after deaeration. Specifically, the plasmonic effect-driven ionic current decreased by approximately 61 % after N_2 deaeration, which closely corresponds to the reduction in dissolved oxygen concentration, as shown in Fig. 2f. These results strongly support that the dominant change of ionic current is due to the plasmon-mediated electrochemical reaction. In contrast, the ionic current driven by the pure thermal effect remains essentially constant regardless of deaeration, further reinforcing our conclusion. This constancy arises because the changes under pure thermal stimulation are primarily attributed to variations in the diffusivity behavior of ions.

The photochemical effects on the ionic current were further examined using laser irradiation with different wavelengths. Fig. 2g shows the current generated by laser irradiation as a function of wavelength. The current generated by the 532 nm wavelength laser exhibited a higher change compared to the current generated by the 808 nm wavelength laser. This is mainly attributed to the energy barrier of $Au-O_2$ on the surface, which is approximately 1.9 eV [34]. While 532 nm and 808 nm wavelength laser have energies of 2.33 eV and 1.53 eV, respectively, the 532 nm wavelength laser enables the hot electrons to be injected into O_2 , resulting in O_2 dissociation on the surface, whereas the 808 nm wavelength laser does not [13]. Additionally, Figure S13 illustrates the current change under laser irradiation for a device to

assess the feasibility of plasmonic reactions occurring at the Ag/AgCl electrodes. The result confirmed that there is no photocurrent at the electrodes by laser irradiation. It is worth noting that additional species may be generated on the gold surface from the electrolyte, potentially affecting the ionic current. When electrolytes are exposed to ambient air, carbon dioxide-derived species, including bicarbonate and carbonate, can be formed and should be considered. These species are known to act as proton sources in the hydrogen evolution reaction on gold surfaces [36,37]. However, the resulting ionic products from such reactions are mainly anionic species, such as hydroxide ions, which can contribute to the overall ionic current and influence ion transport and surface charge as additional anionic species [38].

To explore the current difference within a narrow temperature range, current measurements were conducted under selected temperatures in the presence of the pure thermal effect, as shown in Figure S14. The results show that the current changes from 0.15 nA to 0.19 nA with a 2 °C temperature increase, demonstrating that the pure thermal effect-based ionic current does not show a drastic increase within a small temperature deviation under the same structural conditions of the NCNM, especially considering the inherently low value of the pure thermal-induced current. In contrast, the current changes from 0.31 nA to 1.20 nA under laser irradiation within a similar temperature range (Fig. 3j and S5d). On the other hand, this shows that the increase in ionic current cannot be explained by the increased temperature solely, suggesting that the plasmonic effect plays a dominant role in the ionic current change. The ionic current changes were characterized within a broader temperature range to further assess the influence of pure

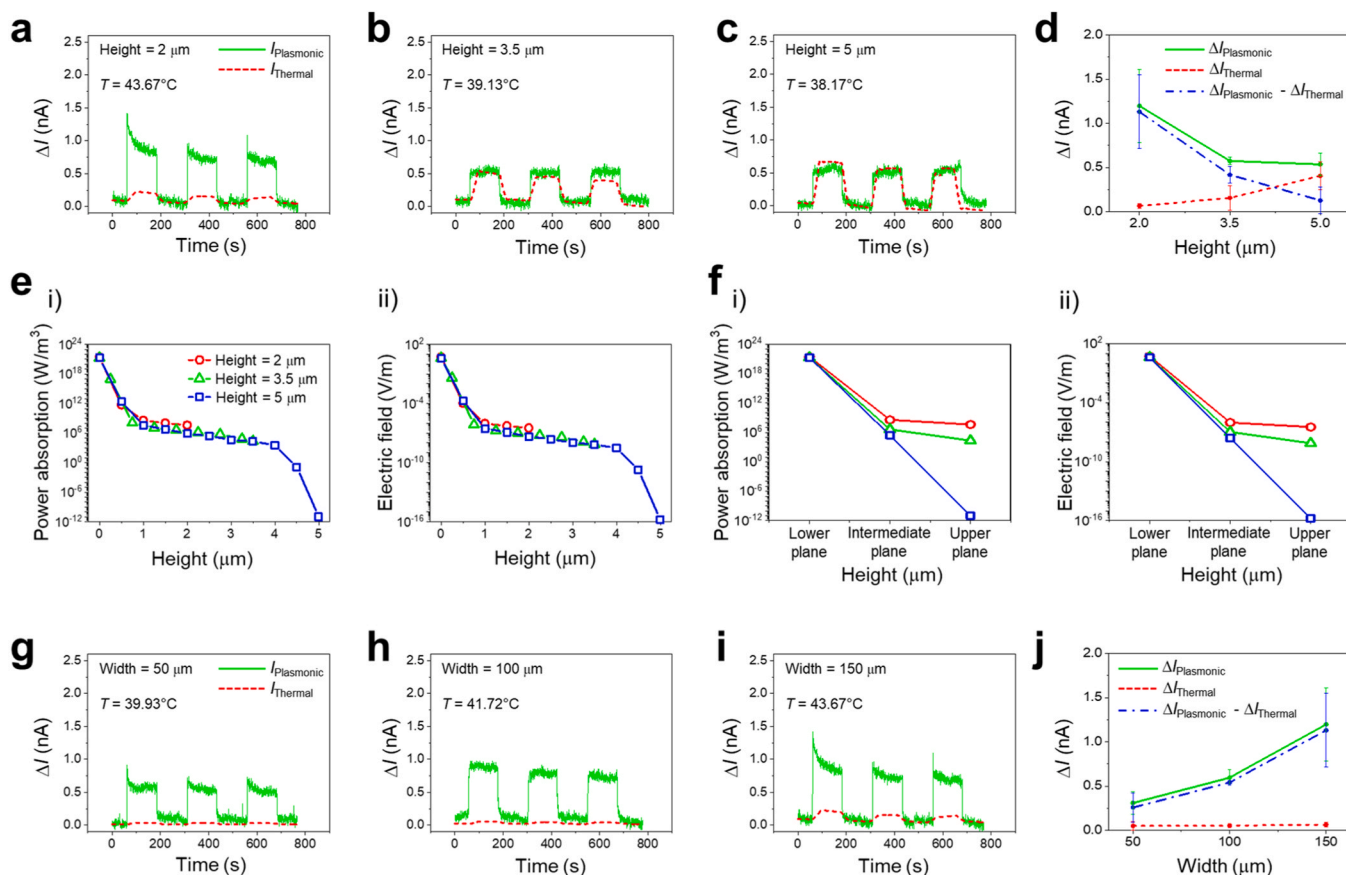


Fig. 3. Structural analysis on plasmon-mediated process in the proposed platform a)–d) Current measurement results and average values under varied height of the structure. Average values, along with their error bars, were derived from data obtained from a minimum of three devices (# of devices = 3). e) FDTD simulation results of maximum power absorption and electric field intensity under varied height of the structure. f) FDTD simulation results of maximum power absorption and electric field intensity on designated planes of the structure at different heights. g)–j) Results and average values under varied width of the structure. Average values, along with their error bars, were derived from data obtained from a minimum of three devices (# of devices = 3). The standard height and width of the NCNM are 2 μm and 150 μm , respectively, with a laser intensity of 300 mW and 1 mM KCl.

thermal effects. As shown in Figure S15, the current change exhibits a generally proportional increase with temperature, achieving an average value of approximately 0.4 nA at 60 °C. In comparison, the plasmon-mediated effect induces a larger current change of approximately 1 nA under standard structural conditions, where the bridge channel has a height of 2 μm and a width of 150 μm . These results indicate that the plasmon-mediated process plays a more dominant contributor to the current change relative to the pure thermal effect.

3.3. Analysis of plasmon-mediated ionic current through various structural properties

Fig. 3a–d show the current for different structure heights and the overall trend of their average values. The ionic current generated by the plasmonic effect is greater than that generated by the pure thermal effect at the lower height, indicating that the plasmonic effect is dominant. However, interestingly, the plasmon-mediated current decreases from an average of 1.13 nA to 0.13 nA, while the pure thermal-mediated current increases from an average of 0.07 nA to 0.41 nA as the height increases. This is because the reduced laser transmittance with increasing height, which inhibits the generation of plasmon-mediated current at the region of low laser transmission because the NCNM consists of close-packed 3D nanoparticles, which induces high absorption and scattering [39]. This can lead the limitation of generation of hot electron and increase of temperature by laser irradiation in NCNM with greater height, since the light absorption and scattering mostly occur at a low height (the laser radiates upward from the bottom) [39,40]. Conversely, the amount of ion transport driven by pure thermal stimuli increases as the cross-sectional area of the nanochannels increases, suggesting that changes in the cross-sectional area have a major influence on the ionic current driven by the pure thermal effect, comparable to the change of ionic diffusivity in the NCNM.

Finite-difference time-domain (FDTD) simulations were conducted to analyze the effect of laser transmittance and power absorption in the NCNM at different heights. Figure S7 shows the overall schematic and modeling setup for the FDTD simulation. To match the experimental conditions, calculations were performed using structural models with heights of 2, 3.5, and 5 μm . Fig. 3e presents the calculation results of the maximum power absorption and electric field intensity at different heights, respectively. First, the maximum power absorption of all structures decreases and levels off at around 1 MW/m^3 near a height of 1 μm . The effect of the plasmonic-mediated process can be also explained through the maximum electric field intensity, which significantly decreases and levels off around 0.1 $\mu\text{V}/\text{m}$ near 1 μm height. Additionally, both the maximum power absorption and electric field intensity sharply decrease when the height exceeds 4 μm . This trend is clearly shown in Fig. 3f presenting the calculation results of maximum power absorption and electric field at designated planes. At the intermediate plane, the maximum power absorption is approximately 70, 4, and 0.22 MW/m^3 , while the electric field intensity is about 0.44, 0.14, and 0.02 $\mu\text{V}/\text{m}$ for the models with the heights of 2, 3.5, and 5 μm , respectively. These declines support the reduced laser transmittance at the higher region of the NCNM. That is, this change is even more pronounced at the upper plane. For example, the 2- μm -high structure exhibits approximately 300 times higher power absorption, and 17 times higher electric field intensity compared to the 3.5- μm -high structure, while the values for the 5- μm -high structure are nearly zero. Overall, the reduction in laser transmittance with increasing height results in more ineffective regions for the plasmon-mediated process in the NCNM structure. In other words, greater NCNM thickness hinders ionic transport driven by plasmon-induced charge density changes, eventually decreasing the net ionic current generated. Figures S8 and S9 show 2D plots of the maximum power absorption and electric field intensity at the planes corresponding to Fig. 3f, respectively.

Fig. 3g–i show the current for different widths of the structure. It is evident that the current increases as the width increases, owing to the

larger contact area exposed to the stimulations. The overall trend of ionic currents and their average values are presented in Fig. 3j, demonstrating that both the plasmonic and the pure thermal effect-induced currents increase from 0.26 nA to 1.13 nA and from 0.05 nA to 0.07 nA, respectively.

3.4. Analysis of plasmon-mediated ionic current through various photochemical conditions

Fig. 4a–c show the current for different laser intensities. The current increases with higher laser intensity because of the enhanced absorbed optical power within the structure. Fig. 4d presents the overall trend of ionic currents and their average values, showing that both the photochemical and the thermal effect-induced currents increase from 0.35 nA to 1.13 nA and from 0.05 nA to 0.07 nA, respectively. Both the plasmonic and the pure thermal effects a linear relationship with laser intensity and temperature, respectively [33]. Fig. 4e–g show the current for different electrolytic concentrations. The ionic current increases with the increase of electrolytic concentration, which can be attributed to the rise in K^+ ion concentration. However, the increase in ionic current is not directly proportional to the increase of electrolytic concentration, attributed to the reduced EDL effect within the pores as the ionic concentration increases, leading to a decrease in the ion selectivity of the NCNM. Fig. 4h presents the overall trend of ionic currents and their average values, indicating that the currents induced by the photochemical and thermal effects increase from 0.36 nA to 1.62 nA and 0.08 nA to 0.24 nA, respectively. Figure S16 shows the changes of ionic current with varying applied voltage. In both cases, the ionic current increases as the potential amplitude increases, which can be attributed to the enhanced formation of surface plasmons and the increased electroosmotic current [41,42].

As seen in the overall results, the current based on the plasmonic effect rises rapidly at the beginning of stimulation, while the current based on the pure thermal effect increases gradually. This is because the pure thermal effect-based ionic current is directly influenced by the temperature increase and thus changes according to Peltier control. In contrast, under standard height and width of 2 μm and 150 μm , respectively, the plasmonic effect-based current is primarily driven by the photochemical and photothermal effect, leading to a rapid initial change in current by the electrochemical reactions. The subsequent changes in the plasmonic effect-based ionic current after the initial response appear to be induced by the combined effects of the ζ_w change, additional reactions involving electrochemical species, and fast temperature increase. Moreover, spike-like current changes can be observed at the moment of signal switching in the plasmonic effect-based current change, which can be attributed to induced photovoltage [15]. Additionally, repeated laser irradiation may lead to partial surface saturation and reduced photochemical activity due to the accumulation of photoelectrochemical products near the surface, thereby reducing the spike-like change of current [43].

In addition to the discussed properties, factors such as particle size and gold shell thickness may also be considered. Larger particles shift the absorption and LSPR peaks toward longer wavelengths [44,45], and increase the pore size of the NCNM, which diminishes EDL effects and ion selectivity [18]. These changes can reduce plasmonic ionic current enhancement. Conversely, smaller particles and thicker gold shells tend to shift the LSPR peak toward shorter wavelengths, which may also diminish current enhancement [46].

The error in measuring the overall temperature changes of the NCNM caused by laser irradiation, used to obtain the temperature value for the pure thermal effect, may occur when using an IR camera. However, as the ionic current changes due to the pure thermal effect are significantly lower compared to those based on the plasmonic effect (Figure S14), this study still demonstrates that the plasmonic effect is dominant in terms of ionic current [47]. Additionally, we minimized potential errors by calibrating the temperature measurements obtained from the Peltier-based

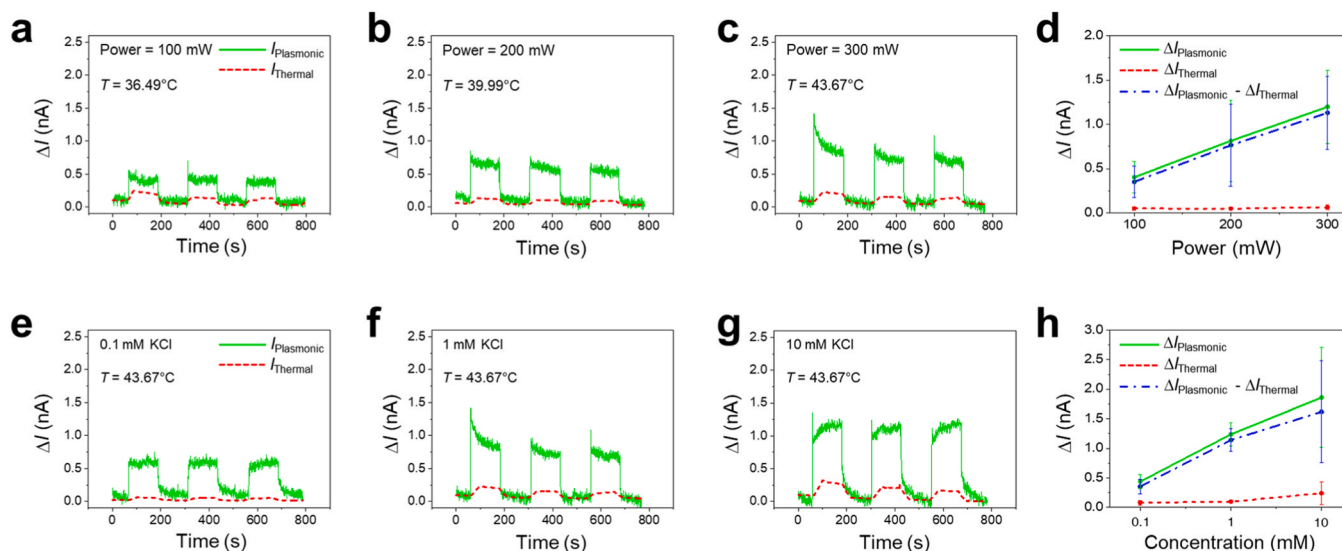


Fig. 4. Ionic current measurement results under various photochemical conditions. a)–d) Results and average values under varied laser intensity. e)–h) Results and average values under varied KCl concentration. Average values, along with their error bars, were derived from data obtained from a minimum of three devices (# of devices = 3). The standard height and width of the NCNM are 2 μm and 150 μm , respectively.

TCD and the IR camera (Figure S4).

4. Conclusion

In this study, we developed a plasmonic NCNM-integrated micro-/nanofluidic device to characterize ionic current enhancement induced by the plasmon-mediated process occurring on the NCNM surface. Our analysis confirmed that the change of space charge density, the increase of effective ζ_w , by the plasmon-mediated process is significant. Deaeration of the electrolyte and laser irradiation with different wavelengths further proved that plasmonic electrochemical reactions play a major role in the ionic current changes. An increase in the width of the NCNM boosts both the contact area with the laser and the cross-sectional area, leading to an increase in both plasmonic and pure thermal effect-based currents. In contrast, changing the height of the NCNM shows opposite trends; increasing the height reduces the plasmonic effect, while the pure thermal effect current increases due to the reduced laser transmittance in 3D lattice structures. Increasing the laser intensity leads to a linear increase in both plasmonic and pure thermal effects, attributed to formation of surface plasmon and an enhanced ionic diffusivity, respectively. While increasing ion concentration enhances ionic current, a linear relation was not observed unlike structural and optical changes. To the best of our knowledge, this study represents the first attempt to investigate the plasmon-mediated process using an ionic current-based measurement method in electrolytes. Furthermore, the direct and efficient conversion of light into ionic transport, facilitated by the plasmonic effect within the nanofluidic system, highlights the versatile potential of the proposed platform. Applications include the development of high-power, photo-induced energy harvesting devices and ionic pumps, as well as the design of wavelength-selective micro-/nanochannels such as fluidics-based rhodopsin by controlling the material and size of the metal nanostructures.

CRediT authorship contribution statement

Seo Dongwoo: Writing – original draft, Validation, Data curation. **Kim Taesung:** Writing – review & editing, Supervision, Project administration, Funding acquisition, Data curation. **Park Jungyul:** Writing – review & editing, Supervision, Funding acquisition, Conceptualization. **Park Gyubin:** Writing – original draft, Software, Data curation. **Kim Jaehyun:** Data curation, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.snb.2025.137957.

Data availability

Data will be made available on request.

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