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Programmable Multiple Plasmonic Resonances of Nanoparticle Superlattice for Enhancing Photoelectrochemical Activity

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Building nanoparticle (NP) superlattices formed in a complex fashion by subsets that can be explored separately presents a promising approach to realize the next generation of superlattices for different applications. Here, by incorporating self-aligned and geometrically different subsets of Au NPs into one matrix with the assistance of multi-pore anodic alumina oxide templates, scaled-up NP superlattices are constructed with programmable multiple plasmonic resonances. The inter-peak spectral distance is tailored in a broad wavelength range from less than 50 nm up to about 1000 nm through altering not only the size and height of each subset, but also the number and nature of the NP subset. Importantly, a mechanical oscillator model is developed to elucidate the microscopic origin of the spectral programmability and to reproduce the parameter dependence of the multiple plasmonic resonances. A photoelectrochemical cell using Au NP superlattice embedded photoanodes is investigated as a proof-of-concept, demonstrating a high photoresponse improvement of about 260% compared to that of bare film reference. In light of the compatibility of this technique with other plasmonic materials and the geometrical tunability, these findings enable systematic optical controlling toward optical devices with multimodal plasmonics.

1. Introduction

2D metal nanoparticle (NP) arrays show characteristic responses to visible and near-infrared electromagnetic waves via collective electron oscillations, so-called localized surface plasmon resonances. This opens up new routes for manipulating light at nanoscale and controlling the flow of light in a plane.[1–3] So far, arrayed NPs have been investigated intensively with the assistance of various top-down and bottom-up techniques, giving rise to inherent narrow-band plasmonic resonance.[4,5] Although such plasmonic resonance could be spectrally controlled by tailoring the NP geometry to match different requirements of active bands, programmable plasmonic operations at broad regions or multiple discrete wavelengths are still challenging. A programmable plasmonic operation shall foster a wide range of applications such as broadband photodetectors,[6,7] solar energy harvesting systems,[8–10] multi-modal lasing,[11] second harmonic generation with dual plasmonic resonances,[12,13] etc. To address this issue, great efforts have been made to explore anisotropic NPs such as nanorods with different aspect ratios[14,15] or back-folding into the first surface Brillouin zone.[16] However, the resulting multiple resonance modes over broad bands are either highly polarization-dependent or intrinsically not independent from each other. On the other hand, plasmonic superlattices that combine multiple subsets of NPs in one matrix potentially provide an alternative route, which is followed in this work.

Considering the structural complexity of multi-component systems, it is necessary to build a family of NP superlattices...
in a continuously geometry-tunable fashion, so that each subset can be systematically investigated to understand their individual geometrical features. The practical realization and utilization of such plasmonic superlattice requires a high level of simultaneous controlling for both the NP geometries and their relative positioning as well as large-scale low-cost productivity. For example, electron beam lithography is capable of precisely positioning multi-set NPs and tailoring NP size individually, but it is difficult to control the height of each-set NP independently over a large area, considering the challenging alignment of the different write-steps.\[17,18\]

As another example, self-assembly approaches are able to integrate diverse NPs into targeting devices by multiple step operation.\[19,20\] However, positioning and orienting a large amount of different NPs with nanometer precision in a reproducive way still remains a crucial roadblock.\[21,22\] Moreover, from the perspective of complex electromagnetic interactions within a superlattice configuration that originates from the near-field coupling among neighboring NPs,\[23,24\] effective modeling for better understanding and predicitng plasmonic resonance is also needed on the basis of previous works.\[25\] Therefore, it is imperative to develop an effective fabrication-and-analysis platform both for in-depth fundamental research and for future practical application of plasmonic NP superlattices.

In this work, we developed a template-assistant top-down method to construct a library of Au-NP superlattices and provided a quantitative investigation over the optical influence of each subset by combining numerical simulation and oscillator model. Aided by multi-pore anodic aluminum oxide (AAO) templates characterized by independent geometrical controllability for each subset of pores and self-alignment of different subsets, highly ordered NP superlattices were realized over centimeter scales. Accordingly, multiple plasmonic resonances with polarization independence were obtained where different modes are shiftable simultaneously or independently, leading to spectral programmability in a broad range. Then, a mechanical oscillator model was developed to reproduce multiple plasmonic resonances and hence elucidated the microscopic origins of optical programmability in conjunction with Finite-difference time-domain (FDTD) simulations. Finally, the advantages of these Au NP superlattices were unveiled by embedment into CdS-film photoelectrochemical (PEC) anodes, which demonstrated high resonance-mode dependence of about 260% improvement in photocurrent density.

2. Results and Discussion

2.1. Optical Response of Two-Subset NP Superlattices

The realization of Au NP superlattices started from an AAO template consisting of typically two subsets of pores, denoted as square A and circular B pores in Figure 1a. First, an array of nanodents was patterned on the surface of an Al-foil by mechanical deformation assisted by a Ni stamp (Figure S1, Supporting Information), which guided the evolution of square A pores and accordingly defined their sites.\[26,27\] Under the electric-field assisted self-alignment effect during anodization,\[28\] the circular B pores are automatically situated at the fourfold junction sites of the square A pores, which is in favor of relative positioning between A and B pores with nanometer resolution over centimeter scales. It is noteworthy that two subsets of pores were sequentially opened due to the presence of two barriers which blocked dual pores on the opposite sides, enabling independent size tunability for the two subsets of pores, as illustrated in Figure S1, Supporting Information. Scanning electron microscope (SEM) images in Figure 1b show that the resulting cubes and cylinders were symmetrically interlaced according to the spatial configuration of the square A and circular B pores. As expected, the as-replicated NPs inherited the geometrical features of the corresponding pore counterparts. By virtue of the self-alignment and independently geometrical tunability regarding the two subsets of pores, the as-fabricated NP superlattice gained a reliable structural uniformity over a large area (Figure 1c), as further supported by the unique color arising from diffraction effect in the periodic pattern that spans over the whole sample area (Figure 1d).

The optical response of NP arrays was characterized by light absorbance spectra measured with UV-Vis spectroscope, where dual absorbance peaks at about 650 nm and 800 nm were observed for the NP superlattice (Figure 1e). In contrast, only one dominant absorbance peak at around 700 nm or 740 nm was found for the single-set cubes or the single-set cylinders, respectively (see b1 and b2 in Figure 1b). FDTD-simulated absorbance spectra show a good coincidence with the experimental results, especially two main peaks for the NP superlattice. To elicit the cause of the dual peaks for the NP superlattice, 2D electrical field maps at the peak wavelengths were calculated, as summarized in Figure 1f. Stronger electric field enhancements were observed in the vicinity of cubes at 650 nm and cylinders at 800 nm. In particular, the electric field profiles around the cubes and the cylinders are similar to those of the single-set counterparts at the peak wavelengths (Figure S2, Supporting Information), implying that the absorbance peaks at 650 nm and 800 nm may originate predominantly from the plasmonic resonance excited in the cubes and cylinders, respectively. The simulations also suggest that the maximum electric field enhancement magnitude (about 1.8, logarithmic scale) around Au cubes at 650 nm is larger than that (about 1.3, logarithmic scale) around Au cylinders at 800 nm, which is in good accordance with the experimental and theoretical absorbance values at the short-wavelength peak in Figure 1e. Note that strong electric fields induced by the cubes and cylinders are overlapping within the interstitial spaces at both peak wavelengths, which accounts for the spectral shift of both absorbance peaks after putting cubes and cylinders together as compared with that of the original single sets.\[29,30\] To explore the polarization dependence of the optical response regarding the Au NP superlattice, a series of simulations were performed by increasing the polarization-angle from 0° to 90° (Figure 1g). Minimal variation with the polarization angle was observed due to the symmetric arrangement of NPs, indicating that Au NP superlattices can serve as polarization-independent dual-mode plasmonic oscillators at normal incidence.
2.2. Spectral Programming of Two-Subset NP Superlattices

To broaden the technical impact of NP superlattices in various applications, the optical response in terms of resonance wavelength was modulated for NP superlattices by altering the NP size. By virtue of the aforementioned geometrical controllability for the two subsets of pores in AAO templates, the pores as well as the replicated NP equivalents were precisely tailored in size. Figure 2a illustrates the absorbance spectra of Au NP superlattices with different size combinations. For simplicity, we only changed the size (namely, diameter) of the cylinders while fixing the size (namely, length of edge) of the cubes in the NP superlattice. Obviously, decreasing the cylinder size from 240 to 190 nm (samples I→II) resulted in a blue shift for the cylinder-dominated long-wavelength peak. When the Au cylinders were downsized to about 140 nm (samples II→III), two peaks were merged into one at about 670 nm. With further reduced cylinder size (samples III→IV), two peaks were observed at shorter wavelengths again. The experimental absorbance spectra are well reproduced by the FDTD-simulated spectra (Figure 2b), confirming the high reliability for the plasmonic dual-peak response of NP superlattices enabled by this technique. In addition to the peak shift from about 800 to 600 nm supported by the cylinders, the cube-dominated peaks were shifted simultaneously from 660 to 710 nm although the cube size always remained the same. This phenomenon might stem from the above-mentioned near-field coupling between neighboring different-set NPs. Therefore, programmability of plasmonic dual-peak resonance can be expected with a further change of the cube size.

To provide more spectral controlling over NP superlattices, the NP-height dependency of the optical response
was also investigated. Different from other well-established
techniques, the heights of two subsets of NPs in the super-
lattice can be independently adjusted with a combination
of a sequential pore opening of AAO templates and a two-
step physical vapor deposition (PVD) process (Figure 3a).
Four Au-NP superlattices with identical geometries but dif-
terent cube-heights were fabricated as a demonstration
of this “design knob”. The cylinder height was fixed to be
100 nm, while the cube height was decreased step by step
(cf. Figure S3, Supporting Information, and Figure 3a). It
was found that the long-wavelength peaks originating from
Au cubes exhibited an obvious red shift from about 750 to
940 nm as the height decreased from 100 to 15 nm (dashed
green arrows in Figure 3b), while the peaks originating from
the cylinders barely shifted (dashed blue line in Figure 3b).
Consequently, the spectral distance between the two main
peaks was broadened from about 110 to 300 nm. Both the
peak position and the peak-shift tendency with the cube-height
reduction were also supported by the numerical simulations
(Figure 3c). Systematic simulations were further conducted
to explore the spectrally tunable possibility, showing that the
inter-peak spectral distance could be broadened to over
1000 nm by, for example, further decreasing the cube height,
increasing the cube size, and/or altering the dielectric envi-
ronment (Figure S4, Supporting Information). Theoretically,
the red shift of long-wavelength peak with cube-height
decrease can be ascribed to the fact that thinning down cubes
shall decrease the amount of the displaced electrons and the
exposed ions of positive charge which leads to the suppressed
restoring force of the displaced electron gas and thus the red
shift of absorbance peak.[31,32] The dependence of the short-
wavelength peak on cylinder height was also explored by sim-
ulations (Figure 3d). Similar to that of the cube-height reduc-
tion, reducing Au-cylinder height from 100 to 15 nm shall
lead to a red shift of the short-wavelength peak from about
635 to 700 nm, while the long-wavelength peak of the Au
cubes remain around 750 nm. Accordingly, the spectral dis-
tance between two main peaks is decreased from about 115 to
50 nm. It is worth noting that, distinct from a simultaneous
shift of the two peaks with the alteration of NP size, these
two peaks can also be shifted separately in a wide wavelength
range through changing the height of each subset of NPs.

2.3. Oscillator Model of NP Superlattices

To quantitatively analyze the microscopic origins underlying
the optical response of NP superlattices, an analytical model
consisting of interacting harmonic oscillators was proposed
(Figure 4a). The physical analogy between the oscillator model
and the plasmonic resonance in NP superlattices is detailed as
follows. For example, for the Au cubes, the dipolar and quad-
rupolar resonance modes are modeled by the oscillators with
the angular frequencies \( \omega_d \) and \( \omega_q \), respectively, which are

![Figure 2. Optical characterization of Au NP superlattices with different sizes. a) Experimental and b) FDTD-simulated absorbance spectra and c) SEM images of Au NP superlattices I–IV. These four samples have identical cube size of about 120 nm and different cylinder size, that is, diameter, (from top to bottom): about 240, 190, 140, and 80 nm. All NPs are 100 nm in height. Dotted blue and green arrows refer to the wavelength shifts of the cylinder- and cube-dominated peaks with the cylinder-size decrease, respectively. Scale bars: 400 nm.](image-url)
obtained by \( \omega = 2\pi c \lambda_{\text{max}} \), where \( \lambda_{\text{max}} \) indicates the peak wavelength of the normalized extinction cross-section of isolated cubes shown in Figure S5, Supporting Information, and \( c \) is the speed of light in vacuum. The springs with \( k_2 \) and \( k_3 \) model the coupling between dipolar and quadrupolar resonance modes in a cube and that between neighboring cubes, respectively. The plasmonic resonances in the cylinders are modeled analogously \( (\omega_{d,q}, k_{3,4}) \). The interaction between cubes and cylinders is described by the spring constant \( K \). The \( m_{1-6} \) represent the mass of the displaced electrons, which are simply set to be 1 (that is, \( m_{1-6} = 1 \)\(^{[33]} \)). Friction coefficients \( r_{1-6} \) account for the power dissipation of each resonance mode stemming from radiative decay processes and non-radiative decay via, for example, intraband electron-hole excitations. The displacements \( x_{1-6} \) of electron \( m_{1-6} \) from their equilibrium points fulfill\(^{[34,35]} \)

\[
\begin{align*}
    m_1 \ddot{x}_1 &= -\omega_1^2 m_1 x_1 - r_1 x_1 + k_1 (x_1 - x_i) + F \\
    m_2 \ddot{x}_2 &= -\omega_2^2 m_2 x_2 - r_2 x_2 + K (x_2 - x_i) + k_2 (x_2 - x_i) + F
\end{align*}
\]

\[
\begin{align*}
    m_3 \ddot{x}_3 &= -\omega_3^2 m_3 x_3 - r_3 x_3 + k_3 (x_3 - x_i) \\
    m_4 \ddot{x}_4 &= -\omega_4^2 m_4 x_4 - r_4 x_4 + k_4 (x_4 - x_i) + k_5 (x_4 - x_i) + F \\
    m_5 \ddot{x}_5 &= -\omega_5^2 m_5 x_5 - r_5 x_5 + k_5 (x_5 - x_i) + F \\
    m_6 \ddot{x}_6 &= -\omega_6^2 m_6 x_6 - r_6 x_6 + k_6 (x_6 - x_i) + F
\end{align*}
\]

Through assigning appropriate values to the coupling coefficients (Table S1, Supporting Information), the absorbed mechanical power is well matched with the theoretical and experimental light absorbance spectra, demonstrating the validity of the oscillator model for elucidating the optical response of plasmonic superlattices (Figure S6, Supporting Information).

A major advantage of such an oscillator model (1)–(6) over, for example, numerical FDTD calculations is the insight that can be gained by studying the influence of the individual parameters. To do so, Figure 4b traces the transformation of Figure 2’s sample I (strongly coupled NPs) into Figure 2’s
sample IV (weakly coupled NPs) as the model parameters are changed step-by-step. For the case of NP-size variation, the increase (panel I→II) of the resonance frequencies ($\omega_d$ and $\omega_q$) corresponding to the cylinder-size decrease leads to the blue shift of the long-wavelength peak. In particular, the two main peaks are apparently merged into one, which can be ascribed to the near-field-coupling-induced resonance hybridization between two rather broad modes having similar resonance energies (e.g., $\omega_d = 1.71$, $\omega_q = 1.9$, $K = 0.52$). Next, the coupling strength between the same kind of NP is changed (panel II→III). This yields a redshift of the peak when the coupling strength decreases, for example, for $k_3$ from 0.78 to 0.01, which corresponds to the gap enlargement between neighboring cylinders from about 150 nm to 300 nm. The peak redshift induced by the coupling decrease is confirmed by the FDTD simulation (Figure S7a, Supporting Information). The single peak is split into two after performing the next step (panel III→IV), changing the coupling strength between the cubes and cylinders from 0.52 to 0.01 which corresponds to the extended gap between cubes and cylinders. Again, the peak splitting by reducing the coupling effect (i.e., increasing inter-particle gap) between cubes and cylinders can be supported by the FDTD simulation (Figure S7b, Supporting Information). As expected, modifying the friction coefficient (panel IV→V) only determines the peak intensity and width, rather than the peak wavelength. Analogously, Figure 4c traces the transformation

Figure 4. Harmonic-oscillator description for the optical response of NP superlattice. a) Mechanical oscillator model of six masses ($m_1$–$m_6$) coupled with springs, cf. Eq. (1)–(6). $m_1$ and $m_2$ are driven by a periodic harmonic force $F = F_0 \exp(-i\omega t)$, corresponding to the electromagnetic excitation. b) Power dissipation by the oscillator system based on NP superlattices with different NP sizes. The panels at the top and bottom in panel b refer to sample I and IV of Figure 2, respectively. Power dissipation by the oscillator system based on NP superlattices with different NP heights. The panels at the top and bottom in panel c refer to sample I and IV of Figure 3d, respectively. The absorbed power spectra of the other panels are derived by changing the parameters in the top panel to that in the bottom panel stepwise. For example, the model parameters ($\omega$, $k$, $K$, $r$) are changed as follows (from top to bottom): (I) $\omega_T$, $k_T$, $K_T$, $r_T$; (II) $\omega_B$, $k_T$, $K_T$, $r_T$; (III) $\omega_B$, $k_B$, $K_T$, $r_T$; (IV) $\omega_B$, $k_B$, $K_B$, $r_T$; (V) $\omega_B$, $k_B$, $K_B$, $r_B$, $r_T$, where the subscripts of “B” and “T” represent that the parameters are from the bottom panel and top panel, respectively.
of Figure 3d’s sample 1 into its sample IV with the NP-height decrease: red shifts are observed for the peaks when the resonance frequencies ($\omega_a$ and $\omega_b$) are decreased corresponding to the cylinder-height reduction (panel I→II). Unlike the peak mergence for the case of size variation in Figure 4b, the NP superlattices with different heights always maintain two peaks although the resonance modes in cylinders and cubes possess similar energies when the cylinder height is 15 nm (e.g., $\omega_a = 1.47$, $\omega_b = 1.55$). The dissimilar phenomenon stems most likely from the weaker near-field coupling strength $K \approx 0.1$. Afterward (panel III→IV), the coupling strength $K$ weakens from 0.1 to 0.06 which is in accordance with the fact that shortening the cubes further reduces the near-field overlap between the cubes and cylinders\cite{32,37} and accounts for the fixed peak wavelength in Figure 3.

The result of dual-peak resonances in NP superlattices derived from this oscillator model should be applicable to superlattices with any arrangement involving two subsets of NPs, because the model is based on the inherently plasmonic features of isolated NPs. As such, we applied it for example to two subsets of overlapping cylinders and cubes, where four vertical grooves were deliberately introduced into the outer cylinders to let the inner cubes come into effect (Figure S8a, Supporting Information). The experimental and FDTD-simulated light absorbance spectra demonstrate that this NP superlattice also possesses a wider plasmonic function region than its counterparts to one set of NPs (Figure S8b,c, Supporting Information). As expected, the optical response is well reproduced by the oscillator model with a large coupling strength $K$ (e.g., 0.58) due to the fact that the cubes and cylinders spatially overlap (Figure S8d, Supporting Information).

### 2.4. Spectral Programming of Three-Subset NP Superlattices

To further enrich the spectral properties beyond the dual-peak resonances, superlattices with more subsets of NPs are highly promising. Therefore, NP superlattices consisting of three different subsets of Au NPs were fabricated with ternary-pore AAO templates (Figure S9, Supporting Information). A representative SEM image and schematic configuration of such superlattice can be found in Figure S5a, including cylinders (~170 nm in size) and two kinds of cubes (about 110 and 80 nm in size). The resultant absorbance spectrum shows three absorbance peaks located at 550, 620, and 700 nm, respectively. Moreover, the morphology and arrangement of the three-set NPs can be adjusted at the relevant fabrication steps from the anodization to the selective etching.\cite{28} When two different heights were introduced into three-set NP superlattices (15 nm for cubes and 100 nm for cylinders), absorbance peaks were changed significantly to 630, 720, and 850 nm, respectively (Figure 5b). Three distinct absorbance peaks can also be observed when a separated subset of NPs was introduced into the NP-overlapping superlattice (Figure 5c). Thus, three or even more subsets of NP superlattices could deliver programmable multi-peak resonance in a much broader spectral range.

### 2.5. Photoelectrochemical Enhancement with NP Superlattices

To explore the merit of multi-peak resonance in solar energy harvesting, thin Cds-film photoanodes equipped with Au NP superlattices were chosen as a model system. Four Cds films underlain with small cubes, large cubes, small-cubes/large-cubes, and small-cubes/large-cubes/cylinders were fabricated for comparison, where a bare Cds film was used as the reference. In Figure S10, Supporting Information, NPs are indicated by the diffraction peaks (111) and (200) of fcc Au crystal (JCPDS No. 65–8601), and the rest of peaks are indexed to the (002), (103), (112), and (104) diffraction of wurtzite Cds crystal (JCPDS 41–1049). Figure 6a shows a set of chopped photocurrent densities from the photoanodes illuminated by 455 nm filtered visible light. The photocurrents were monotonically increased with the introduction of Au superlattices from zero- to three-subset NPs, for example, enhancement of 262% from 0.47 to 1.23 mA cm$^{-2}$ was achieved at −0.2 V (vs. Ag/AgCl). As shown in Figure S11, Supporting Information,
the photocurrent density decays rapidly at the first 10 min and thereafter remains at the relatively stable value, with a small decay less than 10% after 100 min PEC operation. Incident-photon-to-current efficiencies (IPCE) were also measured, in which the photoanode with three-subset NPs has a significant IPCE enhancement in the whole range of 450–750 nm (Figure S12, Supporting Information). The specific enhancement can be easily identified with normalized IPCE curves compared with two photoanodes with only one-set NPs characterized by a single peak at about 570 and 660 nm respectively, the photoanode with two-subset NPs combines the function regions of the constituent components (Figure 6b). In addition to the broadband function, the enhancement amplitude was also strengthened with two-subset NPs. This phenomenon was further supported by the photoanode with three-subset NPs, with even stronger and broader IPCE improvement, substantially boosting solar energy conversion in the vicinity of the CdS-bandgap corresponding wavelength. Note that the onset potential of all photoanodes in Figure 6a remained the same, revealing that Au NPs were not involved in the chemical reaction occurring at the electrolyte/semiconductor interface.[38,39] Consequently, the PEC-performance improvement should stem from the increased light absorption in the photoanodes, which was confirmed by the normalized absorption spectra where a similar trend with that of the normalized IPCE curves was observed (Figure 6c). Because the identical condition was employed for the CdS-film growth, the plasmonic resonance excited in Au-NP superlattices turn out to be the determinative factor of the increased light absorption, which originates from not only the multi-modes resonances that broaden the light absorption band, but also the strong electric field coupling between neighboring NPs that strengthens the light trapping of CdS films across the interstitial spaces of neighboring NPs. It is noteworthy that, after-treatment (e.g., thermal annealing, surface protection) can be further performed to reduce the recombination of photogenerated electron/hole pairs and potentially exploit the multi-mode induced efficient light trapping to the full.[41,42]

3. Conclusion

In conclusion, a library of Au NP superlattices consisting of two/three subsets of NPs have been constructed on centimeter scales. The resulting multiple plasmonic resonances were programmed in a broad wavelength range by systematically tuning the size and height for each subset of NPs. Considering the enrichment of the AAO template, more subsets of controllable NPs combined into one matrix are obtainable. Subsequently, the geometrical tunability independence over more constituent subsets will enable a higher spectrally programmable degree for multiple plasmonic resonances through elaborately controlling the near-field coupling strength between the same as well as the different constituent subsets. Thus, we believe that the highly accessible NP superlattice provides a blueprint for developing spectrum-programmable and complex plasmonic library with potential utilizations in a wide range of fields such as PEC catalysis, optics, optoelectronics, and biological diagnostics, etc.

4. Experimental Section

**Fabrication of Au NP Superlattices:** As schematically shown in Figure S1, Supporting Information, the fabrication process of Au NP superlattices mainly includes eight steps: (1) Using a Ni mold with periodic nanopillars under a pressure of 12 kN cm−2 for 2 min, electro-polished Al foils were imprinted to obtain an array of square-arranged 400 nm periodicity nanodent on its surface. (2) A constant voltage of 160 V was exploited to anodize the imprinted area of Al foil in 0.4 M H3PO4 solutions at 15 °C for 10 min, achieving an array of square pores (denoted as A pores) with a thick barrier layer at the bottom of each A pore. In particular, these pores can be further enlarged in 5 wt% H3PO4 solutions at 30 °C with an etching rate of about 2 nm min−1. (3) Upon the pore walls of the as-anodized A pores, a 10 nm thick TiO2 layer was coated by a Picosun SUNALETM R-150 atomic layer deposition (ALD) system, acting as a protective layer to prevent A pores from chemical etching in the subsequent steps. The ALD deposition was conducted at 300 °C and each cycle consisted of 0.1 s TiCl4, 5 s N2 purge, 0.1 s H2O, and 5 s N2 purge with a growth rate of about 0.05 nm cycle−1. In an important step, the TiO2 layer on the topmost surface of AAO template...
needs to be milled off by Gatan PECSTM so that the barrier of B pores can be opened completely. (4) Polyethylmethacrylate (PMMA) solution was dripped onto the anodized area and then dried naturally, serving as a sacrificial layer to protect AAO templates from cracking. Afterward, the unoxidized Al foil was removed in a mixture solution, (27 wt% CuCl₂ and 3 wt% HCl), followed by dissolving the PMMA layer into acetone. By immersing the AAO template into 0.1 M NaOH solution at 30 °C for 30 min, another set of circular pores (denoted as B pores) was opened at the fourfold junction sites of neighboring A pores. Particularly, the circular B pores can be further reshaped into the cross-shaped pores by virtue of anisotropic etching rate for the B-pore walls in 5 wt% H₃PO₄ solutions. (5) The AAO template with completely opened B pores and blocked A pores were transferred onto an ITO substrate. (6) The barriers of the square A pores were milled off to achieve a template with two subsets of opened pores. (7) Using the two-subset template as a shadow mask for PVD, Au was evaporated onto the ITO substrate. (8) After peeling off the AAO template, a NP superlattice with two subsets of Au cubes and Au cylinders was produced on the ITO substrate. The NP height can be controlled by PVD parameters such as growth rate and time.

Fabrication of CdS Photoanodes: A two-electrode electrochemical cell was exploited for CdS film deposition in which the as-prepared Au NP arrays on ITO substrates and a Pt plate acted as the working and counter electrodes respectively. The electrochemical electrolyte included 3.6 g CdCl₂ 1.6 g S, and 100 mL dimethyl sulfoxide (DMSO). The solution should be heated to 130 °C while being stirred and remained for more than 30 min to completely dissolve the S powder. The CdS semiconductor membranes were deposited under the constant current mode of 1 mA cm⁻² without stirring. Finally, a strip of copper tape was bonded to the exposed ITO area of the electrode and sealed by an insulating epoxy. The active electrode areas were measured to be about 0.8 cm².

PEC Measurement: Solar radiance was simulated by an Oriel solar simulator (300 W Xe lamp, AM1.5 global filter) which was calibrated to 1 sun using a standardized Si photodiode (Model 818, Newport). PEC performance of CdS photoanodes was evaluated using AM 1.5 illuminations (100 mW cm⁻²) by a three-electrode electrochemical cell configuration in which Na₂S/Na₂S₂O₃ (0.2 M/1 M) aqueous solution, Pt mesh, and Ag/AgCl were used as the electrolyte, the counter electrode, and reference electrode, respectively. A QEPVS1-b Quantum Efficiency Measurement System (Newport) was utilized to perform IPCE measurement which was performed in a two-electrode configuration with the same electrolyte of Na₂S/Na₂S₂O₃ aqueous solution without external bias.

Optical Characterization: The optical characterization was performed with a Varian Cary 5000 UV–vis-NIR spectrophotometer. All illumination was conducted under normal incidence and without polarization. For the optical absorbance spectra of Au NP arrays, a light spot size of about 20 mm² was exploited for measurement. The absorbance of an ITO wafer was measured to serve as a background spectrum of 0% absorbance in normalization. As for the CdS photoanodes, the absorption efficiencies were calculated by (100-R-T)%, where R and T represent reflection and transmission of the incident light.

FDTD Simulation: FDTD simulations were carried out using the software package from Lumerical Computation solutions, Inc. 3D layouts were used in this work. All NPs were situated on the SiO₂ substrate covered by a 100 nm ITO layer whose top surface is parallel with the xy plane and at z = 0 nm. The experimental data from Johnson and Christy[48] along with Palik’s Handbook of Optical Constants of Solids[49] were used to model in the simulation Au and SiO₂, respectively. Data from the Sopra Material Database was used for the optical property of ITO.[43] All NP geometries and the inter-NP distances in the simulation were set according to the experimental observation. To calculate the electric field distribution and the optical absorbance spectra, periodic boundary conditions were applied in the x and y directions, and perfectly matched layers (PML) start in the z direction at z = ±1000 nm. A plane-wave light source, propagating in the ±z direction and locating at z = 500 nm, was used for illumination. The polarization of the incident light was always chosen along the x direction, except for the investigation in the polarization independence of light absorbance. The electric fields around Au NPs were recorded by a 2D field profile monitor at z = 0 nm. The transmitted power (T) was measured by a 2D power monitor embedded into the SiO₂ substrate at z = −500 nm. The light absorbance spectrum was calculated by log₁₀(T/T₀), where T₀ indicates the transmitted power of a bare ITO substrate without Au NPs. The normalized extinction cross-section was obtained via a so-called total-field scattered-field source (TFSF) propagating along the –z direction and covers the 3D volume: 400 nm ≤ x,y ≤ −400 nm, 300 nm ≤ z ≤ −100 nm. PML layers cut the x axis at x = ±600 nm, y axis at x = ±600 nm, z axis at x = 1000 nm and −500 nm, respectively. Au NPs were centered at the site of (x, y, z) = (0, 50, 0) nm. A box of 2D power monitors situated outside TFSF source (namely, x = ±500 nm, y = ±500 nm, z = −200 nm, z = 500 nm) measured the net power scattered by Au NP, and another box of 2D power monitors in TFSF source (namely, x = ±300 nm, y = ±300 nm, z = 200 nm, z = −50 nm) measured the absorbed power by Au NP. Then, the sum of the absorbed power and scattered power was divided by the incident intensity and by the NP cross section to obtain the normalized extinction cross section.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

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