Enhanced Dye Degradation through Multi-Particle Confinement in a Porous Silicon Substrate: A Highly Efficient, Low Band Gap Photocatalyst

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A platform is introduced for fabrication of a reusable and highly efficient low band gap photocatalyst by confining gold nanoparticles (AuNPs) in the pores of a nanopatterned Si monolith (AuNSM). Due to their size, a maximum of two AuNPs can assemble in a single pore, thus preventing agglomerations. Their access to the analyte provides more active sites for redox reaction, leading to enhanced efficiency. While proximity of nanoparticles enhances coupling efficiency, confinement prevents rapid recombination of photogenerated charge carriers, a major factor contributing to low efficiency of photocatalytic materials. Degradation of methyl orange (MO) is used to determine the photocatalytic efficacy of AuNSM compared to 1) bare silicon and 2) AuNPs randomly dispersed on silicon. After 90 min of exposure to UV light (λ = 353 nm) in the AuNSM, the MO absorption is <1%, indicating near complete degradation, while it is still 85% and 70% for systems (1) and (2), respectively. Finite element method simulations of the confined structure suggest that the AuNPs act as a mediator/receptacle for photogenerated charges rather than a source of them at this wavelength and thus enhance the performance of the photocatalyst by creating more effective Schottky junctions—preventing recombination of electrons and holes—rather than by a localized surface plasmonic resonance effect.

1. Introduction

Heterogeneous photocatalysis technology is always looking for an ideal photocatalyst, one that is reusable and that possesses high photocatalytic efficiency, a large specific surface area, and a response to the broadband spectrum of sunlight. Semiconductor photocatalysts have found various applications and are a potential candidate for future sustainable fuel generation from solar light. However, semiconductor heterostructures typically have drawbacks such as rapid recombination of photogenerated charge carriers, narrowband response to light, and lower efficiency. These drawbacks could be overcome by various methods such as nanostructuring of the semiconductor surface to increase absorption density to create more charge carriers for photocatalysis, and formation of heterostructure with plasmonic materials to increase photocatalytic efficiency across the broad solar spectrum. Recently, photocatalysis has received lots of attention as a possible solution to some of the most fundamental issues in sustainable development, such as renewable energy production, water treatment, and air purification.[1–3] In one scheme, several semiconductor photocatalysts are deposited alongside metallic co-catalysts: holes are confined in the semiconductor rods, while the delocalized electrons get transferred onto the metal co-catalyst.[4,5] The advantage of this system is good control over the charge separation. These co-catalysts show great promise for water splitting, due to their lower activation potentials for hydrogen generation and enhanced photocatalytic function.[3,5]

Here, we introduce a new recyclable heterogeneous co-catalyst made of gold nanoparticles (AuNPs) confined in a nanoporous Si monolith (AuNSM) using block-copolymer nanopatterning (Figure 1). The novel aspect of our design takes advantage of confinement without compromising the exposure of metal to the solution as the nanoparticles are not fully embedded in the semiconductor. Otherwise, the deeply embedded nanoparticles in the semiconductor photocatalyst having limited contact with the solution could act as charge recombination centers and lower the efficiency of the photocatalyst. Moreover, metal
nanoparticles in confined space volumes could also cause synergistic interactions between the nanoparticles and the support, thereby changing the electronic properties of the heterostructure.\textsuperscript{[6–8]} Due to the high surface energy of metal nanoparticles, they have a strong tendency to agglomerate into clusters,\textsuperscript{[9,10]} and as a result, control of their assembly and applications cannot be attained without appropriate designs. Therefore, it is imperative to design a hybrid photocatalyst system, which can suppress agglomeration and facilitate better photocatalyst activity. In this work, we address the agglomeration problem by confining limited numbers of the nanoparticles in similar size cavities of a nanopatterned Si substrate. One of the major factors contributing to low efficiency of photocatalytic materials is the recombination of excited electrons and holes; our design allows for better charge separation because of the large interaction area of the AuNPs and the silicon substrate within the pores. Even though this heterostructure was not experimentally tested at visible wavelengths range, our finite difference time domain (FDTD) simulations predict that this system has significantly greater electric field enhancement which potentially leads to a significantly faster redox reaction. Compared to semiconductor CdS,\textsuperscript{[11]} nanocrystals and TiO\textsubscript{2},\textsuperscript{[12]} nanoparticles with 95% and 97% efficiency of methyl orange (MO) degradation after 300 and 420 min UV light illumination respectively, our heterostructure photocatalyst achieved near complete MO degradation after 90 min illumination. Block-copolymer soft nanolithography is a versatile, robust, and cost-effective technique to make nanostructured surfaces and produce various types of surface morphologies.\textsuperscript{[13–18]} The structural dimensions such as pore size, pore depth, and surface area are adjustable by simply employing different block-copolymers with varying interaction parameters ($\chi$), volume fraction of blocks ($f$), and fine-tuning microphase separation parameters,\textsuperscript{[15,18–20]} In this study, we have used poly(styrene)-block-poly(methyl methacrylate) (PS-b-PMMA) block-copolymer to define an etch mask for producing a nanoporous Si substrate, with AuNPs encapsulated in the nanopores for photocatalytic applications. As one of the most prevalent organic pollutants in waste water, MO has become a great concern due to its potential carcinogenic, mutagenic, and bactericide properties. Therefore, MO deposited on AuNSM was chosen as a model reaction to examine the photocatalytic activity of the catalyst platform. Si is a cheap and abundant semiconductor that has revolutionized the microelectronics industry.\textsuperscript{[21]} Si quantum dots, nanowires, mesoporous silica and other composites have been used in photocatalytic applications.\textsuperscript{[22,23]} However, to the best
of our knowledge, porous nanostructured Si as a template for confining metal nanoparticle co-catalysts to produce field enhancement has not been investigated. The advantages of our heterogeneous system are 1) its high surface area\(^{(24)}\) 2) the Si photocatalytic monolith can be easily recycled and separated from the reaction system (whereas, homogeneous powder catalysts cannot be easily reused); and 3) the close proximity of the metal nanoparticles confined in the nanopores enhances coupling efficiency and prevention of electron-hole recombination. Moreover, metal co-catalysts embedded in nanopores control the reaction kinetics efficiently by adjusting the absorption and loading capacity, where the accessibility of analyte to the active sites is high. These materials also allow for controlling the contact time, which is a key parameter for increasing selectivity and limiting the occurrence of secondary reactions.

2. Results and Discussion

2.1. Morphological Analysis of the Nanoporous Silicon Monolith

To fabricate the NSM, we employed PS-b-P(MMA) block-copolymer with the PMMA as the cylinder forming microdomain and the PS as the major matrix of the block-copolymer film. Block-copolymer systems have been explored as an alternative route to overcome conventional lithography methods. Due to immiscibility between two blocks, joined by a covalent bond, block-copolymers self-assemble to periodic nanosized structures, typically with repeat distance of 10–100 nm. Figure 1A shows a PS-b-P(MMA) phase separated film on a silicon substrate. The center-to-center pitch in the block-copolymer film measured by atomic force microscopy (AFM) is 48 ± 2 nm and the diameter of the cylinders is 25 ± 5 nm. The nanopatterned template was employed as the etch mask to produce nanopore arrays in Si through the pattern transfer process. The details on preparation of the film and the etch process can be found in the experimental section. The PMMA block (the dots in Figure 1A) was selectively removed through a dry etch process.\(^{(25)}\)

The resulting porous PS matrix (Figure 1B) was employed as an etch mask for the fabrication of the nanoporous Si substrate. Pattern transfer into the Si substrate was performed by inductively coupled plasma (ICP) etching using C\(_4\)F\(_8\) and SF\(_6\) process gases. This resulted in a well-defined nanoporous Si substrate, with pore depth of ~60 nm (Figure 1D). No considerable disordered or missing patterns were observed for the Si substrate after etching. The inset in Figure 1C is a high-magnification scanning electron microscopy (SEM) image, indicating wide range ordering of the nanopores. The diameters of the nanopores in the film varied from 25 ± 5 nm with a spacing of 45 ± 3 nm and depth of 60 nm, which is a close match with the original template mask. To study the effect of confinement on photocatalysis, we synthesized AuNPs and confined them in the pores of the NSM.

Figure S2, Supporting Information, shows SEM images of the thiol-capped AuNPs with an average diameter of 18 nm. AuNSMs were prepared by spin coating of the AuNP solution on the nanoporous Si substrate. The insertion procedure was repeated twice to ensure the nanopores were fully loaded with AuNPs. Figure 1D is a cross-sectional SEM image of the AuNSM, where the bright spots represent AuNPs in the nanopores.

2.2. The Effect of Confinement on the Kinetics of Photocatalytic Reaction

To verify the effect of enhanced coupling in AuNPs when confined in Si nanopores on photocatalysis, MO was chosen for dye degradation on UV-light exposure. The AuNSM system is believed to improve the degradation rate due to the greater interaction area of the porous silicon substrate with the MO dye and the AuNPs compared to flat silicon. In the AuNSM, contact between each AuNP and the nanoporous Si creates a Schottky junction and thus an internal electric field that prevents recombination of electrons and holes. Based on experimental data, we believe the AuNPs confined in nanoporous Si are important for separating the electrons and holes generated upon light absorption in the AuNSM and thus these electrons are driving the degradation of the dye. We have also verified our hypothesis by two control experiments, where UV light absorbed on 1) a flat silicon substrate and 2) AuNPs on flat silicon produced significantly less degradation of the dye. This indicates that electron-hole separation is facilitated effectively in AuNSM compared to flat silicon and to randomly dispersed AuNPs on Si. Figure 2A represents a schematic of AuNPs deposited on bare Si (top image, Figure 2A) and AuNPs embedded in the NSM (bottom image, Figure 2A). The photocatalytic activity of three systems was tested: 1) unpatterned Si; 2) AuNPs randomly dispersed on Si (Figure 2B); 3) AuNSM where synthesized AuNPs were deposited and confined in the pores of a NSM (Figure 2C). All the substrates were cleaned with deionized (DI) water. After deposition of AuNPs, the samples were left overnight to dry then rinsed with DI water to remove any surface adducts or AuNPs hinged outside of the pore structures. X-ray photoelectron spectroscopy (XPS) spectra of AuNSM samples before and after catalytic use are shown in Figure 3. The nearly identical amount of gold on the surface before and after use indicates that AuNPs are confined in the pores, otherwise they would have been washed away through the rinsing process.

MO dye (0.25 mmol mL\(^{-1}\)) in DI water was deposited onto all three sets of substrates: bare Si, randomly dispersed AuNPs on Si, and AuNSM. The substrates were irradiated with UV light (353 nm) for a range of time intervals (5–90 min). The irradiated substrates were rinsed in equal volumes of DI water and this “wash” (active spectra) was used in the UV–vis spectrometry. In Figure 2D–F, the UV–vis spectra of the degraded MO dye wash from the different types of modified Si is shown after 10, 50, and 90 min of exposure. Scheme S1, Supporting Information, describes the steps. We observe that after 15 minutes, the active spectra—i.e., the absorption of light by the wash—is lowest for the AuNSM template, indicating the MO dye has already been degraded. This suggests that catalytic efficiency is higher in the AuNSM than in other systems. Specifically, after 90 min of irradiation time (Figure 2F), most of the dye on the AuNSM has been degraded completely, whereas the dye on the bare Si substrate and on the AuNPs on bare Si substrate were degraded partially or very little. These results further support our hypothesis that the confinement in AuNSM photocatalyst enhanced the photochemical activity and/or the synergistic interactions between the NPs and the Si support that changed the electronic properties of heterostructure, which enhanced the dye degradation. From the active spectra (Figure 2D–F),
it can be inferred that the addition of AuNPs to bare Si also improves the photocatalytic performance (slightly better than bare Si, but significantly less than the AuNSM system). This may be due to an increased number of photogenerated electrons in the AuNPs compared to bare Si or the possibility of charge separation by transfer from the substrate to the AuNP. For comparison, a solution of dye containing AuNPs was exposed for 90 min in the same experimental setup but the degradation was negligible. This indicates that simple UV exposure is not enough to degrade the dye and also that AuNPs in solution (most likely isolated) do not degrade the dye either.

In the absorption spectrum of MO, an absorption peak was observed at 464 nm (Figure 4A). The decrease in the intensity of the absorption peak at 464 nm indicates the possible cleavage of the azo group (—N=N—), which is a chromophoric functional group. In Figure 4B, the peak absorption is plotted against exposure length for the four substrates. The dashed line is a fit to a single exponential. For the AuNSM system, the fit gives a decay constant of 4 min (the necessary exposure time for the absorption to decrease to 1/e of its original value). (The fits for the other substrates would require more data points.) The progressive decolorization of the MO dye on AuNSM at different time intervals is illustrated in Figure 4C. After 90 min irradiation time, most of the dye was decolorized indicating complete degradation. Figure 4D shows the reflectivity measurements of the three different modified Si substrates, where the reflectivity in the AuNSM is comparatively lower than nanoporous Si and bare Si. This indicates AuNSM has higher absorption density.
to cause enhanced photocatalytic degradation of MO dye due to the possibility of charge separation and transfer of hot carriers from the Si to the AuNPs.

The plausible mechanism of the MO degradation due to UV exposure is proposed to be the following: Degradation of MO solution by the cleavage of the $-\text{N} = \text{N} -$ bond to two different chemical amines structures ($-\text{NR}_2$) (Scheme S1). The $-\text{N} = \text{N} -$ double bond in azo dyes is the chromophoric functional group for color, which is prone to decomposition upon photoexcitation. Photocatalysis via light absorption induces the generation of charge carriers such as hot electrons. These electrons are very effective at causing the degradation of the dye.[26] In addition, we presume the acceleration of the photocatalysis could be through the coupling of AuNPs and the silicon substrate. The degradation process leveled off after ~90 min, indicating that all of the MO dye had been degraded (Figure 4A). These results indicate that the AuNSM photocatalyst support enhanced the photochemical activity. From Figure 4B, it can be seen that the MO dye degradation on the AuNSM at different time intervals of UV-light exposure is higher than bare Si (the data in Figure 4B were normalized to the dye absorption for zero exposure time). This might be due partially to the increased surface area of the porous Si substrate ($\approx 3\times$ more than bare Si) providing more active sites for photoreaction and leading to a greater interaction area with the MO dye. In addition, AuNPs confined in Si nanopores could also cause synergistic interactions between the NPs and the Si support, and thus change the electronic properties of the heterostructure, this also facilitates charge separation which enhances the dye degradation.[6,26,27] These interactions also take advantage of the high surface area of the nanoporous Si compared with the bare Si to increase the photocatalytic efficiency.[24] To understand the mechanism of the photocatalysis, our control experiments with different substrates showed that: 1) photocatalytic degradation of MO dye on bare Si had a slow reaction rate, this could be ascribed to the unavoidable rapid recombination of photogenerated charge carriers in the Si, that decreases the photocatalytic MO degradation. 2) Deposition of the noble metal NPs on semiconductors suppressed the electron-hole recombination. This semiconductor/metal heterostructure, pumps in photogenerated electrons, and facilitates an interfacial charge-transfer process due to its high Schottky barrier at the metal/semiconductor interface.[28,29] However, efficiency of the randomly distributed NPs over the Si substrate on the photocatalytic MO degradation is too small. We presume the low efficiency is because of fewer photogenerated charge carriers to induce the MO degradation. 3) In our system, confinement of the AuNPs in the Si nanocavities enlarges the excitation space and encourages transfer of hot carriers from the Si support to enhance the photocatalytic efficiency. Moreover, it could also be that the nanopores serve as a
template to stack AuNPs resulting in a short separation and a higher enhancement factor. This could be ascribed to the generation of hot carriers, which combined with Si semiconductor cause excitation of electronic or vibrational transitions in MO dye molecules to accelerate the photodegradation.\[30\]

### 2.3. Electromagnetic Simulations

FEM simulations were performed for the three different systems used in our experiment. The simulations were used to gain insight into the relative photocatalytic performance of each system. The sizes of the pore and AuNP were taken from the SEM images (25 ± 5 nm and 18 ± 3 nm, respectively) and the geometry was set up to simulate a periodic triangular lattice for each substrate. While it is unlikely that the AuNPs on bare Si formed a triangular lattice, it is expected that they were isolated individual particles on the surface and thus the simulated geometry was an adequate approximation. FEM simulations were performed using the software COMSOL\[31\] and used plane wave excitation at a wavelength of 353 nm. Maps of power loss in the different systems indicating that porous silicon has higher power loss density thus implying more photogenerated carriers. FDTD simulation of the AuNPs confined in porous Si. E) Single AuNP in a nanopore and F) dimer of AuNPs in a nanopore both at plasmon resonance. G) Maximum electric field enhancement as a function of wavelength.

Figure 5. A) Scheme S1 depicting proposed mechanism for photocatalytic degradation of MO dye on AuNSM. AuNSM photocatalyst support enhanced the photochemical activity due to the large surface area of the porous Si substrate and improved extraction of hot charge carriers into the AuNPs, effective at causing the degradation of the dye. B–D) FEM simulation of different systems at exposure wavelength 353 nm. Maps of power loss in the different systems indicating that porous silicon has higher power loss density thus implying more photogenerated carriers. FDTD simulation of the AuNPs confined in porous Si. E) Single AuNP in a nanopore and F) dimer of AuNPs in a nanopore both at plasmon resonance. G) Maximum electric field enhancement as a function of wavelength.

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From our simulation outcome, it is likely that the main reason for fast photocatalytic degradation of MO is due to creating a large volume of Schottky junctions near the AuNP/Si interface, which provide extra paths for electron–hole separation and fast charge lane to the active sites.

It has been reported that metallic NPs that are separated by distances of a few nanometers show high amplitude of electromagnetic field\(^{[26,32–34]}\) that is ascribed to the strong coupling between adjacent NPs. Moreover, the synergy of noble metals (such as Au and Ag) and semiconductor nanoparticles in photocatalytic heterostructures enhances photocatalytic efficiency by significant suppression of the electron–hole recombination generated upon photoexcitation.\(^{[28]}\) Indeed, our original hypothesis was that confining multiple nanoparticles (AuNPs) in nanostructured spaces (Si pores) would increase the near-field enhancement significantly in comparison to randomly dispersed nanoparticles on the same substrate. In a photocatalytic system, this enhancement should be able to drive the reactions at significantly higher rates. Therefore, the AuNSM system is expected to be photocatalytically active at visible wavelengths due to its plasmonic response. To investigate the extent to which the system could be affected by the range of exposure wavelength, FDTD simulations were carried out on AuNP ensembles in a Si nanopore. We simulated the electric field enhancement for multiple plasmonic AuNPs confined in nanostructured spaces, in visible wavelength range and demonstrated that the enhancement of near-field is due to plasmonic coupling. We found that the electric field enhancement due to plasmonic coupling for multiple AuNPs embedded in a nanopore is greater than for dispersed and/or individual NPs; this enhancement contributes strongly to the plasmon-driven photocatalysis efficiency. The generation of plasmon-induced hot charge carriers is directly related to the local electric field \(|E(r)|^2\) inside the plasmonic particles\(^{[35]}\).

\[
\text{Hot charge carrier density} = \frac{1}{V_{\text{MFP}}} \int r \left| E(r) \right|^2 \, dr
\]

where \(V_{\text{MFP}}\) is the volume within a distance of the mean free path from the surface inside \(r_g\) up to active interface \(r_{\text{MFP}}\). Due to the small size of our particles, we can consider all the electrons of the entire volume of the particle.\(^{[34]}\) Smaller particles also have the advantage that they scatter less compared to larger ones and therefore their plasmon absorption yield is higher.\(^{[34]}\) so more hot charge carriers can be injected into the semiconductor Si substrate, and direct transfer of the hot charges from the AuNPs (20 nm in diameter) to MO dye can occur simultaneously. For example, Boerigter et al. reported direct charge excitation as the dominant role in the degradation of methylene blue.\(^{[36]}\) In this case, the electric field at the surface of the plasmonic system is the determining factor. Figure 5 shows the local electric field enhancement of a single AuNP (Figure 5E) in a nanopore (28 nm diameter), compared to a dimer of touching AuNPs (Figure 5F). FDTD calculations indicated the significant increase in near field enhancement as a function of wavelength, shown in Figure 5G, and red shift from \(\approx 630 \text{ nm}\) to \(\approx 735 \text{ nm}\) due to the dimer of AuNPs with a close-packed hotspot in the Si nanopore. Experimental verification of visible range will be the focus of future work.

3. Conclusions

In summary, we have studied how confining AuNPs in a porous Si template can significantly enhance the photocatalytic activity of MO. The pores prevent agglomeration of nanoparticles and eliminate the need for any functionalization. Confinement of the AuNPs in the Si nanocavities prevents electron–hole recombination and facilitates the transfer of hot carriers from the Si support to accelerate the photocatalytic efficiency. Since the nanoparticles are not fully buried in the semiconductor matrix, the number of active sites for redox reaction is plentiful. All these factors contribute to higher efficiency of our heterogeneous photocatalyst. We have developed a block-copolymer templated nanoporous Si monolith (NSM) to achieve the confinement of the AuNPs and their arrangement in close-packing set. Close-packing enhances the electromagnetic field and increases the synergistic interactions between the nanoparticles and the nanoporous support, thereby changing the electronic properties of the photocatalytic heterostructure. Full degradation of the MO dye on the AuNSM was successfully achieved on exposure to UV light for 90 min, at least three times faster than reported in the literature, compared to unmodified or bare Si substrates, where no or minimal degradation was observed. FEM simulation demonstrates in our system where the Si pore and AuNPs have similar dimension, nanocavities have large absorption density around the pore of the AuNSM compared to bare Si and porous Si. At a wavelength of 353 nm, the interparticle interaction in the pores seems negligible, indicating that the AuNPs act as a mediator/receptacle for photogenerated charges rather than a source of them at this wavelength. This suggests confining the AuNPs in Si pores enhances the performance of the photocatalyst by creating more effective Schottky junctions and thus preventing recombination of electrons and holes rather than localized surface plasmonic resonance effect. Nonetheless, we believe that this proposed mechanism of electron transfer between the AuNPs and Si warrants further study—in particular utilizing characterization such as Kelvin probe microscopy to study the work function of the materials.\(^{[37,38]}\) The recyclable, low-band gap photocatalytic system has economic and environmental advantages that promote implementation of catalytic and separation processes in continuous flow mode, with the advantages associated with easier phase separation and product recovery, enhanced safety, and easier operation. We anticipate that this system can be applied to fabrication of various other nanomaterials for photocatalytic applications.

4. Experimental Section

**Materials** Poly(styrene)-r-poly(methyl methacrylate) ((PS-r-PMMA); Arkema), propylene glycol methyl ether acetate (PGMEA), PS-b-PMMA, Si wafer, hydrogen tetrachloroaurate(III) trihydrate, 11-mercaptopoundecanoic acid, sodium borohydride, and MO dye were used. Other solvents were used as received unless otherwise stated.

**Preparation of the Nanoporous Silicon Template—Preparation of Block-Copolymer Film:** The preparation of self-assembled diblock-copolymer thin films on Si wafers was performed in four steps: wafer cleaning and oxidation, polymer brush formation, thin film formation, and annealing.

Step 1 involved wafer cleaning and oxidation. A (100) Si wafer was treated with fresh piranha solution \((\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2)\) with a volume ratio of...
were used for broadband and single peak scans, respectively. To make sure the degradation of the dye was analyzed by the decrease in the absorption of MO.

measurements. The degradation of the dye was analyzed by the decrease

time durations (5–90 min). The irradiated substrates were washed in
equal volumes of distilled water to extract the dye for UV–vis absorption
measurements. The degradation of the dye was analyzed by the decrease in the absorption of MO.

X-Ray Photoelectron Spectroscopy: An XPS/UPS Omicron MultiProbeXP X-ray photoelectron spectrometer was used to determine the elements present in the samples. The system uses an aluminium source (1486.6 eV, 300 W) and an XM 1000 monochromator. Step-sizes of 0.5 eV and 0.2 eV were used for broadband and single peak scans, respectively. To make sure AuNPs are confined in the Si pores, XPS spectra of samples were collected before and after photocatalytic use (Figure 3). XPS was also performed on nanopatterned Si (without gold) to show the stability of the substrate (Figure S4, Supporting Information). SEM image of the samples after use confirms the pores are intact (Figure S5, Supporting Information).

Optical Characterization: Absorption measurements of the extracted dye were taken using a PerkinElmer LAMBDA 1050 UV–Vis–NIR spectrophotometer fitted with an integrating sphere. The samples were placed on a holder within the sphere and scanned over the wavelength range 250–700 nm in steps of 3 nm with an integration time of 0.7 s. Reference measurements of distilled water and of the original dye solution were also taken.

FEM Simulation: The absorption of the different substrates was simulated with the FEM using COMSOL Multiphysics. A hexagonal unit cell of side length 28 nm (to correspond to a pitch of 48 nm) was used with spherical AuNPs that had a diameter of 22 nm. Periodic boundary conditions on sides perpendicular to the substrate surface, absorbing boundary conditions on sides parallel to the substrate surface, and a plane wave light source with a wavelength of 333 nm were used. The substrates simulated were bare silicon, silicon with a single AuNP, and nanoporous silicon containing two AuNPs. For porous silicon, a pore diameter of 20 nm and a depth of 60 nm were used. The dielectric permittivity Au (Rakic) and Si (Aspnes) were used for gold and silicon, respectively.

FDTD Simulation: The electric field enhancement due to multiple AuNPs in a Si nanopore was simulated with the FDTD method, through the open-source software package MEEP. The dielectric function of AuNPs (20 nm in diameter) was approximated by a Lorentz–Drude model using experimental data obtained from Rakic et al. Periodic boundary conditions were placed on all sides of the simulation cell (pore size = 28 nm, pitch = 48 nm, depth = 60 nm) and an artificial absorber layer was placed parallel to the plasmonic array at the end of the simulation cell to block transmission through the cell. The plasmonic arrays and nanopores were hexagonally arranged.

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.
Data Availability Statement

Research data are not shared.

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