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Plasmonic Charge Transfers in Large-Scale Metallic and Colloidal Photonic Crystal Slabs

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The challenges in plasmonic charge transfer on a large-scale and low losses are systematically investigated by optical designs using 1D-plasmonic lattice structures. These plasmonic lattices are used as couplers to guide the energy in an underneath sub-wavelength titanium dioxide layer, resulting in the photonic crystal slabs. So far, photodetection is possible at energy levels close to the semiconductor bandgap; however, with the observed hybrid plasmonic–photonic modes, other wavelengths over the broad solar spectrum can be easily accessed for energy harvesting. The photo-enhanced current is measured locally with simple two-point contact on the centimeter-squared nanostructure by applying a bias voltage. As lattice couplers, interference lithographically fabricated conventional gold grating provides an advantage in fabrication; this optical concept is extended for the first time toward colloidal self-assembled nanoparticle chains to make the charge injection accessible for large-scale at reasonable costs with possibilities of photodetection by electric field vectors both along and perpendicular to the grating lines. To discuss the bottleneck of unavoidable isolating ligand shell of nanoparticles in contrast to the directly contacted nanobars, polarization-dependent ultrafast characterizations are carried out to study the charge injection processes in femtosecond resolution.

1. Introduction

The light–matter interaction at the nanoscale induces the collective oscillation of charge carriers in a metallic nanostructure.[1] These conduction band electrons have enormous energy densities that can be utilized for various photophysical processes,[2] such as photocatalysis,[3–6] photovoltaics,[7–9] and photodetection.[10–12] Such electrons have been popular in the nanophotonics community as hot-electrons[2,8,13,14] because of possessing much higher energy, even higher than room temperature thermal excitation.[12,15] These hot-electrons from metallic nanostructures with sufficient high energies, when in close vicinity of a semiconductor, can overcome the Schottky barrier ($\phi_{SB} = \phi_M - \chi_S$) and get injected into the conduction band ($E_{CB}$) of the neighboring semiconductor[3,16] here $\phi_M$ is the work function of the metal and $\chi_S$ is the electron affinity of the semiconductor.[8] This transfer of charged carriers can be enhanced by a structured metal surface,[17,18] through the process of localized surface plasmon resonances.[14] In general, whenever a localized surface plasmon is excited, it relaxes both radiatively and non-radiatively.[8] In the case of radiative relaxation, they re-emit a photon whereas for nonradiative relaxation they decay by Landau damping to form energetic electron–hole pair[19] (within 1–100 fs). These hot-carriers follow Fermi-Dirac distribution, which can again relax by electron–electron scattering processes such as Auger transitions (within 100 fs to 1 ps). In the end, these electrons interact with the lattice phonons and dissipate in terms of local heat on the longer time scale (100 ps to 10 ns).[2,8] Such plasmon-induced charge carriers (both hot electrons and hot holes[20]) can undergo direct or indirect transfer to the adjacent...(continued on next page)
acceptor, depending on the dynamics of the excitation.[21] Since plasmons are predominantly radiatively damped oscillations, it is definitely challenging to increase the yield of charge-carrier extraction from the plasmonic structure into the acceptor states.[22]

To compete with the radiative damping in plasmonic nanostructures, several hybridization strategies[23–25] have been implied to suppress such losses, one of which is to introduce waveguide-like characteristics to the plasmonic excitation. This is possible on structures supporting both localized plasmon resonances as well as waveguide modes, where the coupling of these two states results in hybrid resonance by forming waveguide-plasmon polaritons.[26,27] This optical concept combines mode confinement along with the reduction of radiative losses through a prolonged lifetime of the photonic character, shown via narrow linewidth. Such metal bars on a dielectric waveguide were initially reported by Giessen et al. as metallic photonic crystal slabs (mPhCs) to produce waveguide-plasmon polaritons.[28] Gómez et al. investigated the photoinduced electron transfer in the strong coupling regime as an application of such waveguide-plasmon polariton modes, where electron-beam lithography induced gold nanobars on titanium dioxide films[22] resulted in the mPhCs, limited to smaller area (<0.5 mm²). An efficient route toward the realization of such mPhCs over a large scale is indeed required to easily execute simple optical characterizations. The colloidal approach offers such scalability ensuring large-scaled plasmonic nanostructures[29] ranging in centimeter squared area. Thus to complete the picture, colloidal photonic crystals should be implemented in photonic–plasmonic coupling over macroscopic scale, resulting in plasmonic charge transfers to adjacent semiconductor region. Previously in a 1D mPhC slab, the guided-mode resonance[30] (GMR) mechanism was employed to confine energy in a semiconductor waveguide for enhanced absorption[27] where the photonic features could be tuned through waveguide thickness and grating periodicity to achieve strong coupling.[22,26] Unlike metallic bars, colloidal plasmonic chain responds to polarization states both parallel and perpendicular to the grating lines giving rise to longitudinal and transverse chain modes, respectively at separate frequencies.[31,32] Thus, by tuning the polarization instead of periodicity, the effect of coupling in the formation of hybrid modes can be gathered from a single structure with a constant period. For charge transfer applications, the shape of the plasmonic resonating structure,[7,13] as well as its contact area to the semiconductive neighbor material is crucial[33,34] which can be easily controlled using colloidal plasmonic blocks.[35,36] Very recently, plasmonic blocks with gold nanorods as the core and silver nanocuboids as the shell have been synergistically resonated with photonic waveguide modes through tuning of incidence angle.[37] The hybrid mode resulted in enhanced hot electron generation leading to increased photocatalytic reaction, as compared to non-hybrid LSPR excitation.

In the present work, we explore such waveguide-plasmon coupled systems fabricated with cost-efficient bottom-up approaches. mPhCs produced over a large macroscopic area by scalable laser interference lithography[38,39] and physical vapor deposition[40] show direct contact of the metallic nanobars to the adjoining semiconductor TiO₂ waveguide. Moreover, we introduce colloidal photonic crystal slabs (cPhCs) toward exploring hot-electron based charge transfer mechanisms by using colloidal-grown gold nanoparticles (AuNPs) with undesired isolating ligand shell (2 nm). These AuNPs are arranged in form of dimer chains[31,41] via directed self-assembly[42] methods that form the plasmonic grating component of the cPhC slabs. Such cPhCs have been recently explored by us for sensing application and linewidth control.[38] In the current study focused on plasmonic charge transfers in both mPhC and cPhC slabs, we are interested to observe the effect of direct and separated contact between metal/semiconductor junctions on plasmonic charge transfer mechanisms. Both mPhCs and cPhCs (see schematics in Figure 1a) have been optically characterized via steady-state transmittances as well as transient ultrafast measurements. This is an important step toward optoelectronic device development, which should turn the ligand shell barrier into an advantage in the future.

2. Result and Discussions

2.1. Metallic and Colloidal Photonic Crystal Slab Concepts for Hot-Electron Injection

To identify the energy confinement of the metallic and colloidal photonic slabs, we conduct the finite-difference time-domain (FDTD) modeling (see Figure 1b). Note, the localized field enhancement should be present in both metallic and semiconductor for efficient charge carrier generation.[10,27] For suppressing the radiative losses of plasmonic excitation, the hybrid mode shows narrow linewidth in both photonic slabs only at specific polarization. As a design criterion, the plasmonic mode has to match with the photonic mode to produce the coupled features. This is done by a suitable choice of 500 nm grating periodicity with a specific fill factor and 200 nm waveguide thickness. The fill factor is defined by the ratio of the bar width or particle chain width to the periodicity with a value of 0.50 and 0.32, respectively. For a constant period, the fill factor directly relates to the bar width which is again related to the plasmonic resonant wavelength.[43] The calculated transmission spectra always show a narrow hybrid feature followed by a broad plasmonic mode. For mPhCs, the hybrid mode can be observed at 763 nm under transverse magnetic (TM) polarization. The hybrid features of plasmon and photonic mode can be observed by the electric field plot at this particular wavelength. The broad resonance observed at 1106 nm is similar to that of pure plasmonic nature and is excluded in the current discussion as a trivial case. To be complete, the pure plasmonic and photonic counterparts of the photonic slabs (Figure S1, Supporting Information) are discussed in Text T1, Supporting Information. For cPhCs, the hybrid mode is excited at 851 nm under transverse electric (TE) polarization with a pure plasmonic mode at 1049 nm. Note, the change of polarization, from TM to TE, is necessary to excite the hybrid modes under the same periodicity condition. Among the transverse and longitudinal chain modes, only the latter can be hybridized with the current 500 nm periodicity.[38] It is also important to distinguish between a charge transport case supported by the hybrid modes and the reference cases of non-hybridization under counter
polarization. The resonant features, observed at TE: 849 nm and TM: 918 nm for the mPhC and cPhC slabs, respectively, are extended via electric field plots. This confirms the existence of pure modes in these hybrid structures showing waveguide confinement at 849 nm and plasmonic mode at 918 nm. These optical concepts can be materialized using photolithography and colloidal self-assembly techniques into large-scale photocurrent devices.

2.2. Large-Area Fabrication of the m/c Photonic Crystal Slabs

Laser interference lithography, physical vapor deposition, and directed self-assembly techniques have been used to fabricate the photonic crystal slabs on centimeter length scales (shown in Figure 2). The schematics in the figure represent the mPhC and cPhC structures, respectively with their step-wise fabrication procedure reported in detail in Text T2, Supporting Information, where Figures S2 and S3, Supporting Information provide the lift-off and self-assembly approaches, respectively. For either of these, the basic photonic component is represented by a PhC structure with photoresist (PR) grating and semiconductor TiO2 waveguide as described in the Experimental Section. The PR grating formed by laser interference lithography offers an extremely fast manufacturing process compared to serial fabrication techniques like direct-laser writing or electron beam lithography. The grating profile needs to be modulated

Figure 1. Metallic and colloidal photonic crystals for hot-electron injection. a) An asymmetric photonic waveguide with a metallic grating or a colloidal grating can result in different types of photonic crystals. b) In-depth investigation of the i) mPhCs and ii) cPhCs with the unit cell as shown in the first column. The resonant wavelengths for each of the cases are identified from the transmittance minima. Corresponding electric fields at resonant wavelengths in both TE and TM modes are calculated through FDTD field monitors showing strong confinement for the hybrid TM excitation 763 nm and hybrid TE excitation at 851 nm for the mPhCs and cPhCs based systems.
according to the final targeted hybrid device that can be easily achieved through control of exposure dosage and developing time. For generating mPhCs through lift-off techniques (details in the Experimental section), a rectangular grating profile is a prerequisite. In contrast, for the assembly of NPs toward realizing the cPhCs, both sinusoidal, as well as rectangular profile, can be used to impart directed self-assembly techniques (details in the Experimental section).

Once the structure is fabricated, these are characterized under scanning electron microscopy (SEM). Figure 2a-ii,b-ii provides large area SEM images of the fabricated sample surfaces of the PhCs. Magnified view in the inset provides an estimation over five periods of such structures. Figure 2a-iii,b-iii displays the cross-sectional view of such structures obtained through a focused-ion beam (FIB) cut. Details of such FIB technique are provided in Text T2, Supporting Information. The surface characterization and height profiles of the fabricated structures have been confirmed by atomic force microscopy measurements that are shown in Figure S4, Supporting Information. As a reference, a photonic structure with randomly arranged nanoparticles is also prepared. Figure S5, Text T3, Supporting Information describes such randomly arranged NPs fabricated using a simple drop-casting method on a TiO₂ coated glass substrate. For light-trapping applications as well as spectroscopic characterization, it is important to excite the structure with plane waves rather than a focused light beam. Our large-area fabrication allows both period and angle-dependent characterization. Conventional spectroscopic methods such as polarized UV–vis–NIR spectroscopy are carried out with plane beams on a centimeter-sized spot area. For a reasonable signal to noise ratio, it is recommended to have infinite lines inside the spot area which is facilitated in our large-scaled fabrication.

2.3. Dispersion Relation of m/c Photonic Crystal Slabs Covering the Vis–NIR Range

Dispersion diagrams also referred to as band diagrams, are used to explore PhC slabs in terms of ω(k), where ω is the optical frequency and k is the wave vector of the supported modes. These plots provide information about the guided fields, including the number of supported modes, and are used to connect the photonic energies to their modes of propagation, essential in studying the optical bandgaps. The frequency versus propagation vectors can also be plotted simply in terms of wavelength versus periodicity to establish similar dispersive natures. Before coming to such dispersion relations, we discuss our experimental result with previously introduced simulated results (see Figure 3a-i,b-i). A good match is observed in both the metallic and colloidal PhC slabs irrespective of the incident polarization. We now theoretically extend the fixed periodicity of 500 nm into a broad range of 300–800 nm to obtain the dispersion relations (Figure 3a-ii,b-ii). Generally, the pure photonic (dashed white lines) and plasmonic modes (dotted white lines) cross each other resulting in an anti-crossing (see the dark contours obtained from the transmittance minima). The dashed and dotted lines are calculated using either a plasmonic or a photonic constituent only; corresponding contour plots for both the mPhCs and cPhCs are given in Figure S6, Text T4, Supporting Information. The anti-crossing is already introduced as the hybrid modes at a fixed periodicity, corresponding to the TM and TE polarization investigation on the mPhCs and cPhCs, respectively. With such periodicity alteration, any desired wavelength within the vis–NIR range can be targeted to result in hybrid states concerning hot-electron generation. With our interference-lithography approach, various grating periodicities can be easily attained. Such structures are similarly characterized and displayed as...
For mPhCs, three periodicities recorded are 300, 400, and 500 nm, whereas, for the cPhCs, three periodicities of 500, 520, and 560 nm are used. To prove the polarization dependency behind the anti-crossing behavior, the non-hybrid cases are also calculated and provided with experimental data points in Figure 3a-iii, b-iii. It should be noted that dispersion relations can also be extracted through angular scan on structures with a fixed periodicity. For the current structure under the observation (500 nm periodicity), we have obtained such dispersion diagrams using both calculated and experimental data. These data are provided in Figure S7, Text T4, Supporting Information for both the mPhC and cPhC slabs. This angle of incidence parameter provides the device developer further tunability and degree of freedom to attain the hybrid resonance precisely.

2.4. Two-Probe Photoresponse Measurements

In Figure 4, we discuss the photoconducting properties of three selected geometries over an excitation wavelength range between 365 and 1050 nm at normal incidence (discreet LED sources). Importantly, to the introduced photonic crystal slabs, we compare the photoresponse characteristics with well-known randomly arranged AuNPs on TiO$_2$ waveguide$^{[5,15]}$ to highlight the colloidal approach. For reference to these results, we also add a comparison with the bare TiO$_2$ slab. The current density ($J$) is the measured current ($I$) per active area of the collection ($A = \text{area between the electrodes}$; $A = 0.0099 \text{ cm}^2$) under periodic excitation of different LED wavelengths and a bias voltage of 1 V (schematic in Figure S8, Supporting Information) which comprises of the photo-induced current ($I_{ph}$) and the dark current ($I_d$). Power and spectra of such LED sources are given in Table S1 and Figure S9, Text T5, Supporting Information, respectively. We have used a two-probe contact scheme for our photoresponse measurement, which is simply fabricated by further depositing gold electrodes parallel to the grating lines. This unconventional approach for plasmonic charge transfer detection does not alter the optical characteristics in contrast to conventional photodetection schemes$^{[12,15]}$ that require additional layers for electrical characterization. The reported photo-detectors operated in varied geometries with top and bottom electrodes and conducting in-between layer, where the photo-generated electrons in the collected current are fully induced by the absorbed photons. In our present scenario, the existing current generated by the voltage bias (1 V) at the two sides of the
TiO$_2$ slab is modulated in magnitude by light absorption and the consequent change in conductivity of the TiO$_2$ slab. Thus, our strategic deployment results in a much simpler characterization to observe this modulation caused by the plasmonic charge transfers, while preserving the optical characteristics of the fabricated m/c PhC slabs. We proceed stepwise through the wavelength selective photoresponses in Figure 4 starting from a bare TiO$_2$ slab, isolated nanoparticle, nanoparticle aggregation, and finalize the discussion with the findings from the photonic crystal slabs.

Figure 4. Plasmonic charge transfer detection through generated photocurrent. The current density (J) data for three different systems: a) random NPs on semiconductor, b) mPhC slab, and c) cPhC slab operating under unpolarized LEDs sources of wavelengths i) 365 nm, ii) 550 nm, iii) 660 nm, iv) 780 nm, v) 880 nm, and vi) 1050 nm for periodic excitation (on-off states). The dashed curve in (a-i) represents the bare TiO$_2$ response to the 365 nm wavelength. For all the measurements, a bias voltage of 1 V is applied.
For excitation at 365 nm wavelength on a bare TiO$_2$ slab corresponding directly to the semiconductor bandgap, we observe a sharp increase (dashed line in Figure 4a) in the current density to a maximized state followed by stabilization to a lower current density value. After termination of the exposure ($\approx$10 s), the current density falls rapidly to the level of the dark measurements ($J_d$). The bare TiO$_2$ responses for different wavelengths are also shown separately in Figure S10, Text T10, Supporting Information. As we proceed from the bare surface to simple nanoparticle aggregations and finally toward more complex photonic crystal slabs, the area of the TiO$_2$ layer exposed directly to the incident excitation gets significantly reduced resulting in decreased current density values. Interestingly, the randomly arranged AuNPs based structure at 365 nm exhibits higher ($\approx$1.94 times) than the bare TiO$_2$ case (solid vs dashed), which can be contributed to the enhanced scattering and absorption from nanoparticles.[49] In all these cases, where metals are included, we observe a slow rise and a relatively faster fall in the photoresponse except at cPhC slabs, where the additional PR layer increases the decay time. At 565 and 660 nm light exposures, we observe current modulation due to the charge transfers mediated by localized surface plasmon resonance of single nanoparticles[50] at 504 nm and aggregations[51] at 686 nm, (Figure S5c, Supporting Information), respectively. For the mPhC slabs, periodic exposure at 565 nm creates a weak photoresponse covered with background noises; the response becomes stronger as the excitation wavelength is increased toward the hybrid modes. The maximum current density can be observed at 780 nm excitation (hybrid mode at 763 nm), which decreases as the excitation wavelength further increases. Thus, compared to bare TiO$_2$, an enhancement in the current of $\approx$68 times has been recorded with mPhCs at 780 nm. A similar conclusion can be drawn toward cPhC slabs showing significant photoresponses only at 780 and 880 nm (hybrid mode at 836 nm). Thus an enhancement in the current by $\approx$20- and $\approx$24-fold has been recorded at these two wavelengths while comparing the performances of the cPhC slabs over the bare TiO$_2$ structures. The excitation at 1050 nm is close to the plasmonic resonance (1038 nm, Figure 3b-ii) of the cPhC slabs; still, the plasmons decay in a radiative way rather than via non-radiative hot electron generation as observed from the current density data corresponding to such wavelengths. The span of the ordinates, that is, the $J$ values in these 2D plots covering the area of interest (565 to 1050 nm) is kept constant for a better qualitative comparison. Since the photoresponse is also a function of the source power, the “incident photon to current conversion efficiency” ($IPCE$),[5,15] defined as the ratio of photo-enhanced current density ($J_{ph} = J - J_d$) and irradiance, is taken into account for better comparison (Figure 5a). Also known as “external quantum efficiency,” this is a straightforward way[52] to compare photoresponse of solar cells and phototransistors by correlating the photogenerated electrons to the incident photons, unlike the “internal quantum efficiency,”[43] which takes into account of the photons absorbed. Details of the photo-dependent device parameters to evaluate these performances can be found in Table S2 and Figure S1, Text T5, Supporting Information, where $J_{ph}$ is averaged over five cycles of the “on/off” states. The error bars in Figure 5a provide the standard deviation of the recorded $IPCE$ over these cycles. The data confirm the random particles to be effective at lower wavelengths.

Figure 5. $IPCE$ calculation and polarization-dependent current density. a) $IPCE$ of the three resonant geometries, that is, random NPs, mPhCs, and cPhCs are calculated and plotted in logarithmic scale using unpolarized light for photoexcitation at wavelengths of interest. Current density ($J$) plot for b) mPhCs and c) cPhCs of 500 nm periodicities under polarized collimated illumination with 780 nm LED source and a bias voltage of 1 V, showing the cases of b, i) hybrid mPhCs , c, i) hybrid cPhCs, b, ii) non-hybrid mPhCs, and c, ii) non-hybrid cPhCs.
However, at higher wavelengths like 780 nm, both mPhCs and cPhCs show an advantage over random NP arrangements. Further, at 880 nm, the cPhC provides a distinct performance among all the three systems under observation.

To highlight the significance of the polarization onto the existence of the supported hybrid modes, polarized photoreponse measurements are repeated at the single wavelength of 780 nm that is effective in charge transfer for both of the photonic crystal slabs. Figure 5b,c, shows the differences in $J$ under the polarization reliant hybrid and non-hybrid cases in mPhC and cPhC slabs. Due to the reduction of the polarized source power, we observed half the intensity, yet quick responsivity of the enhanced signal for TM polarization while using the mPhC slabs (Figure 5b-i). Switching to the TE polarization resulting in a non-hybrid case, where plasmons cannot be excited, we observe only the effect of the dark current (Figure 5b-ii). For the cPhC slabs, the hybrid configuration under TE polarization shows photoreponse as compared to the non-hybrid case of the TM polarization (Figure 5c-i). At this current wavelength of operation, the single or aggregated nanoparticles cannot be excited (shown before in Figure 4a-iv), which also resulted in only a dark current in the TM polarization (Figure 5c-ii). Thus, these results confirm the use of polarization states as photo-switches to initiate and terminate the resulting current. Further by altering the degree of polarization, “photo-switchable gate” based phototransistors can be achieved out of these m/c PhCs, which is discussed in the Conclusion section. Although our simple measurements demonstrated the necessity of the wavelength selective guiding (by choosing distinct LEDs), as well as the plasmonic–photonic coupling (by polarization-selective hybridization) for the generation of plasmon mediated hot-electrons, its direct comparison to the currently available photodetector devices (Table S3, Text T5, Supporting Information) indicates the necessity of further improvements through optimization of the introduced m/c PhC slabs

2.5. Ultrafast Transient Measurements

So far, we have proved that the photoconducting characteristics as a result of charge transfer are solely dependent on excitation wavelength as well as the polarization. The hybridized modes can significantly reduce the radiative damping of excited plasmons to generate more hot electrons. The injection mechanism of the generated hot electrons into the adjacent semiconductor waveguide can be observed through an ultrafast transient pump-probe method,[22,26] where the amplitude of the signal is directly proportional to the number of electrons injected. The benefits of hybrid modes have been so far characterized by the tuning of the periodicity[22,26] that involves the fabrication of multiple structures. Similar proof with lesser efforts can be provided by externally tuning the incident pump and probe beam polarization incident on our “fixed-period” photonic crystal slabs. We investigate such polarization tuning[53] of the pump-probe signals to unravel the plasmonic non-radiative decay at the femtosecond scale. Metallic PhC slabs have previously been explored under pump-probe systems with different pump and probe wavelengths.[22] Such mPhC slabs required excitation at a lower wavelength (hybrid state) along with probing the TiO$_2$ matrix with broader wavelengths corresponding to the region of absorption. To avoid such a complex setup we have used a simpler scheme (Figure S12, Text T6, Supporting Information), where the pump and probe beams are generated from a common source (Titanium Sapphire laser) operating in the range of 770–830 nm. Additionally, we have introduced sophistication by tuning the individual polarization of the pump and probe to distinguish between the hybrid and non-hybrid cases for both m/c PhC slabs. This technique allows us to pump and probe at the same polarization to repeat literature results whereas proceeding a step further, we can discover other non-radiative decay channels.

Figure 6 shows the ultrafast transient transmittance characteristics of the photonic crystal slabs categorized into hybrid and non-hybrid cases corresponding to different polarization states. Depending on these states, the pump beam excites different resonance mechanism, shown via the characteristic spectra in the inset. These spectra are taken from the experimentally recorded dataset (see Figure 3). The probe beam collects the pump-induced changes in the transmittance at a specific wavelength and polarization state. Starting with the “TM pump/TM probe” polarizations on the mPhC slabs, we observe high amplitude and a moderate lifetime. This high amplitude is related to the hot electron transfer that resulted in photo-enhanced current, as detected from the previous figure (Figure 5b-i). Shifting to the “TE pump/TM probe,” which excites the photonic mode and collects the hybrid mode response, results in a dark current generation. With this polarization-dependent probing, we observe a non-radiative decay channel excited by the photonic mechanism only. This non-radiative decay can be related to a weak energy transfer from the photonic mode to the hybrid mode showing a similar lifetime but reduced amplitude in comparison to the “TM pump/TM probe” case. Interestingly, at the exact opposite case with a “TM pump/TE probe,” we reverse the process to result in a “plateau” instead of a sharp rise, followed by a slower decay of the transient signal. Hence, although exciting the hybrid modes, we can only observe the effect related to a photonic process resulting in no photon to electron conversion and a higher lifetime of the generated electrons. Coming to the more straightforward case of “TE pump/TE probe,” we are excite as well as observing the photonic modes only; the amplitude is similar to the previous case, resulting in no photocurrent case in Figure 5b-ii. With this, we complete the cycle of altering the polarization configurations, thus observing the sequential impact of coming from a hybrid case (“TM pump/TM probe”) to a non-hybrid one (“TE pump/TE probe”).

Changing our focus to the cPhCs, we investigate and confirm similar polarization dependency on the plasmonic charge transfers. Note, that the hybrid modes can now be excited with TE polarization for the cPhC slabs. We start with a “TE pump/TE probe,” to excite and observe the hybridized chain mode related plasmonic charge transfer. Due to the presence of the insulating layer around the nanoparticles, a lower amplitude is obtained reflecting a lesser number of electrons transferred into the semiconductor. This is directly related to the observed photoresponse in Figure 5c-i, which is lower by
an order of magnitude than the hybrid mPhC slabs. For the “TM pump/TE probe” case (analogous to “TE pump/TM probe” case of mPhCs), this excites the photonic mode and collects the hybrid mode response, resulting in a dark current generation. For the “TE pump/TM probe case,” the hybrid mode excitation although made feasible, is hindered by the probing

Figure 6. Pump-probe investigation on the metallic photonic crystals and colloidal photonic crystals: Pump-probe data operated at various pump-probe polarization for a) metallic PhCs and b) colloidal PhCs. Inset shows broadband transmittance spectra of the m/c-PhCs under the stated polarization. c) The amplitude of the rising edge of the pump-probe spectra is plotted and compared from the transient signals of m/c-PhCs under different polarization configurations. These polarization states for the pump-and probe beam are provided separately in the figure. d) The lifetimes of the transferred electrons are calculated for these different polarization configurations of the pump and probe signals affecting the hybrid resonant (mPhCs and cPhCs) systems. The sub-figures (i-iv) representing the different polarizations are addressed in the text.
mechanism resulting in low amplitude but a higher lifetime (analogous to the “TM pump/TE probe” case of mPhCs). As we move to the “TM pump/TM probe” case, the transient signal is diminished explaining the null photoresponse (Figure 5c-ii). In general, the occupation of electrons in the conduction band of TiO₂ results in a broadband transient signal occurring from 600 up to 3000 nm. [54] Since the coupled states also exist in this wavelength span (773 and 836 nm for the mPhC and cPhC structures, respectively), the degenerate pump-probe setup thus becomes handy in the measurement of the transient phenomena. The rise and descent of the ΔT/T spectra thus express the plasmonic hot-electron transfer and the decay of these transferred electrons through electron–electron and electron–phonon scattering. [26] For a direct comparison of the amplitude and lifetime of such transient spectra under the aforementioned polarization configurations, we have provided Figure 6c,d. The lifetimes have been extracted by fitting a single exponential function to the plotted spectra with the observed time frame of 8 ps (Table S4 and Figure S13, Text T6, Supporting Information). For calculating the decay over a longer period (>100 ps), a biexponential function is more suitable [26] to demonstrate the rapid fall (<5 ps), followed by a slower decay. [22] Figure S14, Text T6, Supporting Information provides such fitted decay curve corresponding to the hybrid case in mPhC slabs under “TM pump/TM probe” investigations.

2.6. Plasmonic Charge-Transfer Mechanisms in m/c Photonic Crystal Slabs

Once, acquired with relevant experimental observations, we now discuss these results in terms of the charge transfer mechanisms occurring in these m/c PhCs. It should be noted that several strategies, both direct, [3,26] and indirect, [55] have been employed recently to observe the plasmonic hot-electron transfer in metal/semiconductor heterojunctions. In contrast, we have applied simple electrical and optical schemes to confirm such charge transfers. As realized, the TM (/TE) polarizations for the mPhCs (/cPhCs) can result in hybridized guided modes to excite the constituent plasmonic blocks (Au nanobars or AuNP chains) as well as suppress the plasmonic radiative losses via photonic waveguiding. Figure 7a describes schematically the cross-sectional profile of the m/c PhC structures under electrical characterization. The grating can be considered of periodically arranged Au nanobars or AuNP chains with deposited macroscopic Au electrodes in close contact with the semiconductor TiO₂ layer. The 780 nm LED wavelength, among all the other available LED sources has been successful to excite the hybrid guided modes within the semiconductor slab; this, in turn, has resulted in the generation of metallic nanostructures into the conduction band of the TiO₂ semiconductor layer. These excess electrons in the TiO₂ thus have given the

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**Figure 7.** Plasmonic charge transfer mechanism in m/c PhCs. 
(a) Hybrid structures (mPhCs/cPhCs) with plasmonic nanobars/nanoparticle chains in close association with a photonic waveguide can result in guided modes of specific wavelengths. The schematic explains the guiding of the 780 nm diffracted orders (±1), within the photonic crystal slabs with 500 nm grating periodicity and 200 nm slab thickness to result in plasmonic hot electrons (shown as “e–”). 
(b) Energy diagram showing the charge transfer mechanisms of the hot electrons generated via hybrid plasmonic excitations. These electrons in the metallic nanostructures can be injected into the TiO₂ conduction band to get an enhanced current signal, specific to the resonant excitation wavelengths. 
(c) Influence of a dielectric layer in between metallic nanostructure and semiconductor. i–iii) describe the cases of mPhC slab, cPhC slab, and similar metal/semiconductor junctions with finite dielectric thickness in between them.
enhanced current signal on periodic excitation of the metallic nanostructures, as shown in Figure 4. It should be noted, that the simultaneous guiding, as well as absorption by the metallic nanostructures, was important to realize the coupled photonic–plasmonic mode which is unlikely in the other wavelength cases. Figure 7b shows the generalized energy diagram related to our discussed m/c PhCs with a TiO2 bandgap\[59\] \((E_g = E_{CB} - E_{VB})\) of 3.3 eV. The generation of abruptly high \(J\) for 365 nm (\(hν = 3.4\) eV) points to the fact that excitation with energy higher than this TiO2 bandgap can result in direct electron–hole separation and subsequent transfer of charges to the electrodes. For the plasmonically excited hot-electrons with the kinetic energy larger than the Schottky barrier between gold and TiO2, these electrons can be diffused into the TiO2 layer and collected by the electric field applied between two electrodes.\[56\]-\[57\] The drift current is expressed as \(J_{\text{drift}} = \sigma E\), where \(\sigma\) is the conductivity of TiO2 and \(E\) is the applied electric field.\[58\] Electron–hole pair recombination can be caused by an electron from the electric field between the electrodes.

In the current study, the yield of photo-enhanced current is smaller for the case of cPhCs, in comparison to the mPhCs as further confirmed from the pump-probe measurements with polarizations specific to the hybridization conditions. The number of electrons injected into the charge carriers with sufficient energy and momentum to overcome the Schottky barrier from TiO2 matrix, being directly proportional to the transient signal amplitude, points out the drawback of the cPhCs system. The low current detection for the cPhCs can be attributed to two main reasons: the presence of a non-conductive layer around the particles, and the presence of a non-necessary PR layer for assembly of the particle chains, both of which hinder the electron transfer process. The defects present in the arrangement of the nanoparticle chains in the cPhC slabs also play a crucial role in reducing the efficiency as compared to the continuous bars in mPhC slabs. Figure S15. Text T7, Supporting Information demonstrates a filling rate of around 58% for the particle chains in cPhC slabs. By improving the directive self-assembly process, we can reach a limit of almost cent-percent filling that can also increase the efficiency. Moreover, in contrast to the metallic bars, the surface area in contact with the semiconductor for the spherical nanoparticles is drastically smaller, as observed from the cross-sectional FIB-cut images in Figure 2a-iii,b-iii. This lowers the possibility of electron transfer in cPhC slabs resulting in a lesser magnitude of recorded current densities in photoresponse measurements and diminished amplitude of the pump-probe spectra as compared to the cases of mPhC slabs. As a possible solution, one can re-deposit a TiO2 layer to partially embed the nanoparticle chains, thus increasing the contact surface area. However, this needs careful consideration of the factors such as chances of deviation from the optimum waveguide thickness to favor the plasmonic–photonic coupling.

As a future goal, it thus becomes important for colloidal society to solve the bottleneck of non-conductive polymer coating through the removal of the ligand shell or by replacing it with a conducting polymer that conducts at the exact wavelength of the plasmon resonance.\[59\] By using a conducting ligand, charge carrier transport can be enhanced.\[60\] The challenge is therefore to attach a ligand to the “coinage” metal nanoparticles in a way that favors the electronic exchange. However, this can no longer be referred to as a classic Schottky barrier because of the involvement of two different mechanisms: first, a system with a classical Schottky barrier relating to the transfer of a hot charge carrier to an adjacent semiconductor; and second, the transfer of a hot charge carrier to an attached adsorbent (i.e., polymer ligand). While the mechanisms of the individual systems have been much discussed,\[59\] effects arising from the combination of the two systems are entirely unknown that needs to be thoroughly investigated. Another way to mitigate the problem of the insulating ligands on the Au nanoparticles is to coat the Au nanoparticles with a thin TiO2 shell\[61\] before assembling them onto the TiO2 layer through directive self-assembly. In such cases, the TiO2 shells can even be modified with specific photosensitizers to enhance the plasmonic effects. To get rid of any additional underlying photoresist, different means of transferring colloidal nanoparticle chains\[31,48\] directly onto a semiconductor layer can be explored for such cPhC slabs. The obtained differences between the responses of the mPhC and cPhC slabs in Figures 4 and 6, thus can be visualized in terms of the specified energy diagrams, as shown in Figure 7c. Since the Schottky barrier height plays an important role in the charge transfer, several strategies have been considered recently in modifying the TiO2 layer and lowering the barrier to enhance the photocurrent yield.\[62\] For the current case of Au/TiO2 heterostructure with a typical barrier height \((=1\) eV\[15,22\]), the excited hot-electrons with sufficient kinetic energy can overcome the Au–TiO2 interface and get injected into the conduction band of TiO2, as shown for the mPhC slab case in Figure 7c-i. The Schottky barrier height at the interface between Au and TiO2 can be considered as \(\approx 1.0\) eV, according to the difference between electron affinity of TiO2 (\(\approx 4.0\) eV) and work function of Au (\(\approx 5.0\) eV). Since the property of the metal-semiconductor interface (e.g., defects or non-uniformity\[63\]) affects the characteristics of the junction, the junction height has been reported in the range of 0.9–1.2 eV experimentally.\[62,64,65\] In contrast, the existence of the insulating layer in cPhCs with even 2 nm thickness provides hindrance in the electron transfer process (Figure 7c-ii). Since the polymer ligand comprising this thin-insulating layer is polyethylene glycol (PEG), there may be a presence of defects due to its semi-crystalline nature in a dry environment. However, the insulating nature of PEG provides more hindrance to the charge transfers than the presence of such defect states. A more straightforward conclusion can be drawn with a thick insulator layer right next to the plasmonic nanostructures,\[22\] which would result in null charge transfer as shown in Figure 7c-iii. This can be directly related to the case of an additional PR layer remaining above the TiO2 layer during the grating fabrication.

### 3. Conclusion

In summary, we have demonstrated both conventional and non-conventional plasmonic–photonic coupling in metallic and cPhCs fabricated through cost-efficient and upscalable
get a pure plasmonic counterpart, gold was sputtered directly on glass substrates and lifted-off similarly.

**Gold Nanoparticle Synthesis:** The synthesis of spherical AuNPs was carried out by a seed-mediated growth process.\(^{61}\) As a result 76.9 ± 1.5 nm diameter (averaged over 100 particles) gold nanoparticle capped with hexadecyltrimethylammonium chloride were achieved. In short, PEG stabilized nanoparticles in water were synthesized in three major steps. First, so-called Wulff seeds were produced by reducing tetrachloroauric acid (HAuCl\(_4\)) with sodiumborohydride (NaBH\(_4\)) in the presence of hexadecyltrimethylammonium bromide (CtaB). This process led to 2 nm large single-crystalline nanoparticles. Second, these particles were further grown in size with the help of two more consecutive synthesis steps until they reached the desired particle diameter. During the growth process, HAuCl\(_4\), ascorbic acid, and CtaC served as the Au precursor, reductant, and stabilizing agent, respectively. To achieve the kinetic control and hence to modulate the particle shape, a syringe pump system was used for the last growing step. In the final step, the particles were washed and purified by centrifugation process and set to a surfactant concentration of 2 mM. To provide the long-term colloid stability to the nanoparticles in the colloidal suspension of water, a ligand exchange was performed from CtaB to PEG-6K-SH.\(^{62}\)

**Directed Self-Assembly toward Colloidal Photonic Crystals:** The fabricated dielectric GMR sample was UV flood-exposed (UV-15 S/L, Herolab) at 254 nm for 10 min and subsequently hard-baked at 120 °C for 4 min on a hot plate to reduce the swelling and leaching out of the PR while in contact with the slightly alkaline particle solution. Oxygen plasma treatment (30 s, 0.2 mbar, 80 W, Flecto 10, Plasma Technology) before the convective assembly experiments\(^{69}\) created good wettability of the substrate that was fixed to a motorized translation stage (PLS-85, Physik Instrumente). A cleaned glass slide (Menzel) was mounted above the GMR photonic slab at a distance of 0.5 mm, and 25 Å of NP solution (0.5 mg mL\(^{-1}\), gold, pH 9) was placed in between the gap. The elevated pH value ensured a strongly negative surface charge of the protein coating (~30 mV)\(^{70}\) to provide electrostatic stabilization of the colloidal suspension. A constant linear motion at the rate of 1 μm s\(^{-1}\) was imparted to the stage through a computerized software system to recede the contact line in a direction parallel to the channels. The stage temperature was set to 14 K above the dew point to control the evaporation rate at the meniscus that drove the transport of NPs toward the three-phase contact line. Lateral confinement by the channel geometry and a vertical one determined by the thickness of the liquid film inside the channels enabled the selective crystallization of the metallic nanoparticles into double (dimer) lines to form the cPhCs. To get the pure plasmonic counterpart, the photonic GMR sample was replaced by a glass substrate with negative resist grating, and the process was exactly repeated.

**UV–Vis–NIR Spectroscopy:** UV–vis–NIR Spectrophotometer (Cary 5000, Agilent Technologies) in transmission geometry was used for recording optical responses. A rotatable polarizer was used to investigate the effect of both the polarization (pol), s-pol (TE), or p-pol (TM) where the electric fields were out of the plane and in-plane to the plane of incidence, respectively.

**Finite-Difference Time-Domain Simulations:** A commercial-grade simulator based on the FDTD method was used to perform all the calculations (FDTD: 3D Electromagnetic Simulator\(^{71}\)). For the simulation of the optical response, a plane wave source was used and the frequency points were set equal to that of the wavelength span. Monitor boxes (transmission monitors kept normally to the substrate) were used to obtain the optical responses of the systems. For the dielectric function of gold, data from Palik\(^{27}\) was fitted using six coefficients with an RMS error of 0.2. For the photoresist, TiO\(_2\) layer, and glass substrate, optical constants were used from Sarkan et al.\(^{38}\)

The mesh size in the FDTD region was set to auto non-uniform with an additional mesh overlay of 2 mm applied over the arranged particle geometry. Periodic boundary conditions were applied for X and Z directions with perfectly matching layers along the Y direction. All simulations reached an auto-shut-off of at least 10\(^{-7}\) before reaching 300 fs simulation time.
**Photoresponse Measurements: Gold electrodes (layer thickness: 60 nm, channel length: 220 µm, width: 4500 µm) were deposited by electron-beam evaporation using a shadow mask. For the current applications, the electrodes were placed parallel to the grating structure. The current between two electrodes was measured and recorded by a Keithley SMU (2612B, Keithley) with the probe station (MDI company, Taiwan), to which the Beryllium Copper probe (25 µm radius) were attached. The light sources were LED lights from Thorlabs, with a wavelength of 365 nm, 565 nm, 780 nm (M780L3), 880 nm (M880L3), and 1050 nm (M1050L4), operated via a controlling unit (DC4100). Light was irradiated from the top of the devices with a constant distance between LEDs and devices of 2 cm. The power of the LED sources was measured by a silicon photodetector (S120VC, Thorlabs) connected to an optical power meter (PM100D, Thorlabs). During the photocurrent measurement, a DC bias (1 V) was applied to collect the generated electrons. All the measurements were conducted under ambient conditions.

**Ultrasfast Pump-Probe Spectroscopy:** Femtosecond time-resolved optical pump-probe spectroscopy was carried out in a non-collinear geometry using a Ti:Sapphire based 35 fs amplified system (Astrella, Coherent) operating at 1 kHz pulse repetition rate and 800 nm central wavelength. A beam splitter was used to separate a weak probe pulse from the main laser beam and sent through a computer-controlled linear translational stage. The pump fluence was varied using a continuously variable neutral density filter and the probe fluence was kept fixed at <$5 \mu J/cm^2$ (=100 MWcm$^{-2}$). The pump beam was modulated at 237 Hz with the help of an optical chopper, and the probe signal was detected using the standard lock-in detection scheme at the chopper frequency. To improve the signal to noise ratio, a weak reference beam was also taken on another photodiode and the difference of the signal with the reference was measured on the lock-in amplifier. The time-delay between the pump and probe pulses could be varied continuously in a large range and a step size better than 6 fs. The polarization of pump and probe beams were adjusted through half-wave plates and linear polarizers. The pump and probe beam diameters on the sample were kept at $\sim 1$ and 0.6 mm, respectively. For the mPhC system, the pump fluence = 10.2 GWcm$^{-2}$, probe fluence = 0.8 GWcm$^{-2}$ whereas for the cPhC system, pump fluence = 28 GWcm$^{-2}$, probe fluence = 2 GWcm$^{-2}$.

### 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

The data that support the findings of this study are available from the corresponding author upon reasonable request.

### Keywords

charge transfer, light trapping, photocurrent, plasmonic nanoparticles, self-assembly

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