Noble-metal-free plasmonic photocatalyst: hydrogen doped semiconductors

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The unique capacity of localized surface plasmon resonance (LSPR) offers a new opportunity to overcome the limited efficiency of semiconductor photocatalyst. Here we unravel that LSPR, which usually occurs in noble metal nanoparticles, can be realized by hydrogen doping in noble-metal-free semiconductor using TiO₂ as a model photocatalyst. Moreover, its LSPR is located in infrared region, which supplements that of noble metal whose LSPR is generally in the visible region, making it possible to extend the light response of photocatalyst to infrared region. The near field enhancement is shown to be comparable with that of noble-metal nanoparticles, indicating that highly enhanced light absorption rate can be expected. The present work can provide a key guideline for the creation of highly efficient noble-metal-free plasmonic photocatalysts and have a much wider impact in infrared bioimaging and spectroscopy where infrared LSPR is essential.

Despite four decades of efforts including doping¹⁻³, heterojunction⁴⁻⁵, graphene-based composition⁶⁻⁷, and cocatalyst⁸⁻¹⁰ to improve their photocatalytic performance, large-scale application of photocatalysts, such as TiO₂ and ZnO, is still significantly inhibited by their narrow light absorption range and large carrier recombination rate¹⁰⁻¹². More recently, the localized surface plasmon resonance (LSPR) of noble metal nanoparticles (NPs) is introduced into the field of photocatalysis¹³⁻¹⁴, and the unique capacity of LSPR to amplify electromagnetic field and scatter electromagnetic radiation for a wide range of solar light wavelengths offers a new opportunity to overcome the limited efficiency of semiconductor photocatalyst. For example, depositing Ag or Au nanoparticles on TiO₂ significantly enhance the photocatalytic quantum efficiency and extend the light absorption range¹⁵⁻¹⁷. Our group also synthesized the classic Ag@AgX (X = Cl, Br, I) plasmonic photocatalysts¹⁸⁻²¹ which show remarkable absorption over the whole ultraviolet and visible light range. However, it is noteworthy that the degradation of noble metals especially silver on exposure to air will significantly reduce the lifetime of this kind of plasmonic photocatalyst²², the high cost and heavy metal pollution will also limit their large-scale application. On the other hand, studies aimed at utilizing near-infrared light constituting about 44% of sunlight are relatively rare²³⁻²⁴. Therefore, exploring a noble-metal-free photocatalyst with LSPR effect in the near-infrared range has great scientific value and practical meaning.

As is known, the LSPR may occur as the free carrier concentration in NPs is large enough, thus we aim to explore the possibility of realizing LSPR in the commonly used semiconductor photocatalyst TiO₂ by heavy doping. Since TiO₂ samples are never perfectly stoichiometric, and are usually in reduced form showing n-type conductivity²⁵, we pay our attention on the n-type doping. To achieve heavy doping, there are two particular requirements of the dopant: solid solubility and donor level. Recently, it is experimentally reported that the electron carrier concentration of TiO₂ could reach 7.8 × 10⁻⁵⁰/cm² after hydrogen plasma treatment²⁵, indicating that hydrogen may have a good solubility and moderate donor level, and they tentatively attribute the strong visible and infrared light absorption to the LSPR induced by this high carrier concentration. By the way, it is one of our purposes to verify the origin of the large carrier concentration and if the concentration could induce LSPR and hence contribute to the light absorption. In addition, the large carrier concentration and interband transition often lead to prominent energy loss. On the other hand, studies aimed at utilizing near-infrared light constituting about 44% of sunlight are relatively rare²³⁻²⁴. Therefore, exploring a noble-metal-free photocatalyst with LSPR effect in the near-infrared range has great scientific value and practical meaning.
Results

Solubility and donor level. In thermodynamic equilibrium, the solubility of dopant in the semiconductor lattice is determined by the formation energy $E_f$ through equation (1)

$$
\eta = N_{sites} \exp (-E_f/kT)
$$

Where $\eta$ is the resultant concentration of dopant, $N_{sites}$ is the number of sites in the lattice where the dopant can be incorporated, $k$ is Boltzmann’s constant, and $T$ is temperature in kelvin. The formation energies of $H_i$ and $O_2$ in charge state $q$ are defined as $33$

$$
E_f(H_i^q) = E(H_i^q) - E(host) - E(H) + qE_F
$$

$$
E_f(O_2^q) = E(O_2^q) - E(host) - E(H) + \frac{1}{2} E(O_2) + qE_F
$$

Where $E(z)$ is the total energy of system $z$. The reference for hydrogen energy is given by an $H$ atom assuming hydrogen plasma environment and that for oxygen energy is given by an $O_2$ molecule since the substituted oxygen atoms generally form $O_2$ molecules. The last term in the formation energy accounts for the fact that $H_i^+$ ($H_i^0$) donates an electron, and $H_i^-$ ($O_2^+$) accepts an electron; $E_F$ denotes the energy of the reservoir with which these electrons are exchanged and is equal to the Fermi level of the system. By the way, we note that if one use $H_2$ molecule as dopant source, the formation energy will be increased by 2.27 eV due to the large binding energy of hydrogen in $H_2$. As a result, the solubility will be significantly reduced.

For $H_i$, a variety of possible interstitial sites are investigated to identify the stable location of $H_i$ in TiO$_2$, and two local stable sites are determined with an energy difference of 0.53 eV between them, which is consistent with a previous report$^{14}$. In the following we mainly focus on the most stable configuration (Figure 1b), since it is the dominant species from the perspective of thermodynamic stability. Figure 2 shows the formation energies of $H_i$ and $O_2$ in different charge states with respect to the Fermi level. The formation energy of neutral $H_i$ is negative with a value of $-1.88$ eV, which indicates a release of energy upon the defect formation; and that of positive $H_i$ is even more negative across the bandgap. Hence we infer that this kind of doping is highly favored according to equation (1), and one may expect an almost indefinite increase in the doping concentration once the hydrogen atom crosses the crystal surface and diffuses into the lattice. Fortunately, it is revealed that the energy barrier for the $H$ atoms to migrate from the crystal surface into the bulk is quite moderate with a value of $0.70$ eV$^{28}$ and the transfer barrier of $H$ atom in the lattice is experimentally determined to be only about $0.09$ eV$^{29}$. Therefore, the incorporation of hydrogen into TiO$_2$ lattice to a high solid solubility is experimentally achievable. However, it has to be kept in mind that the defect formation energy is also a function of its concentration, and it increases with increasing concentration. Thus the doping concentration will not increase infinitely. Nevertheless, the formation energy of $H_i$ corresponding to a concentration of about $7.41 \times 10^{21}$/cm$^3$ is only increased to $-1.33$ eV, then doping concentration in this order of magnitude or higher can be realized in $H_i$ doped TiO$_2$. In addition, it is indicated that $H_2$ readily dissociates and forms two $HO$ species exothermically$^{30}$, thus the high concentration of $H_i$ will not form $H_2$ which eliminates the donor properties of $H_i$.

For the case of neutral $H_2$ defect, the formation energy with a value of $1.84$ eV is obtained. At equilibrium, the $H_2$ concentration is estimated to be on the order of magnitude of $10^{11}$/cm$^3$ by hydrogen plasma treatment at 500°C. And the smaller formation energy of positive $H_2$ across the bandgap implies a larger solubility. Moreover, once the oxygen vacancy ($O_V$) previously forms during the preparation process of TiO$_2$, which is the usual case, the formation energy will reduce to $-3.13$ eV. This large negative value clearly indicates readily occupation of $H$ atoms in the oxygen vacancy sites, thus fully eliminating the oxygen vacancies in the host lattice, and its beneficial results will be discussed in the following.

Figure 1 | The crystal structures used for our calculations. (a) The supercell model. The local geometric structures of (b) $H_i$ and (c) $H_2O$ doped TiO$_2$. The sky blue, red, and pink balls represent Ti, O, and H atoms, respectively.

Figure 2 | Formation energies of $H_i$ and $H_2O$ in different charge states with respect to the Fermi level $E_F$. The range of $E_F$ corresponds to the bandgap with $E_F = 0$ at the VBM.
To achieve effective n-type doping, thus getting high concentration of free carriers in the doped semiconductor at thermodynamic equilibrium as that of metal, the donor level \( D_{1/0} \) of the dopant, which is defined as the Fermi level position where the formation energies of charge states \( 1 \) and \( 0 \) are equal\(^{33}\), must be close to or resonant with the conduction band. Satisfyingly, as shown in Figure 2, the donor levels of both \( H_i \) and \( H_o \) are in resonance with the conduction band, suggesting that the electron can be effectively injected into the conduction band, thus contributing to n-type conductivity. Therefore, the high solubility of \( H \) dopant, together with the shallow donor level, can promise a large carrier concentration, and this results can be used to account for the large n-type conductivity and carrier concentration \((7.8 \times 10^{20}/\text{cm}^3)\) of TiO\(_2\) film after hydrogen plasma treatment observed experimentally\(^{25}\).

Electronic structures. In order to reveal the origin of the high solubility and shallow donor levels of \( H_i \) and \( H_o \), a closer look at the electronic structures of the doped system is helpful. Figure 3a shows the density of states (DOS) of perfect and \( H_i \) doped TiO\(_2\), as well as the projected density of states (PDOS) on hydrogen and oxygen to which the hydrogen bonds. Clearly, there are no defect levels in the bandgap and a sharp peak located at 6.8 eV below the valence band maximum appears upon \( H_i \) doping. The PDOS shows that the peak is a hybridization of \( H_1s \), \( O_2s \), and \( O_2p \) states, and the other superposition states of these three orbitals are located in the conduction band. This picture is consistent with the bonding and antibonding character of the orbitals, which can be understood from the molecular orbital theory, as pictorially presented in Figure 4a: to bond with hydrogen \( 1s \) orbital, the \( 2s \) and \( 2p \) orbitals of the oxygen must form a symmetric \( (a_1) \) combination premised on principles of orbital symmetry matching\(^{37}\), moreover, since the oxygen \( 2s \) and \( 2p \) orbitals are fully occupied, one of the three electrons has to occupy the antibonding orbital which is located in the conduction band without introducing gap states, thus resulting in a shallow donor level in resonance with the conduction band, as indicated in the preceding part. In addition, the strong bonding between hydrogen and oxygen, as implied by the lower lying bonding states, ensures the small formation energy of \( H_i \) and hence large solubility. Furthermore, the electronic charge density distribution of the fully symmetric bonding states between hydrogen and oxygen clearly reveals a
strong polar O-H σ bonding orbital (Figure 5a), which is consistent with the analysis based on molecular orbital theory. Finally, we note that the shallow donor nature of H in anatase TiO$_2$ is also consistent with the prediction of the model of hydrogen universal alignment proposed in Ref. 33 and 38.

For Ho, the occupation of hydrogen atom in the oxygen vacancy site effectively eliminates the gap states introduced by O$_v$ and makes the donor level lie in the conduction band, as shown in Figure 3b, thus contributing more free carriers. This phenomenon can be easily understood due to the formation of hydrogen multicenter bonds with the adjacent three Ti atoms: The PDOS on H and the nearest-neighbor Ti atoms exhibit strong hybridization, which is the indication of strong bonding between H and Ti atoms; Moreover, the PDOS on all three adjacent Ti atoms are almost the same due to the combination of the three Ti 3$d$ dangling bonds to form a symmetric (a$_1$) orbital, and the detailed process of orbital interaction is pictorially illustrated in Figure 4b. Further analysis of electronic charge density distribution of the hydrogen multicenter bonds also reveals that the hydrogen bonds almost equally to the three adjacent Ti atoms (Figure 5b). Therefore, the bonding of H with adjacent Ti atoms makes the antibonding state, which is also the donor level, lie in the conduction band. In addition, since the gap states generally promote the recombination of photogenerated carriers, the removal of these states by hydrogen doping can result in low recombination rate of electrons and holes as revealed by the photoluminescence (PL) emission spectra measurement. Moreover, since hydrogen doping can effectively eliminate the Ti$^{3+}$ ions, the electron paramagnetic resonance (EPR) signal of Ti$^{3+}$ will also disappear after hydrogen doping, as observed in Ref. 25.

Finally, the charge density distribution of the donated electrons by H$_i$ and H$_o$ (Figure 6) shows that the doped electrons by both H$_i$ and H$_o$ are well delocalized among the Ti atoms, indicating effective n-type doping, which is also consistent with the absence of Ti$^{3+}$ spins revealed by the EPR measurement. In addition, the itinerant nature of the doped electron also accounts for the experimentally observed high conductivity. The significant local lattice distortion induced by H$_i$ doping, as shown in Figure 1b, rationalize the formed amorphous disordered shell of TiO$_2$ nanocrystals after hydrogen plasma process, as this process can introduce large amount of H$_i$ into the TiO$_2$ lattice. Although large researches indicate that one free electron is often trapped in Ti atoms forming a polaron, thus limiting the conductivity of electron, we note that when large number of electrons populate in the conduction band, the competition of adjacent polarons through their induced structural distortion may free the trapped electrons, which is also verified by the large electron carrier concentration observed experimentally.

**LSPR properties of heavily doped semiconductor.** The results above indicate that hydrogen is an effective n-type dopant, which can introduce large carrier concentration in the order of magnitude of 10$^{21}$/cm$^3$ or even larger. Then what exactly is the carrier concentration that can realize metal-like optical property-LSPR in TiO$_2$? Here, we note that the LSPR requires the real part of the complex

**Figure 4 | Details of orbital interaction between H and the adjacent host atoms.** (a) The interaction between H 1$s$ orbital and the 2$s$ and 2$p$ orbitals of the oxygen to which the hydrogen bonds in H$_i$ doped TiO$_2$. (b) The interaction between H 1$s$ orbital and the dangling bonds (dbs) of three adjacent Ti atoms in H$_o$ doped TiO$_2$. In both cases, the H 1$s$ orbital combines with the fully occupied symmetry-adapted a$_1$ state, resulting in a bonding state in the valence band (VB) and an antibonding state in the conduction band (CB). The electron that would occupy the antibonding state is then transferred to the conduction band minimum, making both H$_i$ and H$_o$ shallow donors.

**Figure 5 | Electronic charge density distribution of the bonding states between hydrogen and host atoms.** (a) Three-dimensional visualization for H$_i$ doped TiO$_2$, the isosurface is at 0.015 electrons Å$^{-3}$. (b) Two-dimensional contour plot for H$_o$ doped TiO$_2$ and the contour plot is on the plane containing hydrogen and the adjacent three Ti atoms.

**Figure 6 | The charge density distribution of the donated electrons by: (a) H$_i$, (b) H$_o$. The atom notations are the same as that in Figure 1.**
permittivity to be a negative value ($\varepsilon' < 0$ for $\omega < \omega_c$), thus it puts a lower limit on the carrier concentration. To get the permittivity of heavily doped semiconductor, we turn to the Drude model $^{29,30}$ which describes the free electron response to electromagnetic wave as equation (4):

$$
\varepsilon(\omega) = \varepsilon_i + i\varepsilon' = \varepsilon_b - \frac{\omega_p^2}{(\omega^2 + \gamma^2)} + i \frac{\omega_p^2 \gamma}{(\omega^2 + \gamma^2)} \omega
$$

Where $\varepsilon_b$ is the background permittivity which describes the polarization response of the core electrons; $\omega_p$ is the plasma frequency; and $\gamma$ is the Drude relaxation rate which is responsible for the scattering and Ohmic losses. Based on the formula, the critical concentration to achieve metal-like properties ($\varepsilon' < 0$ for $\omega < \omega_c$), here $\omega_c$ is chosen to be corresponding to the wavelength of 1000 nm which is relevant to photocatalysis. From the following equation (5), shorter wavelength will require larger carrier concentration) is given by the following equation (5):

$$
n > \frac{\hbar m^*}{e^2 \varepsilon_b} \varepsilon_b \omega_c^2 + \gamma^2
$$

Where $\varepsilon_b$ is the vacuum permittivity, $e$ is the electron charge, $m^*$ is the carrier effective mass, and $\gamma$ is approximated to be $\gamma = e\mu / \hbar$ in which $\mu$ is the carrier mobility.$^{27}$ For our specific sample TiO$_2$, the parameters used for our calculations and results are listed in Table 1.

Surprisingly, the carrier concentration introduced by hydrogen doping can exceed the required critical concentration producing LSPR. Therefore, we further estimate the LSPR effect of TiO$_2$ with this critical carrier concentration. The model of a 2 nm thick spherical shell with a diameter of 20 nm, which is comparable with the experimental samples$^{28}$, is used in our further calculations. The LSPR absorption spectra and the enhanced electric field are shown in Figure 7. The results show that the LSPR wavelength is in the infrared region of the electromagnetic spectra due to the smaller carrier concentration to achieve metal-like properties ($\varepsilon' < 0$ for $\omega < \omega_c$). In addition, the infrared LSPR of highly doped TiO$_2$ can also be readily used in infrared bioimaging and spectroscopy$^{43,44}$, where extending the LSPR of noble metal NPs further into the infrared region is quite challenging.

On the other hand, the enhanced electric field contour also indicates that the near field enhancement of the LSPR effect of the heavily doped semiconductor is comparable with that of noble metal NPs$^{13,45}$. Similar to the LSPR of noble metal NPs, the LSPR wavelength can also be easily tuned by particle sizes, dimensions, and local dielectric environment, to cover a wide range of wavelengths.

According to the above LSPR properties of doped semiconductor, some reasonable LSPR phenomena can be inferred: as the LSPR wavelength is located in the infrared region, the doped semiconductors will show remarkable absorption in this region (Figure 7) in photocatalytic reactions. As another significant effect of LSPR, the near-field enhancement (Figure 7) will not only increase the light absorption rate but also decrease the recombination of photogenerated carriers$^{15}$, thus significantly improving the overall photocatalytic performance of the systems.

### Discussion

For the specific carrier concentration of the samples ($2.27 \times 10^{20}/\text{cm}^3$) reported by Wang et al$^{25}$, the corresponding wavelength for the real part of permittivity to be negative is estimated to be 5617 nm, then the absorption within 2000 nm as reported in the experiment may be mainly due to the intraband transition of the large amount of free carriers rather than LSPR, it is noted that broad absorption peak ranging from visible region to infrared region due to intraband transition of free carriers has also been observed in heavily Nb-doped TiO$_2$. However, when the interband transition is induced by the ultraviolet light, large number of additional photogenerated electrons will be populated in the surface shell, then it may induce LSPR effect near or within 2000 nm. In addition, the photogenerated electrons are recently reported to induce LSPR in ZnO nanocrystals$^{46}$.

In the present work, according to the Drude model, we have estimated the critical concentration of carriers (6.72 $\times 10^{20}/\text{cm}^3$) [Table 1] for TiO$_2$ to show LSPR in the near infrared region in which some kinds of photocalytic reactions can be driven, this critical concentration is found to be significantly higher than that ($2.27 \times 10^{20}/\text{cm}^3$) obtained in the previous work with citation of Ref. 25. Therefore, we conclude that the absorption within 2000 nm as reported in the experiment should be mainly due to the intraband transition of the large amount of free carriers rather than LSPR. In addition, based on the first-principles calculations, it is inferred theoretically that the critical concentration of carriers can actually been obtained by proper hydrogen plasma doping. Thus future work should be devoted to realizing this promising H-doped TiO$_2$ plasmonic photocatalyst.

By the way, because the absorption spectra in the near infrared region of Ref. 25 originate mainly from the intraband transition of

### Table 1 | The parameters used for our calculations of the critical carrier concentration required to make the real part of the permittivity of semiconductor negative at 1000 nm along with the calculated results

| Sample | Background permittivity $\varepsilon_b$ | Mobility $\mu$ [cm$^2$/V·s] | Effective mass $m^*$ [unit of free electron mass] | Critical carrier concentration [x10$^{21}$/cm$^3$] |
|--------|--------------------------------------|---------------------------|---------------------------------|---------------------------|
| TiO$_2$ | 5.27 | 20.58 | 1.45 | 6.72 |
| ZnO    | 3.822 | 52.6* | 0.3822 | 1.62 |

*The carrier mobility is obtained assuming similar relaxation rate as that of TiO$_2$, satisfactorily, this value is similar to that of heavily Al-doped ZnO.*
carriers rather than the localized surface plasmon resonance (LSPR) absorption of carriers, the LSPR absorption presented in the present work is different from the absorption spectra in Ref. 25. Furthermore, it is exclusively because the doping level of hydrogen in their TiO$_2$-H$_x$ sample is not high enough that the LSPR within 2000 nm cannot be induced, whereas the qualitative trends of PL spectra and EPR data should be identical in the present work and Ref. 25.

Additionally, large amount of experimental and theoretical results indicate that hydrogen also has a large solubility and the donor level of H$_3$ and H$_2$O are also resonant with the conduction band in ZnO, another important photocatalyst$^{33,37,47,48}$, thus high carrier concentration should be expected by hydrogen doping in ZnO, too. Moreover, because of the smaller electron effective mass and background permittivity of ZnO compared with TiO$_2$, the critical carrier concentration for it to exhibit metal-like optical properties at wavelength of 1000 nm is estimated to be only 1.616 $\times$ 10$^{27}$/cm$^3$ assuming similar relaxation rate as that of TiO$_2$, indicating that it may be easier to realize LSPR in ZnO by hydrogen doping. The LSPR absorption spectra and enhanced electric field, as shown in Figure 7, demonstrate similar LSPR properties as that of TiO$_2$, thus also beneficial for photocatalysis.

In summary, we reveal that the strong bonding of hydrogen with the host atoms can ensure large solubility and shallow donor levels of H$_3$ and H$_2$O, consequently, introducing carrier concentration large enough to realize LSPR properties in semiconductor photocatalyst TiO$_2$ at wavelengths relevant to photocatalysis. Moreover, the infrared LSPR absorption can supplement that of noble metal whose absorption is generally in the visible region, thus making it possible for applications where infrared LSPR is essential, such as infrared catalyst systems but also to have a much wider impact in potentially unexpected entirely new discoveries not only to be a key guideline of noble metal NPs. In addition, it is expected that similar LSPR near field enhancement property is shown to be comparable with red LSPR absorption can supplement that of noble metal whose absorption is generally in the visible region, thus making it possible for applications where infrared LSPR is essential, such as infrared bioimaging and spectroscopy.

Methods

The total energies and electronic structures are obtained based on the spin-polarized density functional theory (DFT) calculations using the projector augmented wave (PAW) pseudopotentials as implemented in the Vienna ab initio Simulation Package (VASP) code$^{35,36}$. Heyd–Scuseria–Erzerhöf (HSE06) hybrid functional, which can provide good physical descriptions of defects in wide-bandgap semiconductors$^{37-43}$, is used in our calculations. A 3 $\times$ 3 $\times$ 1 supercell with the lattice parameters [a = 3.776 Å, c/a = 2.212 Å] is used to simulate the bulk TiO$_2$, and a hydrogen atom is introduced into the lattice to simulate the corresponding H$_3$ or H$_2$O doped TiO$_2$. The electron wave function is expanded in plane waves up to a cutoff energy of 400 eV to provide sufficient precision. The Brillouin zone is sampled with 2 $\times$ 2 $\times$ 2 1 $\Gamma$-centered k-points$^{37}$. The atomic positions of all atoms are fully relaxed until the residual force is smaller than 0.02 eV/Å. The total and projected densities of states (TDOS and PDOS) are calculated at the equilibrium volume using the tetrahedron method with Bloch corrections for accuracy$^{44}$.

The LSPR absorption spectra and enhanced electric field distribution are obtained by solving the Maxwell’s equations numerically based on the discrete dipole approximation (DDA) as implemented in the DDSCAT code$^{22-24}$. The DDA approximates the object of interest by an array of polarizable points, and there is no restriction as to which of the array sites is occupied, which means that DDA can represent an object or multiple objects of arbitrary shape and composition. Thus it is very useful for the present study. The permittivity of TiO$_2$ is obtained based on the Drude model as detailed in the Results part. All DDA calculations refer to vacuum as the external dielectric medium. For full convergence of the calculations, an inter-dipole distance of 0.2 nm is used.

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Author contributions
Y.D. and B.B.H. designed the research. X.C.M. and L.Y. performed the density functional theory and DDSCAT calculations. X.C.M. and Y.D. prepared the manuscript. All authors contributed to the scientific discussions.

Additional information
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