Modulating the interaction between gold and TiO$_2$ nanowires for enhanced solar driven photoelectrocatlytic hydrogen generation†

P. Sudhagar,‡a Taeseup Song,‡b Anitha Devadoss,a Jung Woo Lee,c Marta Haro,d Chiaki Terashima,a Volodymyr V. Lysak,b Juan Bisquert,e Akira Fujishima,a Sixto Gimenez*fd and Ungyu Paik*c

The interaction strength of Au nanoparticles with pristine and nitrogen doped TiO$_2$ nanowire surfaces was analysed using density functional theory and their significance in enhancing the solar driven photoelectrocatalytic properties was elucidated. In this article, we prepared 4-dimethylaminopyridine capped Au nanoparticle decorated TiO$_2$ nanowire systems. The density functional theory calculations show (101) facets of TiO$_2$ as the preferred phase for dimethylaminopyridine–Au nanoparticles anchoring with a binding energy of −8.282 kcal mol$^{-1}$. Besides, the interaction strength of Au nanoparticles was enhanced nearly four-fold (−35.559 kcal mol$^{-1}$) at (101) facets via nitrogen doping, which indeed amplified the Au nanoparticle density on nitrided TiO$_2$. The Au coated nitrogen doped TiO$_2$ (N–TiO$_2$–Au) hybrid electrodes show higher absorbance owing to the light scattering effect of Au nanoparticles. In addition, N–TiO$_2$–Au hybrid electrodes block the charge leakage from the electrode to the electrolyte and thus reduce the charge recombination at the electrode/electrolyte interface. Despite the beneficial band narrowing effect of nitrogen in TiO$_2$ on the electrochemical and visible light activity in N–TiO$_2$–Au hybrid electrodes, it results in low photocurrent generation at higher Au NP loading (3.4 × 10$^{-7}$ M) due to light blocking the N–TiO$_2$ surface. Strikingly, even with a ten-fold lower Au NP loading (0.34 × 10$^{-7}$ M), the synergistic effects of nitrogen doping and Au NPs on the N–TiO$_2$–Au hybrid system yield high photocurrent compared to TiO$_2$ and TiO$_2$–Au electrodes. As a result, the N–TiO$_2$–Au electrode produces nearly 270 μmol h$^{-1}$ cm$^{-2}$ hydrogen, which is nearly two-fold higher than the pristine TiO$_2$ counterpart. The implications of these findings for the design of efficient hybrid photoelectrocatlytic electrodes are discussed.

Introduction

Semiconductor photocatalysis and photoelectrochemistry, particularly involving TiO$_2$, is an influential field that plays an important role on environmental remediation and energy conversion applications. The striking features of TiO$_2$ including its high chemical stability in aqueous media, high photoactivity, earth abundance and environmentally benign nature strongly encourage the use of this material as a potential electron acceptor in light driven devices operating under solar radiation.$^{1,2}$ The primary report on photoelectrocatlytic (PEC) water oxidation on TiO$_2$ by Fujishima and Honda$^3$ has promoted a huge body literature on the design of nanostructured photocatalytic materials for realizing the solar driven PEC water oxidation process.$^{4,5}$ Moreover, the photogenerated holes at the valence band of TiO$_2$ energetically favour the oxidation process of chemical components (like pollutants, etc.). This process can be understood as a renaissance of natural photosynthesis utilizing man-made materials. Nonetheless, the short wavelength cut-off property of TiO$_2$ permits accessing only a narrow segment (~5%) of the solar spectrum; resulting in low PEC efficiency.$^6$ Conversely, the VB edge position (~3.2 V vs. NHE) of TiO$_2$ meets the energy requirement for successful PEC water oxidation,
where most of the visible light band gap materials such as CdS, CdSe, GaAs, and GaP fall short. Therefore, developing strategies to amplify the light harvesting efficiency of TiO₂ (greater than 5%) without sacrificing its PEC water oxidation potential is strongly in demand to further improve the PEC performance of TiO₂.

In this context, gold nanoparticle (Au NP) supported TiO₂ hybrid photocatalytic systems have attracted much attention because of their strong light absorption in the visible region, which arises from enhanced scattering and localized surface plasmon resonance (LSPR). Due to LSPR, Au NPs can effectively harvest the electromagnetic energy of the incident light and concentrate it into “plasmonic hotspots”, which in turn can maximize the local field intensity by a factor of 10⁶. Notably, one dimensional (1-D) TiO₂ nanostructures such as nanowires, nanotubes, nanofibers, etc. afford ample room to accommodate the nanoparticles compared to their bulk counterparts. Moreover, the rapid electron transport in the 1-D TiO₂ crystallite framework is highly beneficial for the efficient charge collection at the relevant interfaces. In the case of TiO₂–Au hybrid photocatalytic systems, neither individual Au NPs nor TiO₂ can act as an efficient photocatalyst upon visible-light irradiation, but a proper combination of both materials generates excellent visible-light PEC performances, even significantly enhancing the UV photocatalysis of TiO₂. This indicates that the interfacial interaction between Au NPs and TiO₂ plays a key role in achieving optimum PEC performance.

So far, a number of strategies have been documented in the literature for anchoring the Au NPs on TiO₂ surfaces. For instance, Au NPs were coated on TiO₂ via physical vapor deposition or sputtering as resulting in the formation of inhomogeneous NP coating on the metal oxide host surface. Alternatively, it has been reported that Au NPs can also be deposited on TiO₂ substrates via directly reducing gold salts by chemical reduction or photodeposition. Unfortunately, such deposition techniques affect the supporting semiconductors due to the multiple post-treatment steps. Similarly, controlling the size, shape and distribution of Au NPs using such approaches still remains challenging. Recently, we have demonstrated a straightforward method of anchoring 4-dimethylaminopyridine (DMAP) capped Au NPs on TiO₂ hollow nanowires, which in turn resulted in enhanced photocatalytic performance towards dye degradation. In the present study, we investigate the underlying mechanism behind the single-step anchoring of DMAP capped Au NPs on TiO₂ nanowires and their respective interactions were studied using theoretical simulations based on first principle theory. The interaction between DMAP capped Au NPs and TiO₂ nanowires was modulated via nitrogen doping TiO₂. The influence of nitrogen doping and DMAP capped Au NPs anchoring on TiO₂ band modification was elucidated. The finite-difference time domain (FDTD) method was used to quantitatively analyse the electromagnetic field enhancement in the TiO₂–Au hybrid photocatalytic system. Our theoretical and experimental results demonstrate the synergistic effect of Au NPs (visible light scattering) and nitrogen doping (band gap narrowing effect) on the PEC water oxidation process and the implications of these findings are discussed.

Experimental

Materials

All materials were received from Sigma-Aldrich and used as received.

Fabrication of TiO₂ nanowire arrays

Vertically aligned TiO₂ hollow nanowires onto FTO substrates were grown using ZnO nanorod array templates. First step, ZnO film of 200 nm was deposited on the FTO substrate using radio frequency magnetron sputtering. Following that, the ZnO seed layer coated FTO substrate was immersed into aqueous solution of 0.025 M zinc nitrate hexahydrate and 0.025 M hexamethylene-tetramine and the sample was kept at 85 °C for 10 h for the growth of vertically aligned ZnO nanorod arrays. After ZnO nanorod growth, the substrates were rinsed with deionized water.

In the second step, the TiO₂ layer will be grown on ZnO nanorod arrays as follows: the resultant ZnO NR array template was kept in aqueous solution of 0.075 M ammonium hexafluorotitanate and 0.2 M boric acid. This chemical bath deposition results in the thin layer of TiO₂ coating ZnO nanorods. Subsequently, the TiO₂ coated ZnO electrode is immersed in a 0.5 M boric acid solution for 1 h and the ZnO template is removed and rinsed with deionized water. Finally, vertically aligned TiO₂ NW arrays are obtained. The TiO₂ NW samples were calcined at 500 °C for 0.5 h under an Ar atmosphere.

For nitridation onto TiO₂ NWs, the electrodes were transferred to a chemical vapour deposition (CVD) chamber. The nitridation process was carried out at 500 °C with H₂ and NH₃ with flow rates of 50–200 standard cubic centimetre per minute (sccm) and 100–300 sccm, respectively.

Synthesis of Au NPs

DMAP-capped Au NPs were synthesized using the phase transfer procedure. Briefly, 0.030 M aqueous solution of HAuCl₄·3H₂O was added to 0.025 M tetraoctylammonium bromide (TOAB) in toluene. Then, 0.4 M aqueous NaBH₄ was added drop-wise to the mixture with stirring, causing an immediate reduction to occur. After 24 h, the two phases were separated and the toluene phase was subsequently washed with 0.1 M H₂SO₄, 0.1 M NaOH, and H₂O (three times), and then dried over anhydrous Na₂SO₄. An equal volume of 0.1 M aqueous solution of DMAP was then added. The phase transfer is clearly visible as the dark pink coloured solution transfers from toluene to water due to the addition of DMAP and was completed within 1 h. Assuming a 100% efficient reduction of gold chloride and no losses during transfer and washing steps, the particle size yields a particle concentration of approximately 6.8 × 10⁻⁷ M in the stock solution arising from the nanoparticle synthesis.

Assembly of Au NPs on TiO₂ nanowire arrays

Au NP coating on TiO₂ and N–TiO₂ NW arrays was obtained by immersing the TiO₂ electrodes in positively charged, water soluble DMAP-capped Au NP solution [3.4 × 10⁻⁷ M] for 5 min. The positively charged DMAP-capped Au NPs were attracted towards the negatively charged surface of TiO₂ NWs and N–TiO₂ NWs.
resulting in the facile formation of electrostatically assembled TiO$_2$–Au and N–TiO$_2$–Au hybrid photocatalytic electrodes. After coating Au NPs on these electrodes DMAP molecules were removed by the sintering process.

Theoretical calculations

The energy calculations were performed using the PW91 method generalized gradient approximation (GGA) and the plane wave model using CASTEP program. The supercell of 20 Å × 20 Å × c was used for the calculation, which represents the nanowire length along the tube axis as c. All atoms were described using Vanderbilt ultrasoft pseudopotentials and a cut off energy of 240 eV where a set of k-points was used to expand the electronic wave function based on the Monkhorst–Pack scheme within 5.0 × 10$^{-5}$ eV per atom of total energy convergence. Electron density was investigated with optimized geometries. The binding energies of atoms on the nanotubes were calculated by eqn (1)

$$E_b = E_{\text{nanotube}+\text{atom}} - (E_{\text{nanotube}} + E_{\text{atom}}).$$

Structural and optical characterization

The surface of various TiO$_2$ nanowire arrays was characterized using a field emission scanning electron microscope (FE-SEM, JEM-3100F, Jeol, Tokyo, Japan) and a field emission transmission electron microscope (FE-TEM, JSM 7600F, JEOL, Tokyo, Japan). The chemical environment of pure and N doped TiO$_2$ electrodes was analyzed by X-ray photoelectron spectroscopy (XPS) using an angular resolved electron analyzer with a monochromated Al K$_x$ source (Theta Probe, Thermo Fisher Scientific). The optical diffuse reflectance spectra of the electrodes were recorded in the range of 350–900 nm using a V670 JASCO UV-Vis spectrophotometer. The absorbance of the electrodes was estimated from diffuse reflectance measurements ($R$) directly using the Kubelka–Munk relation, $F.R. = (1 - R)^2/2R$ using in built software from a JASCO UV-Vis spectrometer. We have assumed that the scattering term is similar for photoelectrodes with and without Au loading.

(Photoo)electrochemical characterization

The (photo)electrochemical analysis was done using a three electrode configuration. The as-prepared TiO$_2$, TiO$_2$–Au, N–TiO$_2$ and N–TiO$_2$–Au electrodes (electrode area 1 cm$^2$) were used as the working electrode, Ag/AgCl as the reference and Pt foil as the counter electrode. 0.5 M of Na$_2$SO$_4$ (Sigma Aldrich) (pH = 6.1) was used as the electrolyte for all PEC measurements without any additional additives. Cyclic voltammograms were recorded using an advanced potentiosstat (PGSTAT-30 from Autolab) with a scanning rate of 50 mV s$^{-1}$. The photocurrent measurements were recorded using a solar simulator with a 300 W xenon arc-lamp (Hayashi- LA 251-Xc). The light intensity was calibrated using a silicon photodiode (100 mW cm$^{-2}$). The electrolyte was bubbled with nitrogen gas for 30 min to avoid the presence of oxygen (electron acceptor) in the solution. The IPCE measurements were carried out by employing a 300 W Xe lamp coupled to a computer-controlled monochromator; the photoelectrode was polarized at the desired voltage (1.6 V vs. RHE) using a Gamry potentiostat, and the photocurrent was measured using an optical power meter 70310 from Oriel Instruments. A Si photodiode was used to measure the light intensity to calibrate the system. The output gas samples were collected from the head space of a sealed PEC chamber using an air-tight gas syringe through the manual sampling port in the top of the chamber (flexible cork made of Teflon) and further subjected to gas chromatographic analysis to evaluate the constituents of the gas products.

Theoretical calculations

To get insights into the binding mechanism of positively charged DMAP-capped Au NPs on TiO$_2$ NWs and N–TiO$_2$ NWs, it is important to estimate the binding energies in the hybrid systems. First principles based simulations provide direct evidence of interaction energies between DMAP–Au NPs and the TiO$_2$ semiconductor, which can be used to detect the optimal binding sites and to predict the maximal affinity that a nanoparticle could attain from them. The binding characteristics in TiO$_2$–Au and N–TiO$_2$–Au hybrid photocatalytic systems were analyzed using first principles theory. Firstly, the binding energies between molecular DMAP and Au were estimated. It was found that the DMAP molecule strongly binds to gold with −14.01 kcal mol$^{-1}$ binding energy, which could be ascribed to the high binding affinity of Au atoms towards the pyridine moieties in DMAP.

Recent studies show that the photocatalytic activity of TiO$_2$ strongly depends on its crystal facets. Moreover, it was realized that the deposition of metal nanoparticles (Ag, Au and Pt) onto selective {101} facets of anatase TiO$_2$ crystals with different percentages of exposed {001} and {101} facets can effectively enhance the photocatalytic activity of TiO$_2$ in both photoreduction and photoxidation processes. In this line, we examined the binding nature of DMAP–Au NPs on {101} and {001} facets of TiO$_2$. Fig. 1 shows the optimal binding sites of DMAP–Au NPs on (a) {001} facets and (b) {101} facets of TiO$_2$. The {101} facet of TiO$_2$ shows higher binding energy (−8.282 kcal mol$^{-1}$) towards DMAP–Au NP anchoring compared to the {001} facets of TiO$_2$. Fig. 1c shows the density of the electron cloud at the TiO$_2$–Au hybrid electrode. The reported excellent catalytic activity and band structure modifications of TiO$_2$ upon nitrogen doping$^{36–39}$ inspired us to investigate the effect of nitrogen doping on DMAP–Au NP binding. Fig. 1(d–f) show the binding orientations and density of electron cloud distribution in N–TiO$_2$–Au hybrid electrodes. As anticipated, higher binding energies (−8.86 kcal mol$^{-1}$) were observed for DMAP–Au NPs anchoring on N–TiO$_2$ than on pristine TiO$_2$ NWs (−6.48 kcal mol$^{-1}$) at the {001} surface. This could be ascribed to the higher binding affinity of pyridines and Au towards nitrogen. Strikingly, the binding energies were found to be remarkably enhanced at the {101} surface of N–TiO$_2$ NWs. The N–TiO$_2$–Au hybrid system shows a binding energy of −35.56 kcal mol$^{-1}$ at the {101} surface, which is nearly
four times higher than that observed for the {001} plane of N–TiO2 NWs. This strongly suggests that the Au NPs can be effectively coated onto N–TiO2 by electrostatic attraction.

On the other hand, in view of improving the light harvesting efficiency of TiO2, Au NP decoration found to improve the visible light activity of hybrid materials owing to their strong scattering effect and enhanced absorption at around 520 nm due to the LSPR band. To understand the origin and the extent of improved visible light activity in TiO2–Au hybrid systems, the light scattering effect of Au NPs at TiO2 NWs was further analyzed using the finite-difference time-domain (FDTD). Fig. 2 shows the electric field (E-field) distribution in the perpendicular direction, across the Au NPs at the TiO2-NW surface obtained from FDTD simulations. The permittivity of gold was analyzed using the Lorenz–Drude dispersive model.\(^4\)

\[
\varepsilon_\infty(\omega) = \varepsilon_\infty + \sum_{m=0}^{5} \frac{G_m \Omega_m^2}{\omega_m^2 - \omega^2 + j\omega \Gamma_m} \tag{2}
\]

where \(\varepsilon_\infty(\omega)\) is the relative permittivity at infinity frequency, \(G_m\) is the strength of each resonance term, \(\Omega_m\) is the plasma frequency, \(\omega\) and \(\omega_m\) are the angular and resonant frequency, respectively, and \(\Gamma_m\) is the damping factor or collision frequency. Fig. 2(a) and (b), clearly illustrate the electric field generation around the Au NPs. The electric field extension varies with Au NP loading (spacing) on TiO2. The visible light scattering centres around Au NPs transformed the light reception at TiO2. However, higher loadings of Au NPs on TiO2 found to scatter the major portion of input light, which may reduce the light transmission reaching the TiO2 surface. Thus, it is anticipated that the TiO2–Au hybrid system benefits not only from improved LSPR band facilitated absorption at 520 nm, but also from the light scattering effect of Au NPs, which could effectively improve the light absorption properties of TiO2 itself.

**Experimental results**

From the above discussion, it is inferred that the Au NP decoration at TiO2 NWs could yield high PEC energy conversion efficiency, mainly through light scattering and co-catalyst effects. Moreover, nitrogen doping was found to enhance the interaction between Au NPs and TiO2 as well as the visible light activity of TiO2 by the band gap narrowing effect.\(^3\) In order to understand the role of Au NP decoration and nitrogen doping,
we have designed and fabricated Au NP decorated TiO\textsubscript{2} NW and N–TiO\textsubscript{2} NW arrays onto fluorinated tin oxide (FTO) substrates. Fig. 3 shows the electron microscopy images of nitrided TiO\textsubscript{2} (N–TiO\textsubscript{2}) NW, Au NP coated TiO\textsubscript{2} NW (TiO\textsubscript{2}–Au) and N–TiO\textsubscript{2} NW (N–TiO\textsubscript{2}–Au) arrays, respectively.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of N–TiO\textsubscript{2} NWs clearly reveal their vertically aligned geometry and 1-D structure (Fig. 3a). The N–TiO\textsubscript{2} NWs have a length of \( \sim 5 \) \( \mu \text{m} \), an inner free space of \( \sim 200 \) nm and a shell thickness of \( \sim 50 \) nm, respectively (Fig. 3b). From Fig. 3c and d, a thin amorphous layer is observed on TiO\textsubscript{2}. This layer represents the formation of TiN/TiO\textsubscript{x}N\textsubscript{y} on the TiO\textsubscript{2} NW surface during the nitridation process. Although it was difficult to obtain lattice resolved TEM images at the surface of N–TiO\textsubscript{2} NWs, the X-ray diffraction (XRD) and SAED patterns support that N–TiO\textsubscript{2} NWs maintain their polycrystalline anatase phase (see ESI,† Fig. S1). There are no noticeable changes in the geometry of the NWs after Au NP anchoring (Fig. 3f and j). Au NPs with an average diameter of \( \sim 5 \) nm were observed in the high magnification TEM images (Fig. 3i) (also see ESI,† Fig. S2). These images (Fig. 3h and l) confirm the higher loading of Au NPs on N–TiO\textsubscript{2} NWs compared to pristine TiO\textsubscript{2} NWs.

The effect of nitrogen doping on TiO\textsubscript{2} NWs was studied by X-ray photoelectron spectroscopy. Fig. 4(a) shows the core spectra of Ti 2p in pristine TiO\textsubscript{2} NWs and N–TiO\textsubscript{2} NWs. The shoulder peaks at 459.4 eV and 465.1 eV correspond to Ti 2p\textsubscript{3/2} and Ti 2p\textsubscript{1/2}, respectively.\textsuperscript{41} In N–TiO\textsubscript{2} NWs, these peaks were shifted toward lower binding energy indicating the successful nitrogen doping at the TiO\textsubscript{2} NWs. Upon further examining the N 1s core spectra (Fig. 4b), the peaks at 396.8, 398.8, and 400.6 eV provide a clear picture of the nitrogen environment at TiO\textsubscript{2} NWs. The peak at 396.8 eV is attributed to the existence of atomic \( \beta\)-N in the TiO\textsubscript{2} matrix and the peak at 398.8 eV implies the substitution of O\textsuperscript{2–} by nitrogen ions and thus, results in the formation of N–Ti–O.\textsuperscript{42,43} This confirms the existence of Ti\textsuperscript{3+} due to the incorporation of nitrogen atoms into oxygen lattice sites. The weaker peak at 400.6 eV indicates the interstitial doping which induces an additional impurity state above the valence band of TiO\textsubscript{2}.\textsuperscript{44} The atomic ratio of nitrogen doping carriers was estimated from Fig. 4b and found to be 5.8 wt\%.

The broad features of the O 1s peak in Fig. 4c were deconvoluted using the Gaussian fit (Fig. 4c, inset). Three distinct peaks were observed at 530.9, 532.2 and 533.2 eV representing the lattice oxygen, surface hydroxyl oxygen and surface adsorbed oxygen, respectively. The atomic weight of lattice oxygen at TiO\textsubscript{2} NWs was estimated to be 51.5%, which was reduced to 47.6% upon nitrogen doping. This indicates the possibility of nitrogen atoms occupying the oxygen vacancies. The influence of nitrogen doping on the work function of TiO\textsubscript{2} NWs was examined using ultraviolet photoelectron spectroscopy (see ESI,† Fig. S3). The valence band maximum (VBM) position of TiO\textsubscript{2} NWs at \( \sim 3.26 \) eV was shifted to \( \sim 2.69 \) eV upon nitrogen doping. This indicates that nitrogen doping carriers

Fig. 3  SEM images of (a) N–TiO\textsubscript{2}, (c) TiO\textsubscript{2}–Au and (i) N–TiO\textsubscript{2}–Au electrodes. The TEM images (b–d), (f–h), and (j–l) represent the high magnification TEM images corresponding to N–TiO\textsubscript{2}, TiO\textsubscript{2}–Au and N–TiO\textsubscript{2}–Au electrodes, respectively.

Fig. 4  XPS results of (a) Ti 2p, (b) N 1s and (c) O 1s core spectra of TiO\textsubscript{2} and N–TiO\textsubscript{2} electrodes.
are creating sub-bands or defects above the VB of TiO$_2$ as discussed in the XPS results.

In order to study the contribution of DMAP–Au NPs towards the visible light activity of TiO$_2$–Au and N–TiO$_2$–Au hybrid photocatalysts, diffuse reflectance measurements were performed. The results are shown in Fig. 5a. The Kubelka–Munk absorbance contribution of TiO$_2$ NWs and N–TiO$_2$ NWs was subtracted from the absorbance spectrum of TiO$_2$–Au and N–TiO$_2$–Au hybrids, respectively (Fig. 5b). Both spectra confirm the enhanced scattering induced by the presence of Au NPs, being the LSPR effect negligible for these specimens. Although, Au NP coating at TiO$_2$ and N–TiO$_2$ was carried out under identical conditions, N–TiO$_2$–Au hybrid electrodes showed higher absorbance, indicating higher loading of Au NPs in good correspondence with the TEM measurements (Fig. 2h and l) and the Kubelka–Munk function ($F.R.$) (inset of Fig. 5). This is attributed to the higher binding energy observed at the N–TiO$_2$ surfaces. The broad absorption nature of N–TiO$_2$–Au may be originated from the light scattering effect which amplifies the absorbance of TiO$_2$.\textsuperscript{15}

To test the photoelectrochemical (PEC) water oxidation performance, we measured $J$–$V$ characteristics of these electrodes under the dark and illumination conditions. From Fig. 6a, it was found that the TiO$_2$–Au hybrid electrode showed four times higher photocurrent $\sim 0.4$ mA cm$^{-2}$ than the pristine TiO$_2$ NW electrode (0.11 mA cm$^{-2}$). This photocurrent enhancement may be due to the combined effect of higher optical absorption due to the scattering and co-catalytic effect of Au NPs in water oxidation through the formation of the Au–TiO$_2$ Schottky junction.\textsuperscript{16,17} In addition, it may facilitate the charge separation at TiO$_2$/electrolyte interfaces and thus reduces the recombination of electrons through surface states of TiO$_2$.\textsuperscript{48} In the case of nitrogen doping at TiO$_2$ NWs, the photocurrent density was slightly enhanced (0.22 mA cm$^{-2}$), which might be ascribed to the promotion of visible light activity of TiO$_2$ through the band gap narrowing effect (see ESI,\textsuperscript{†} S3 and S4).

In striking contrast, the photocurrent in the N–TiO$_2$–Au hybrid system was only slightly higher than that in the N–TiO$_2$ NW system. This might be due to excessive Au NP decoration (from Fig. 3l), which may result in forward light scattering blocking the light photons reaching the N–TiO$_2$ NW surface and also reduce the interfacial contact between N–TiO$_2$ and FTO electrodes, thus hindering the photoholes participating in the water oxidation process.\textsuperscript{18} This implies that there exists a trade-off between the enhanced light scattering due to Au NP decoration and visible light photon reception at N–TiO$_2$ NWs, which necessitates the optimization of Au NP loading onto N–TiO$_2$ NWs. We have recently reported that the photoelectrochemical performance of TiO$_2$–Au nanocomposites has a volcano dependence with Au loading.\textsuperscript{28}

Interestingly, the Au NP decorated TiO$_2$ and N–TiO$_2$ electrodes using low concentration stock solution (0.34 \times 10^{-7} M), here referred to as TiO$_2$–Au (low) and N–TiO$_2$–Au (low), respectively, lead to higher photocurrent compared to the high Au concentration samples, as observed in Fig. 6. This photocurrent enhancement strongly suggests minimizing the optical blocking effect through controlling the Au NP loading on N–TiO$_2$.

Furthermore, the stability of electrodes in photocurrent generation is examined with chronamperometric curves (see ESI,\textsuperscript{†} S5). The significant decrease of the photocurrent in both TiO$_2$ and TiO$_2$–Au electrodes may be attributed to the current leakage at TiO$_2$/FTO interfaces to the electrolyte through the naked FTO surface (uncovered TiO$_2$ area). Another plausible reason may arise from Au stability under long time photo-irradiation. However it is not clear at this moment and further research on this topic is needed. It is anticipated that inserting a compact TiO$_2$ blocking layer between TiO$_2$ and FTO layers will hinder the electron flow from the charge collector to the electrolyte.

In order to further corroborate the absence of the plasmonic effect at Au coated TiO$_2$ electrodes, we recorded IPCE spectra (see ESI,\textsuperscript{†} Fig. S6). There is no photocurrent peak at around 550 nm in the TiO$_2$–Au electrode as observed in optical absorption spectra (Fig. 5b). This implies that there is no electron injection from Au nanoparticles to TiO$_2$ by the plasmonic effect. Instead, Au NPs are promoting the optical absorption of TiO$_2$ through the scattering effect. In addition, Au NPs play a critical role as a co-catalyst in the water oxidation process as shown in Fig. S4 (ESI,\textsuperscript{†}). The photoholes generated at the
valence band of TiO₂ and N–TiO₂ are injected into Au NPs and may oxidize the water molecules into oxygen and protons.

Aiming at the technological exploitation of the photocurrent enhancement due to nitrogen doping and loading of Au nanoparticles, we carried out the deposition of these structures on flexible stainless steel (SS) substrates. The flexible photoelectrodes are highly promising in solar-to-hydrogen fuel production owing to their lower weight and cost, compared to FTO, together with more versatile mechanical properties. However, the TiO₂ nanowire fabrication onto flexible SS substrates remains challenging. A similar deposition procedure of TiO₂ on FTO substrates explained in the Experimental section was repeated for fabricating TiO₂ NWs on flexible SS substrates. We adopt the optimized Au NP concentration condition (0.34 × 10⁻⁷ M) from Fig. 6, and reconstructed the TiO₂–Au hybrid systems onto flexible stainless steel (SS) substrates instead of FTO substrates (the sample photo is presented in the inset of Fig. 7a).

The J–V characteristics of Au–TiO₂–SS and N–TiO₂–Au–SS electrodes were tested in the 0.5 M Na₂SO₄ aqueous electrolyte with a three electrode PEC cell step up. The J–V characteristic of N–TiO₂–Au–SS is displayed in Fig. 7a. The higher photocurrent density achieved in N–TiO₂–Au–SS compared to the TiO₂–Au–SS electrode agrees well with the trends presented in Fig. 6. The scattering effect by Au NPs, the band gap narrowing effect by N doping and catalysis at optimal concentration lead to high photocurrent generation at the N–TiO₂–Au–SS sample. A small onset potential shift occurred in this sample towards the negative potential region, also in good agreement with the results shown in Fig. 6. We believe that this cathodic shift can be related to enhanced charge collection at the contact for the N–doped TiO₂.

The gas evolution from the PEC water oxidation experiment was collected for one hour under light illumination at 1 V vs. RHE potential, and analysed using gas chromatography (Fig. 7b). It is observed that TiO₂–Au–SS hybrid electrodes could generate hydrogen of about 120 μmol h⁻¹ cm⁻². Interestingly, the hydrogen generated at N–TiO₂–Au–SS hybrid electrodes was about 270 μmol h⁻¹ cm⁻². The described bendable architecture of N–TiO₂–Au on SS substrates (inset of Fig. 7a) with light weight and low cost can be beneficial for large scale flexible PEC fuel generation. Another advantage of both side conducting nature of SS substrates enables us to design an artificial leaf based (back side coated with the electrocatalyst) on monolithic wireless type solar fuel cells.

Conclusions

Hybrid photocatalytic systems developed by anchoring DMAP–Au NPs on N–TiO₂ nanowires exhibit interesting optical and photocatalytic properties for water oxidation. Nitrogen doping of TiO₂ both maximizes the DMAP–Au NP loading and improves the optical absorption due to the band narrowing effect. DMAP–Au NP anchoring amplifies the visible light activity of TiO₂ and N–TiO₂ via a light scattering effect and also improves the charge recombination at the electrode/electrolyte interface. After optimization of the Au loading on the nanostructured photoelectrodes, N-doped TiO₂ leads to enhanced photocurrent generation and slightly more favourable onset potential on both FTO and SS substrates. Hydrogen generation measured on films deposited on flexible SS substrates was significantly higher on N-doped TiO₂ nanostructures.

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Notes and references