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Modulating the interaction between gold and TiO₂ nanowires for enhanced solar driven photoelectrocatalytic hydrogen generation

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The interaction strength of Au nanoparticles with pristine and nitrogen doped TiO₂ nanowire surface 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 nanoparticles decorated TiO₂ nanowires system. The density functional theory calculations show {101} facets of TiO₂ as the preferred phase for dimethylaminopyridine-Au nanoparticles anchoring with a binding energy of -8.282 kcal/mol. Besides, the interaction strength of Au nanoparticles was enhanced nearly four-fold (-35.559 kcal/mol) at {101} facets via nitrogen doping, which indeed amplified the Au nanoparticle density on nitrided TiO₂. The Au coated nitrogen doped TiO₂ (N-TiO₂-Au) hybrid electrodes show higher absorbance owing to the light scattering effect of Au nanoparticles. In addition, N-TiO₂-Au hybrid electrodes block the charge leakage from electrode to electrolyte and thus reduce the charge recombination at electrode/electrolyte interface. Despite the beneficial band narrowing effect of nitrogen in TiO₂ on the electrochemical and visible light activity in N-TiO₂-Au hybrid electrodes, it results low photocurrent generation at higher Au NPs loading (3.4×10²⁵ M) due to light blocking to N-TiO₂ surface. Strikingly, even with a ten-fold lower Au NPs loading (0.34×10²⁵ M), the synergistic effects of nitrogen doping and Au NPs on N-TiO₂-Au hybrid system yield high photocurrent compare to TiO₂ and TiO₂-Au electrodes. As a result, N-TiO₂-Au electrode produces nearly 270 µmol/hr cm² hydrogen, which is nearly two-fold higher than the pristine TiO₂ counterpart. The implications of these findings for the design of efficient hybrid photoelectrocatalytic electrodes are discussed.

Introduction

Semiconductor photocatalysis and photoelectrochemistry, particularly involving TiO₂, is an influential field that plays an important role on environmental remediation and energy conversion applications. The striking features of TiO₂, including its high chemical stability in aqueous media, high photoactivity, earth abundance and environmental benign nature, strongly encourage the use of this material as potential electron acceptor in light driven devices operating under solar radiation. The primary report on photoelectrochemical (PEC) water oxidation on TiO₂ by Fujishima and Honda, has promoted a huge body literature on the design of nanostructured photocatalytic materials for realizing the solar driven PEC water oxidation process. Moreover, the photogenerated holes at the valence band of TiO₂ 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 TiO₂ permits accessing only a narrow segment (~5%) of the solar spectrum; resulting in low PEC efficiency. Conversely, the VB edge position (~ 3.2 V vs NHE) of TiO₂ 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 their PEC water oxidation potential are strongly demanded to further improve the PEC performance of TiO₂.

In this context, gold nanoparticles (Au NPs) 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 at 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 TiO$_2$.\textsuperscript{17-21} This indicates that the interfacial interaction between Au NPs and TiO$_2$ plays a key role on achieving optimum PEC performance. So far, a number of strategies have been documented in literature for anchoring the Au NPs on TiO$_2$ surfaces. For instance, Au NPs were coated on TiO$_2$ \textit{via} physical evaporation or sputtering resulted in the formation of inhomogeneous NPs coating on the metal oxide host surface.\textsuperscript{22, 23} Alternatively, it has been reported that Au NPs can also be deposited on TiO$_2$ substrates \textit{via} directly reducing gold salts by chemical reduction or photodeposition.\textsuperscript{24, 25, 26, 27} 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 remain challenging. Recently, we have demonstrated a straightforward method of anchoring 4-dimethylaminopyridine (DMAP) capped Au NPs on TiO$_2$ hollow nanowires, which in turn resulted in enhanced photocatalytic performance towards dye degradation.\textsuperscript{28} In the present study, we investigate the underlying mechanism behind the single-step anchoring of DMAP capped Au NPs on TiO$_2$ nanowires and their respective interactions were studied using theoretical simulations based on first principle theory. The interaction between DMAP capped Au NPs and TiO$_2$ nanowires were modulated via nitrogen doping the TiO$_2$. The influence of nitrogen doping and DMAP capped Au NPs anchoring on TiO$_2$ band modification was elucidated. The finite-difference time domain (FDTD) method was used to quantitatively analyse the electromagnetic field enhancement in TiO$_2$-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 PEC water oxidation process and the implications of these findings are discussed.

\section*{Experimental}

\subsection*{Materials}

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

\subsection*{Fabrication of TiO$_2$ Nanowires Array}

Vertically aligned TiO$_2$ hollow nanowires onto FTO substrates were grown using ZnO nanorod array templates. First step, ZnO film of 200 nm was deposited on FTO substrate using radio frequency magnetron sputtering. Followed that, the ZnO seed layer coated FTO substrate was immered in aqueous solution of 0.025 M zinc nitrate hexahydrate and 0.025 M hexamethylenetetramine and the sample was kept at 85 °C for 10 h for the growth of vertically aligned ZnO nanorods array. After ZnO nanorods growth, the substrates were rinsed with deionized water.

In the second step, TiO$_2$ layer will be grown on ZnO nanorod array as follows: the resultant ZnO NR array template was kept at aqueous solution of 0.075 M ammonium hexafluorotitanate and 0.2 M boric acid. This chemical bath deposition results thin layer of TiO$_2$ coating ZnO nanorods. Subsequently, the TiO$_2$ 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 TiO$_2$ NWs arrays are obtained. The TiO$_2$ NWs samples were calcined at 500 °C for 0.5 h under Ar atmosphere.

For nitridation onto TiO$_2$ NW, the electrodes were transferred to a chemical vapour deposition (CVD) chamber. The nitridation process was carried out at 500 °C with H$_2$ and NH$_3$ with flow rates of 50–200 standard cubic centimetre per minute (sccm) and 100–300 sccm, respectively.

\subsection*{Synthesis of Au NPs}

DMAP-capped Au NPs were synthesized using the phase transfer procedure.\textsuperscript{30} Briefly, 0.030 M aqueous solution of HAuCl$_4$.3H$_2$O was added to 0.025 M tetraoctylammonium bromide (TOAB) in toluene. Then, 0.4 M aqueous NaBH$_4$ 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 H$_2$SO$_4$, 0.1 M NaOH, and H$_2$O (three times), and then dried over anhydrous Na$_2$SO$_4$. 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 the 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.

\subsection*{Assembly of Au NPs on TiO$_2$ Nanowires Array}

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

\subsection*{Theoretical calculations}

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

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

\subsection*{Structural, and optical characterization}

The surface of various TiO$_2$ nanowires array 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 were analyzed by x-ray photoelectron spectroscopy (XPS) using an angular resolved electron analyzer.
with a monochromated Al Kα 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 working electrode, Ag/AgCl as the reference and Pt foil as the counter electrode. 0.5 M of Na₂SO₄ (Sigma Aldrich) (pH=6.1) was used as the electrolyte for all PEC measurements without any additional additives. Cyclic voltammograms were recorded using the advanced potentiostat (PGSTAT330 from Autolab) with the scanning rate 50 mV/s. The photocurrent measurements were recorded using a solar simulator with a 300 W xenon arc lamp (Hayashi LA 251-Xe). The light intensity was calibrated using a silicon photodiode (100 mWcm⁻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 photocell was polarized at the desired voltage (1.6 V vs RHE) with 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 TiO₂ NWs and N-TiO₂ 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 TiO₂ 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 TiO₂-Au and N-TiO₂-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 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 TiO₂ strongly depends on their crystal facets. Moreover, it was realized that deposition of metal nanoparticles (Ag, Au and Pt) onto selective {101} facets of anatase TiO₂ crystals with different percentages of exposed {001} and {101} facets can effectively enhance the photocatalytic activity of TiO₂ in both photoreduction and photo-oxidation processes. In this line, we examined the binding nature of DMAP-Au NPs on {101} and {001} facets of TiO₂. Figure 1 shows the optimal binding sites of DMAP-Au NPs on (a) {001} facets and (b) {101} facets of TiO₂. The {101} facet of TiO₂ shows higher binding energy (-8.282 kcal/mol).
kcal/mol) towards DMAP-Au NPs anchoring compared to the
{001} facets of TiO$_2$ (-6.48 kcal/mol), illustrating the higher
affinity of {101} surfaces towards DMAP-Au NPs anchoring.
Figure 1c shows the density of electron cloud at 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 NPs
binding. Figure 1 (d-f) shows 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) were
observed for DMAP-Au NPs anchoring on N-TiO$_2$ than on
pristine TiO$_2$ NWs (-6.48 kcal/mol) at {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 {011} surface of N-TiO$_2$ NWs.
The N-TiO$_2$-Au hybrid system shows a binding energy of -35.56
kcal/mol at {011} surface, which is nearly four times higher than
that observed for {001} plane of N-TiO$_2$ NW. This strongly
suggests that the Au NPs can be effectively coated onto N-TiO$_2$
by electrostatic attraction.

![Figure 2](image-url)

**Figure 2.** Spatial distribution of electric-field energy density of TiO$_2$-Au hybrid photocatalytic system at different spacing conditions: (a) with few nm spacing and (b) Au nanoparticles in contact (y axis indicated the distance in nm).

On the other hand, in view of improving the light harvesting
efficiency of TiO$_2$, Au NPs decoration found to improve the
visible light activity of hybrid materials owing to their strong
scattering effect and enhanced absorption around 520 nm due to
LSPR band. To understand the origin and the extent of improved
visible light activity in TiO$_2$-Au hybrid systems, the light
scattering effect of Au NPs at TiO$_2$ NWs was further analyzed
using finite-difference time-domain (FDTD). Fig.2 shows the
electric field (E-field) distribution in the perpendicular direction,
across the Au NPs at TiO$_2$-NWs surface obtained from FDTD
simulations. The permittivity of gold was analyzed using Lorenz-
Drude dispersive model.$^{40}$

$$
\varepsilon_r(\omega) = \varepsilon_r\infty + \sum_{n=0}^{\infty} \frac{G_n \Omega_n^2}{\omega_n^2 - \omega^2 + jo\Gamma_n} 
$$

where, $\varepsilon_r(\omega)$ is the relative permittivity at infinity frequency, $G_n$
is the strength of each resonance term, $\Omega_n$ is the plasma
frequency, $\omega$ and $\omega_n$ is the angular and resonant frequency,
respectively, and $\Gamma_n$ is the damping factor or collision frequency.

**Experimental results**

From the above discussion, it is inferred that the Au NPs
decoration at TiO$_2$ NWs could yield high PEC energy conversion
efficiency, mainly through light scattering and co-catalyst effect.
Moreover, nitrogen doping was found to enhance the interaction
between Au NPs and TiO$_2$ as well as enhancing the visible light
activity of TiO$_2$ by band gap narrowing effect.$^{39}$ In order to
understand the role of Au NPs decoration and nitrogen doping,
we have designed and fabricated Au NPs decorated TiO$_2$, NWs
and N-TiO$_2$ NW arrays onto fluorinated tin oxide (FTO)
substrates. Figure 3 shows the electron microscopy images of
nitrided TiO$_2$ (N-TiO$_2$) NWs, Au NPs coated TiO$_2$ NWs (TiO$_2$-
Au) and N-TiO$_2$ NWs (N-TiO$_2$-Au) arrays, respectively.

![Figure 3](image-url)

**Figure 3.** (a), (e) and (i) SEM and images of N-TiO$_2$, TiO$_2$-Au and N-
TiO$_2$-Au electrodes, respectively. Corresponding TEM images were
presented in right hand side of each sample.

Scanning electron microscopy (SEM) and transmission electron
microscopy (TEM) images of N-TiO$_2$ NWs clearly reveal their
vertically aligned geometry and 1-D structure (Fig. 3a). The N-
TiO$_2$ NWs have a length of ~5 µm, inner free space of ~200 nm
and shell thickness of ~50 nm, respectively (Fig. 3b). From Fig.
3c and 3d, a thin amorphous layer is observed on TiO$_2$. This layer
represents the formation of TiN/TiO$_2$N$_x$ on TiO$_2$ NW surface
during the nitridation process. Although it was difficult to obtain
lattice resolved TEM images at the surface of N-TiO$_2$ NWs, the
X-ray diffraction (XRD) and SAED patterns support that N-TiO$_2$
...
NWs maintain their polycrystalline anatase phase (See Supporting information Fig. S1). There are no noticeable changes on the geometry of the NWs after Au NPs anchoring (Fig. 3f & Fig. 3j). Au NPs with an average diameter of ~5 nm were observed in the high magnification TEM images (Fig. 3(i)) (also See Supporting information Fig. S2). These images (Fig. 3b & Fig. 3l) confirm the higher loading of Au NPs on N3TiO2 NWs compared to pristine TiO2 NWs.

The effect of nitrogen doping on TiO2 NWs was studied with X-ray photoelectron spectroscopy. Fig. 4(a) shows the core spectra of Ti 2p in pristine TiO2 NWs and N3TiO2 NWs. The shoulder peaks at 459.4 eV and 465.1 eV correspond to Ti2p3/2 and Ti2p1/2, respectively.41 In N3TiO2 NWs, these peaks were shifted toward lower binding energy indicating the successful nitrogen doping at the TiO2 NWs. Further examining the N1s core spectra (Fig. 4b), 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 TiO2 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 TiO2 NWs was examined using ultraviolet photoelectron spectroscopy (See supporting information Fig. S3). The valence band maximum (VBM) position of TiO2 NWs at ~3.26 eV was shifted to ~2.69 eV upon nitrogen doping. This indicates that nitrogen doping carriers are creating sub-bands or defects above the VB of TiO2 as discussed in the XPS results.

In order to study the contribution of DMAP-Au NPs towards the visible light activity of TiO2-Au and N-TiO2-Au hybrid photocatalysts, diffuse reflectance measurements were performed. The results are showed in Fig. 5a. The Kubelka-Munk absorbance contribution of TiO2 NWs and N-TiO2 NWs was subtracted from the absorbance spectrum of TiO2-Au and N-TiO2-Au hybrids, respectively (inset of Figure 5). Both spectra confirm the enhanced scattering induced by the presence of Au NPs, being the LSPR effect negligible for these specimens. Although, Au NPs coating at TiO2 and N-TiO2 was carried out at identical condition, N3TiO2-Au hybrid electrodes showed higher absorbance, indicating higher loading of Au NPs in good correspondence with the TEM measurements (Fig. 2h & 2l) and Kubelka-Munk function (F.R.) (inset of Figure 5). This is attributed to the higher binding energy observed at the N-TiO2 surfaces. The broad absorption nature of N-TiO2-Au may be originated from the light scattering effect which amplifies the absorbance of TiO2.45
To test the photoelectrochemical (PEC) water oxidation performance, we measured J-V characteristics of these electrodes in the dark and upon illumination conditions. From Fig. 6(a), it was found that TiO$_2$-Au hybrid electrode showed four times higher photocurrent (~0.4 mA cm$^{-2}$) than pristine TiO$_2$ NWs electrode (0.11 mA cm$^{-2}$). This photocurrent enhancement may be due to the combined effect of higher optical absorption due to scattering and co-catalytic effect of Au NPs in water oxidation through the formation of Au/TiO$_2$ Schottky junction. 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$_2$. 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 band gap narrowing effect (See supporting information S3 and S4).

In striking contrast, the photocurrent at N-TiO$_2$-Au hybrid system was only slightly higher than N-TiO$_2$ NWs system. This might be due to excessive Au NPs decoration (From Fig.3 (I)), which may result in forward light scattering blocking the light photons reaching N-TiO$_2$ NWs surface and also reduce the interfacial contact between N-TiO$_2$ and FTO electrode, thus hindering the photoholes participating in the water oxidation process. This implies that there exist a trade-off between the enhanced light scattering due to Au NPs decoration and visible light photons reception at N-TiO$_2$ NWs, which necessitates the optimization of Au NPs 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.

![Figure 6](image)

*Figure 6.* J-V results of PEC water splitting using different photoanode electrodes. Note that two different Au concentrations were used for decorating working electrodes: low – 0.34×10$^{-7}$ M; high - 3.4 x 10$^{-7}$ M).

Interestingly, the Au NPs decorated TiO$_2$ and N-TiO$_2$ electrodes using low concentration stock solution (0.34×10$^{-7}$ M), here referred 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 Figure 6. This photocurrent enhancement strongly suggests minimizing the optical blocking effect through control the Au NPs loading on N-TiO$_2$.

Furthermore, the stability of electrodes in photocurrent generation is examined with chronocoulometric curves (See supporting information 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 electrolyte through 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 compact TiO$_2$ blocking layer between TiO$_2$ and FTO layers will hinder the electron flow from the charge collector to electrolyte.

In order to further corroborate the absence of plasmonic effect at Au coated TiO$_2$ electrodes, we recorded IPCE spectra (See supporting information Fig. S6). There is no photocurrent peak exhibit around 550 nm in TiO$_2$-Au electrode as observed in optical absorption spectra (Figure 5b). This implies that there is no electron injection from Au nanoparticles to TiO$_2$ by plasmonic effect. Instead, Au NPs are promoting the optical absorption of TiO$_2$ through scattering effect. In addition, Au NPs play a critical role as co-catalyst in water oxidation process as scheduled in Figure S4. The photoholes generated at the valence band of TiO$_2$ and N-TiO$_2$ is 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 TiO$_2$ nanowire fabrication onto flexible SS substrates remains challenging. Similar deposition procedure of TiO$_2$ on FTO substrates explained in the experimental session was repeated for fabricating TiO$_2$ NW on flexible SS substrates. We adopt the optimized Au NPs concentration condition (0.34×10$^{-7}$ M) from the Figure 6, and reconstructed the TiO$_2$-Au hybrid systems onto flexible stainless steel (SS) substrates instead of FTO substrates (sample photo presented in inset of Figure 7).

The $j$-$\nu$ characteristics of Au-TiO$_2$-SS and Au-N-TiO$_2$-SS electrodes were tested in 0.5M Na$_2$SO$_4$ aqueous electrolyte with three electrode PEC cell step up. The $j$-$\nu$ characteristic of N-TiO$_2$-Au-SS is displayed in Figure 7 (a). The higher photocurrent density achieved in N-TiO$_2$-Au compared to TiO$_2$-Au electrode agrees well with the trends presented in Figure 6. The scattering effect by Au NPs, band gap narrowing effect by N doping and catalysis at optimal concentration leads to high photocurrent generation at the Au-N-TiO$_2$-SS sample. A small onset potential shift occurred in this sample towards negative potential region, also in good agreement with results showed in Figure 6. We believe that this cathodic shift can be related to enhanced charge collection at the contact for the N-doped TiO$_2$.
Figure 7. (a) J-V characteristics of PEC water splitting with different photoanodes (inset: photograph of N3TiO23Au on flexible SS substrate)(b) hydrogen gas evolution from PEC experiments using different photoanodes.

The gas evolution from 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 hybrid electrodes could generate hydrogen of about 120 µmol/hr cm2. Interestingly, the hydrogen generated at N-TiO2–Au hybrid electrodes was about 270 µmol/hr cm2. The described bendable architecture of N-TiO2–Au on SS substrates (inset of Fig. 7a) with light weight and low cost can be beneficial in large scale flexible PEC fuel generation.59

Another advantage of both side conducting nature of SS substrates enable us to design an artificial leaf based (back side coated with electrocatalyst) on monolithic wireless type solar fuel cells.51

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 NPs loading and improves the optical absorption due to band narrowing effect. DMAP-Au NPs anchoring amplifies the visible light activity of TiO2 and N-TiO2 via light scattering effect and also, improves the charge recombination at electrode/electrolyte interface. After optimization of the Au loading on the nanostructured photocathodes, 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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