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ARTICLE

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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 nitrated 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 (3.4×10⁻⁷ M) due to light blocking to N-TiO₂ surface. Strikingly, even with a ten-fold lower Au NPs loading (0.34×10⁻⁷ 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 cm⁻² 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.^{1, 2} The primary report on photoelectrocatalytic (PEC) water oxidation on TiO₂ 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 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.⁶ 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.^{7, 8} 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).⁹⁻¹¹ 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 10⁶.¹² 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.¹³ Moreover, the rapid electron transport at 1-D TiO₂ crystallite framework is highly beneficial for the efficient charge collection at the relevant interfaces.^{14, 15} 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,¹⁶ but a proper combination of both materials generates excellent visible-light PEC performances, even

significantly enhancing the UV photocatalysis of TiO₂.¹⁷⁻²¹ This indicates that the interfacial interaction between Au NPs and TiO₂ 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 TiO₂ surfaces. For instance, Au NPs were coated on TiO₂ *via* physical evaporation or sputtering resulted in the formation of inhomogenous NPs coating on the metal oxide host surface.^{22, 23} 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.^{24, 25, 26, 27, 28} 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 TiO₂ hollow nanowires, which in turn resulted in enhanced photocatalytic performance towards dye degradation.²⁹ 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 were modulated via nitrogen doping the 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 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 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 Nanowires Array

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 FTO substrate using radio frequency magnetron sputtering. Followed that, the ZnO seed layer coated FTO substrate was immersed into 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, TiO₂ 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 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 NWs arrays are obtained. The TiO₂ NWs samples were calcined at 500 °C for 0.5 h under Ar atmosphere.

For nitridation onto TiO₂ NW, 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.³⁰ 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 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.

Assembly of Au NPs on TiO₂ Nanowires Array

Au NPs coating on TiO₂ and N-TiO₂ NWs arrays was obtained by immersing the TiO₂ electrodes in positively charged, water soluble DMAP-capped Au NPs 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 TiO₂-Au and N-TiO₂-Au hybrid photocatalytic electrodes. After Au NPs coating on these electrodes DMAP molecules were removed by sintering process.

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)

$$E_b = E_{\text{nanotube+atom}} - (E_{\text{nanotube}} + E_{\text{atom}}). \quad (1)$$

Structural, and optical characterization

The surface of various TiO₂ 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 TiO₂ electrodes were analyzed by x-ray photoelectron spectroscopy (XPS) using an angular resolved electron analyzer

with a monochromated Al K α source (Theta Probe, Thermo

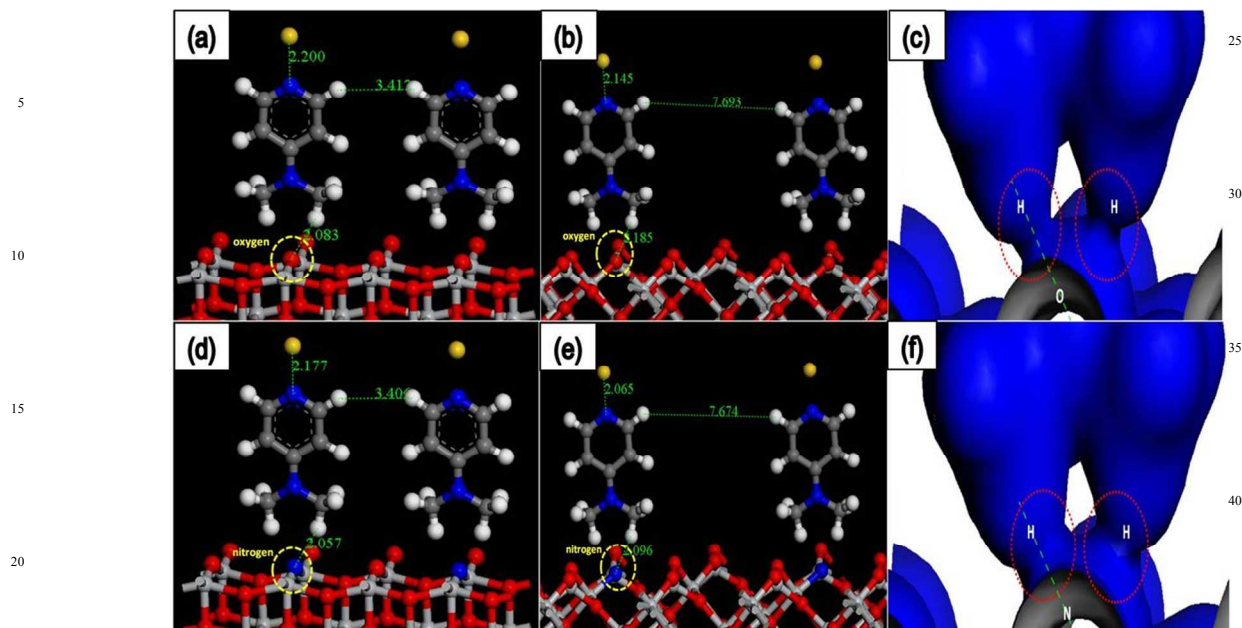


Figure 1: The optimal orientations of TiO₂ (a, b) and N-TiO₂ (d, e) surface illustrating the binding mechanism of DMAP-Au NPs at {001} and {101} planes, respectively. The electron density distribution estimated at TiO₂-Au (c) and N-TiO₂-Au (f) electrodes.

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, $F.R. = (1 - R)^2 / 2R$ with in build software from JASCO UV-Vis spectrometer. We have assumed that the scattering term is similar for photoelectrodes with and without Au loading.

(Photo)- electrochemical characterization

The (photo)-electrochemical analysis was done using a three electrode configuration. The as-prepared TiO₂, TiO₂-Au, N-TiO₂ and N-TiO₂-Au electrodes (electrode area 1 cm²) were used as 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 (PGSTAT-30 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 photoelectrode 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.³¹⁻³³ 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.^{34, 35} 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) towards DMAP-Au NPs anchoring compared to the {001} facets of TiO₂ (-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 TiO₂-Au hybrid electrode.

The reported excellent catalytic activity and band structure modifications of TiO₂ upon nitrogen doping³⁶⁻³⁹ 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-TiO₂-Au hybrid electrodes. As anticipated, higher binding energies (-8.86 kcal/mol) were observed for DMAP-Au NPs anchoring on N-TiO₂ than on pristine TiO₂ 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 {101} surface of N-TiO₂ NWs. The N-TiO₂-Au hybrid system shows a binding energy of -35.56 kcal/mol at {101} surface, which is nearly four times higher than that observed for {001} plane of N-TiO₂ NW. This strongly suggests that the Au NPs can be effectively coated onto N-TiO₂ by electrostatic attraction.

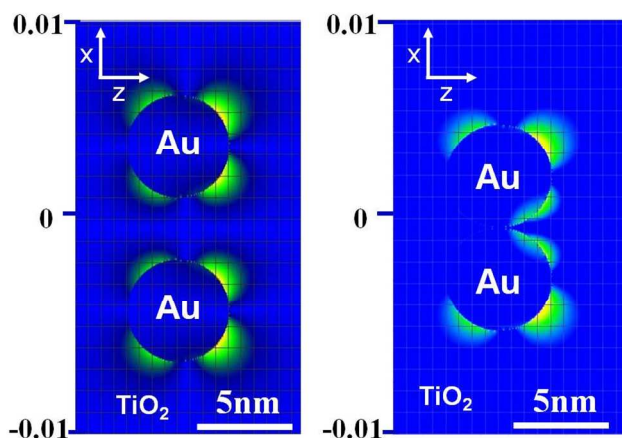


Figure 2. Spatial distribution of electric-field energy density of TiO₂-Au hybrid photocatalytic system at different spacing conditions: (a) with few nm spacing and (b) Au nanoparticles in contact (y axis indicated the distance in nm).

On the other hand, in view of improving the light harvesting efficiency of TiO₂, 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 TiO₂-Au hybrid systems, the light scattering effect of Au NPs at TiO₂ 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 TiO₂-NWs surface obtained from FDTD simulations. The permittivity of gold was analyzed using Lorenz-Drude dispersive model.⁴⁰

$$\epsilon_r(\omega) = \epsilon_{r,\infty} + \sum_{m=0}^5 \frac{G_m \Omega_m^2}{\omega_m^2 - \omega^2 + j\omega\Gamma_m} \quad (1)$$

where, $\epsilon_r(\omega)$ is the relative permittivity at infinity frequency, G_m

is the strength of each resonance term, Ω_m is the plasma frequency, ω and ω_m is the angular and resonant frequency, respectively, and Γ_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 NPs 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 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 NPs decoration at TiO₂ 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 TiO₂ as well as enhancing the visible light activity of TiO₂ 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 TiO₂ NWs and N-TiO₂ NWs arrays onto fluorinated tin oxide (FTO) substrates. Figure 3 shows the electron microscopy images of nitrated TiO₂ (N-TiO₂) NWs, Au NPs coated TiO₂ NWs (TiO₂-Au) and N-TiO₂ NWs (N-TiO₂-Au) arrays, respectively.

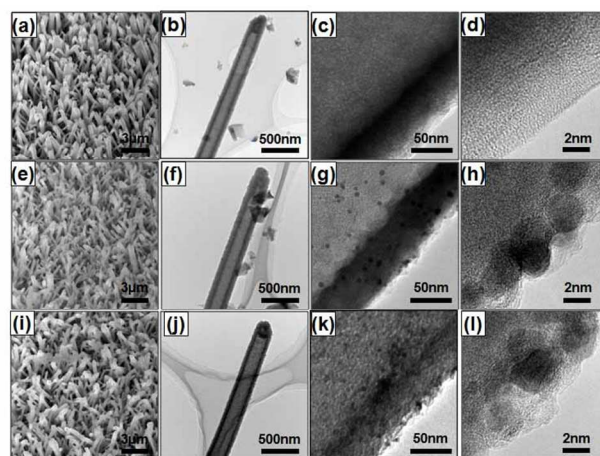
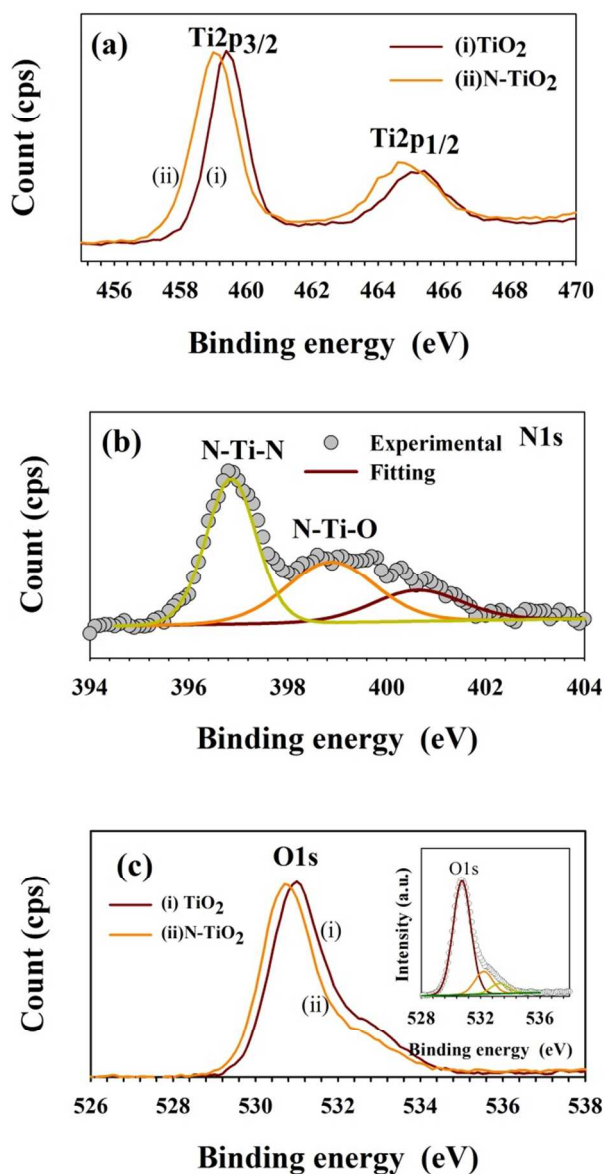


Figure 3. (a), (e) and (i) SEM and images of N-TiO₂, TiO₂-Au and N-TiO₂-Au electrodes, respectively. Corresponding TEM images were presented in right hand side of each sample.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of N-TiO₂ NWs clearly reveal their vertically aligned geometry and 1-D structure (Fig. 3a). The N-TiO₂ 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 TiO₂. This layer represents the formation of TiN/TiO_xN_y on TiO₂ NW surface during the nitridation process. Although it was difficult to obtain lattice resolved TEM images at the surface of N-TiO₂ NWs, the X-ray diffraction (XRD) and SAED patterns support that N-TiO₂

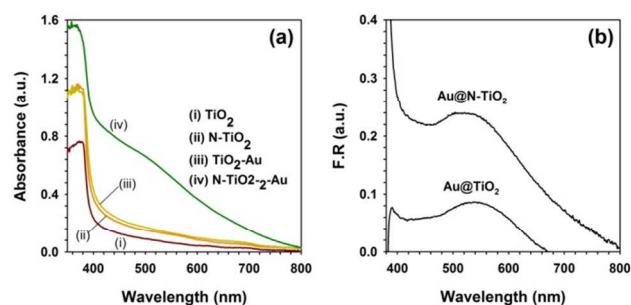
NWs maintain their polycrystalline anatase phase (See Supporting information Fig.S1). There are no noticeable changes on the geometry of the NWs after Au NPs anchoring (Fig. 3f & Fig. 3j). Au NPs with an average diameter of ~ 5 nm were observed in the high magnification TEM images (Fig. 3(i)) (also See Supporting information Fig.S2). These images (Fig. 3h & Fig. 3l) confirm the higher loading of Au NPs on N-TiO₂ NWs compared to pristine TiO₂ NWs.



10 **Figure 4.** XPS results of (a) Ti 2p (b) N1s and (c) O1s core spectra of TiO₂ and N-TiO₂ electrodes.

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 N-TiO₂ NWs. The shoulder peaks at 459.4 eV and 465.1 eV correspond to Ti2p_{3/2} and Ti2p_{1/2}, respectively.⁴¹ In N-TiO₂ 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), the peaks at 396.8, 398.8, and 400.6 eV provide a clear picture of

nitrogen environment at TiO₂ NWs. The peak at 396.8 eV is attributed to the existence of atomic β -N at TiO₂ matrix and the peak at 398.8 eV implies the substitution of O₂⁻ by nitrogen ions and thus, results in the formation of N-Ti-O.^{42, 43} This confirms the existence of Ti³⁺ 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 TiO₂.⁴⁴ The atomic ratio of nitrogen doping carriers was estimated from Fig. 4(b) and found to be 5.8 wt%. The broad features of O1s peak in Fig.4c were deconvoluted with 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 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.



45 **Figure 5.** Absorbance spectra of TiO₂ and N-TiO₂ electrodes in the presence and absence of Au NPs; (b) Kulbelka-Munk relation of Au NPs decorated at TiO₂ NWs and N-TiO₂ NWs.

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 Kulbelka-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, N-TiO₂-Au hybrid electrodes showed higher absorbance, indicating higher loading of Au NPs in good correspondence with the TEM measurements (Fig. 2h & 2l) and Kulbelka-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 TiO₂-Au hybrid electrode showed four times higher photocurrent $\sim 0.4 \text{ mAcm}^{-2}$ than pristine TiO₂ NWs electrode (0.11 mAcm^{-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/TiO₂ Schottky junction.^{46, 47} In addition, it may facilitate the charge separation at TiO₂/electrolyte interfaces and thus reduces the recombination of electrons through surface states of TiO₂.⁴⁸ In the case of nitrogen doping at TiO₂ NWs, the photocurrent density was slightly enhanced (0.22 mAcm^{-2}), which might be ascribed to the promotion of visible light activity of TiO₂ through band gap narrowing effect (See supporting information S3 and S4).

In striking contrast, the photocurrent at N-TiO₂-Au hybrid system was only slightly higher than N-TiO₂ 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-TiO₂ NWs surface and also reduce the interfacial contact between N-TiO₂ and FTO electrode, thus hindering the photoholes participating in the water oxidation process.¹⁸ 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-TiO₂ NWs, which necessitates the optimization of Au NPs loading onto N-TiO₂ NWs. We have recently reported that the photoelectrochemical performance of TiO₂/Au nanocomposites has a volcano dependence with Au loading.²⁸

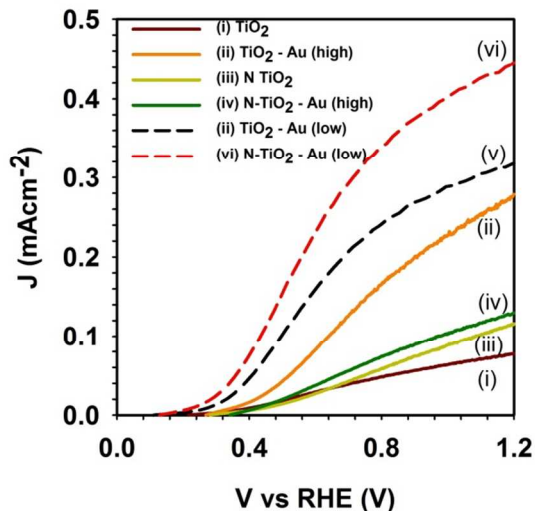


Figure 6. J-V results of PEC water splitting using different photoanode electrodes. Note that two different Au concentrations were used for decorating working electrodes: low – $0.34 \times 10^{-7} \text{ M}$; high- $3.4 \times 10^{-7} \text{ M}$.

Interestingly, the Au NPs decorated TiO₂ and N-TiO₂ electrodes using low concentration stock solution ($0.34 \times 10^{-7} \text{ M}$), here referred as TiO₂-Au (low) and N-TiO₂-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-TiO₂.

Furthermore, the stability of electrodes in photocurrent

generation is examined with chronoamperometric curves (See supporting information S5). The significant decrease of the photocurrent in both TiO₂ and TiO₂-Au electrodes may be attributed to the current leakage at TiO₂/FTO interfaces to electrolyte through naked FTO surface (uncovered TiO₂ 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 TiO₂ blocking layer between TiO₂ 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 TiO₂ electrodes, we recorded IPCE spectra (See supporting information Fig. S6). There is no photocurrent peak exhibit around 550 nm in TiO₂-Au electrode as observed in optical absorption spectra (Figure 5b). This implies that there is no electron injection from Au nanoparticles to TiO₂ by plasmonic effect. Instead, Au NPs are promoting the optical absorption of TiO₂ 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 TiO₂ and N-TiO₂ 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 TiO₂ nanowire fabrication onto flexible SS substrates remains challenging. Similar deposition procedure of TiO₂ on FTO substrates explained in the experimental session was repeated for fabricating TiO₂ NW on flexible SS substrates. We adopt the optimized Au NPs concentration condition ($0.34 \times 10^{-7} \text{ M}$) from the Figure 6, and reconstructed the TiO₂-Au hybrid systems onto flexible stainless steel (SS) substrates instead of FTO substrates (sample photo presented in inset of Figure 7).

The *j-v* characteristics of Au-TiO₂-SS and Au-N-TiO₂-SS electrodes were tested in 0.5M Na₂SO₄ aqueous electrolyte with three electrode PEC cell step up. The *j-v* characteristic of N-TiO₂-Au-SS is displayed in Figure 7 (a). The higher photocurrent density achieved in N-TiO₂-Au compared to TiO₂-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-TiO₂-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 TiO₂.

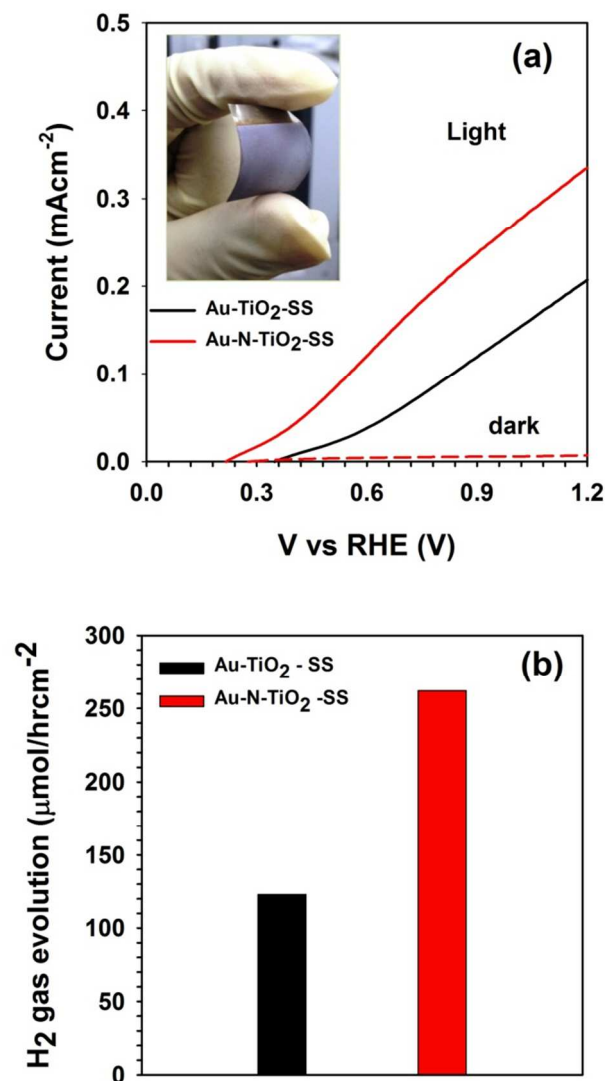


Figure 7. (a) J-V characteristics of PEC water splitting with different photoanodes (inset: photograph of N-TiO₂-Au on flexible SS substrate)(b) hydrogen gas evolution from PEC experiments using different photoanodes.

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 cm⁻². Interestingly, the hydrogen generated at N-TiO₂-Au hybrid electrodes was about 270 μmol/hr 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 in large scale flexible PEC fuel generation.^{49, 50} 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 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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