DOI: 10.1002/cctc.201300715



# Disordered Mesoporous $TiO_{2-x}N_x$ +Nano-Au: An Electronically Integrated Nanocomposite for Solar H<sub>2</sub> Generation

Kumarsrinivasan Sivaranjani,<sup>[a]</sup> Sivaraman RajaAmbal,<sup>[a]</sup> Tanmay Das,<sup>[b]</sup> Kanak Roy,<sup>[a]</sup> Somnath Bhattacharyya,<sup>[b]</sup> and Chinnakonda S. Gopinath<sup>\*[a, c, d]</sup>

We report on H<sub>2</sub> generation by photocatalysis driven by simulated white light by electronically integrated Au nanoparticles with multifunctional, disordered mesoporous  $TiO_{2-x}N_x$  (Au-NT) nanocomposites. Solar H<sub>2</sub> generation (1.5 mmol h<sup>-1</sup> g<sup>-1</sup>) from aqueous methanol has been demonstrated with Au-NT nanocomposites. The water splitting activity of Au-NT is attributed to the 21.1 ps lifetime of charge carriers observed from fluores-cence lifetime measurements, which indicates a high electron-injection efficiency from nano-Au to the conduction band of TiO<sub>2</sub>, and hence charge separation as well as utilization. This is directly supported by the observation of a high photolumines-cence emission intensity with Au-NT that highlights the energy transfer from nano-Au to TiO<sub>2</sub>. The p–n heterojunction observed between the Au (001) and TiO<sub>2</sub> (101) facets helps to-

wards the higher charge separation and their utilization. A low mesochannel depth (< 10 nm) associated with disordered mesoporous  $TiO_{2-x}N_x$  helps the charge carriers to move towards the surface for redox reactions and hence charge utilization. Visible-light absorption, as a result of the surface plasmon resonance of nano-Au, is observed in a broad range between 500 and 750 nm, which helps in harvesting visible-light photons. Finally, electronically integrated nano-Au with  $TiO_{2-x}N_x$  in Au-NT is evident from Raman and X-ray photoelectron spectroscopy measurements. All of these factors help to achieve a high rate of H<sub>2</sub> production. It is likely that a higher rate of H<sub>2</sub> production than that reported here is feasible by strategically locating Au clusters in porous  $TiO_2$  to generate hot spots through electronic integration.

## Introduction

The visible-light-driven photocatalytic water splitting reaction (WSR) is projected to be an indispensable solution to meet a significant part of the clean and sustainable energy demand on a global level.<sup>[1]</sup> The production of H<sub>2</sub>, a clean fuel, from water and sunlight by the overall water splitting reaction (OWSR) is an ultimate goal to sustain the globe in a better way.<sup>[1-3]</sup> In spite of many efforts in the past, the OWSR by visible-light-driven photocatalysis is yet to produce a breakthrough in terms of a quantum efficiency of  $\geq 10\%$ , which is the mini-

[a]	Dr. K. Sivaranjani, S. RajaAmbal, K. Roy, Prof. C. S. Gopinath Catalysis Division
	CSIR-National Chemical Laboratory Dr. Homi Bhabha Road, Pune 411 008 (India) Fax: (+91)20-2590-2633
	E-mail: cs.gopinath@ncl.res.in
[b]	T. Das, Prof. S. Bhattacharyya Department of Condensed Matter Physics and Materials Science Tata Institute of Fundamental Research 1 Homi Bhabha Road, Colaba, Mumbai 400 005 (India)
[c]	Prof. C. S. Gopinath Center of Excellence on Surface Science CSIR-National Chemical Laboratory Pune 411 008 (India)
[d]	Prof. C. S. Gopinath CSIR-Network of Institutes for Solar Energy (NISE) CSIR-NCL Campus Pune 411 008 (India)
	Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/cctc.201300715

mum benchmark to consider commercialization. From the rate of slow progress of the OWSR witnessed in the last few decades, in our opinion, the achievement of 10% efficiency might be considered as a long-term solution for energy demands. Nonetheless, H<sub>2</sub> production through the WSR with a sacrificial agent, such as methanol or glycerol, might be considered as a short-term goal, as it avoids the four-electron process to produce O<sub>2</sub> in the OWSR.<sup>[4,5]</sup> There are significant numbers of reports available on the WSR and OWSR, and more concerted efforts are necessary to produce a sustainable photocatalyst system.<sup>[1–5]</sup>

Among the materials available,  $TiO_2$  is considered to be the best candidate for photocatalysis for a variety of reasons, such as photostability, low toxicity, large abundance, cost effectiveness, and high oxidation potential.<sup>[6]</sup> However, a large band gap and fast charge-carrier recombination are the major drawbacks of  $TiO_2$ . There have been many efforts in the past to make  $TiO_2$  a visible-light-active photocatalyst through metal ion doping, anion doping, surface sensitization, etc.<sup>[7-12]</sup> Nitride anion doping is considered to be the most suitable path to reduce the band gap of  $TiO_2$  and bring about the absorption of more visible light.<sup>[9, 10]</sup> It has been demonstrated that nitride or anionic nitrogen is responsible for the band-gap reduction and visible-light absorption in  $TiO_{2-x}N_x$ .<sup>[9,11]</sup>  $TiO_{2-x}N_x$  has been prepared successfully by various methods.<sup>[9,11-16]</sup>

Along with visible-light absorption, the probability of charge-carrier recombination should be suppressed or mini-

mized to increase the quantum efficiency. The introduction of mesoporosity in TiO<sub>2</sub> increases the rate of diffusion of charge carriers from the bulk to the surface.<sup>[14,17]</sup> Specifically, disordered mesoporosity is known to reduce the diffusion length of charge carriers as the depth of the mesopores is a few nanometers (<10 nm),<sup>[14,18]</sup> unlike several hundred nanometers in conventional mesoporous materials, such as MCM-41 and SBA-15.<sup>[19-21]</sup> These types of mesopores.<sup>[14,22]</sup> This disordered mesoporous framework provides an easy route for the diffusion of reactants and products because of low diffusion barriers.

It is known that noble metal cluster deposition on TiO<sub>2</sub> results in an electron sink through selective storage of electrons.<sup>[23]</sup> Interestingly, nano-Au or Ag deposits on TiO<sub>2</sub> cause more visible-light absorption through surface plasmon resonance (SPR) bands.<sup>[24]</sup> It is known that the final properties of an Au/TiO<sub>2</sub> system, especially for WSR activity, mainly depend on the preparation procedure. Bamwenda et al. prepared Au/TiO<sub>2</sub> and Pt/TiO<sub>2</sub> photocatalysts by different preparation routes and showed that their WSR activity from aqueous ethanol solution depends on the preparation procedure.<sup>[25]</sup> Recently Murdoch et al. have shown that photocatalytic activity is independent of the Au cluster size between 3 and 12 nm and Au/anatase gives a two orders of magnitude higher rate of H<sub>2</sub> production than on rutile TiO2.<sup>[26]</sup> Subramanian et al.<sup>[27]</sup> demonstrated a negative shift of the Fermi level ( $E_{\rm F}$ ) of a Au/TiO<sub>2</sub> nanocomposite; a higher negative potential shift has been observed with the  $E_{\rm F}$ of Au/TiO<sub>2</sub> with decreasing Au particle size. Hence, the resulting composite materials are more reductive than pure TiO<sub>2</sub>. Furthermore, lifetime measurements indicate that charge injection occurs from TiO<sub>2</sub> to Au. However, exactly the opposite to the above, electron injection from Au to the conduction band (CB) of TiO<sub>2</sub> was suggested because of the strong localization of plasmonic near fields close to the Au–TiO<sub>2</sub> interface.<sup>[28,29]</sup> Notably, the preparation methods are different in the above reports, and it is very likely that the method of preparation influences the electron-injection mechanism. Apart from the above controversies, the mechanistic aspects of the Au/TiO<sub>2</sub> system and the integration of nano-Au with TiO<sub>2</sub> is less understood.  $^{\mbox{\tiny [27-29]}}$  However,  $\mbox{\rm H}_2$  production with Au-TiO\_2 composites through the WSR demonstrates its high potential,[25-29] and a better understanding would lead to the application of these materials with better activity.

A tandem approach has been employed to synthesize an electronically integrated composite of nano-Au and disordered



**Figure 1.** a) Wide-angle PXRD pattern and b) UV/Vis absorption spectra of xAu-NT nanocomposites. Inset in a) is shown the low-angle XRD patterns. The photograph (top) shows the color variation with increasing Au content of xAu-NT with sample labels as  $A = N-TiO_2$ , B = 0.01Au-NT, C = 0.03Au-NT, D = 0.05AuNT, E = 0.10AuNT, and F = 0.30Au-NT.

and a significantly long lifetime of electrons (21 ps). These composite materials show decent activity towards H<sub>2</sub> generation from aqueous methanol solution under simulated white light. This work is part of ongoing studies in our laboratory on materials development for visible-light-driven photocatalysis.<sup>[11-14,18,30-34]</sup>

#### **Results and Discussion**

Powder X-ray diffraction (PXRD) patterns of all xAu-NT materials, in which x indicates the nominal amount of Au loaded [at%], are shown in Figure 1a. All the peaks in the XRD patterns could be indexed to the anatase phase of TiO<sub>2</sub> (JCPDS File 21-1272).<sup>[34, 35]</sup> All of the peaks are broad, which indicates the nanocrystalline nature of the materials. The crystallite size was calculated by using the Debye–Scherrer equation, and the results are shown in Table 1. Up to 0.10Au-NT, there is no feature observed in the XRD patterns that corresponds to metallic

mesoporous  $TiO_{2-x}N_x$  (Au-NT) in a single step by a simple solution combustion method (SCM). The Au-NT composite material possesses desirable properties, such as nano-Au clusters with SPR in a broad visible-light range,  $TiO_{2-x}N_x$  with disordered mesoporosity, low mesochannel depth ( $\leq 10$  nm) and high surface area, electrically interconnected nanoparticles (EINP),<sup>[18]</sup>

Table 1. Physicochemical properties of the xAu-NT materials.							
Material	Surface area [m²g <sup>-1</sup> ]	Pore Diameter [nm]	Pore volume [cm <sup>3</sup> g <sup>-1</sup> ]	Crystallite size [nm]	Bulk Au [at %] <sup>[a]</sup>		
N-TiO <sub>2</sub> (NT)	234	7	0.44	6.8	0		
0.01Au-NT	218	8.2	0.37	6.0	0.009		
0.03Au-NT	200	8.1	0.4	6.2	0.026		
0.05Au-NT	213	8	0.43	6.9	0.045		
0.10Au-NT	171	9.6	0.41	8.0	0.11		
0.30Au-NT	157	6.8	0.27	8.8	0.28		

Au. However, 0.30Au-NT shows a peak at  $2\theta = 44^{\circ}$  that corresponds to the (200) plane of metallic Au.<sup>[35]</sup> This supports the good dispersion of nano-Au clusters on xAu-NT (x  $\leq$  0.1).

The inset in Figure 1 a shows the low-angle XRD patterns of all of the xAu-NT materials. The mesoporous nature of the Au-NT materials was confirmed by a feature at around  $2\theta = 1^{\circ}$ . Only one peak was observed, which indicates the disordered mesoporosity.<sup>[14,34]</sup> Unlike ordered hexagonal mesoporous materials, such as MCM-41 and SBA-15, no other low-angle features were observed, <sup>[19–21]</sup> which highlights the disordered mesoporous nature that results from the intergrowth of fundamental particles. A high Au loading (x=0.3) affects the mesoporosity of the materials significantly. A gradual decrease in the intensity of the low-angle peak at  $2\theta = 1^{\circ}$  indicates increasing pore blockage by nano-Au clusters. However, all of the *x*Au-NT materials possess disordered mesoporosity along with nanocrystallinity.

The UV/Vis spectra of the xAu-NT nanocomposites are shown in Figure 1 b. The absorption edge of TiO<sub>2</sub> remains at around 380 nm, in spite of N doping.<sup>[14]</sup> The color photograph in Figure 1 displays the xAu-NT nanocomposites. N-TiO<sub>2</sub> is pale yellow, and upon Au introduction, a blue to grayish blue color develops gradually. On increasing the Au loading to 0.1 at % and above, the color changes increasingly towards dark blue. The SPR features of nano-Au in these composite materials cause more visible-light absorption between 500 and 750 nm.<sup>[26,27]</sup> This light absorption is a result of the collective oscillation of electrons of the Au particles in response to optical excitation.<sup>[27]</sup> Visible-light absorption between 500 and 750 nm demonstrates the surface plasmon state energy, at least, between 1.65 and 2.5 eV above the  $E_{\rm F}$  of Au, which indicates the production of energized electrons. This SPR peak intensity increases with increased Au loading, and the position of the peak depends on the Au particle size or aggregation and the surrounding environment.<sup>[36,37]</sup> Hence visible-light photons can be harvested by using xAu-NT nanocomposites. Indeed, TEM studies of 0.1Au-NT show the size distribution of Au clusters (Figure 3), which suggest that different size particles lead to a broad absorption in the visible-light regime. However, the pore volume and surface area decrease with increasing Au content, especially at  $x \ge 0.1$  (Table 1), which indicates increased pore blockage as a result of Au clusters in the pores. Apart from SPR, nano-Au clusters act as an electron sink by forming Schottky barriers with TiO<sub>2</sub> and the active sites for H<sub>2</sub> evolution. Thus nano-Au in xAu-NT increases the visiblelight absorption significantly.

 $N_2$  adsorption-desorption isotherms and the Barrett–Joyner– Halenda (BJH) pore size distribution of xAu-NT are shown in Figure 2. All materials show a type IV isotherm with an H<sub>2</sub> hysteresis loop, which is typical for disordered mesoporous materials.<sup>[14,22]</sup> xAu-NT nanocomposites show a narrow pore size distribution with an optimum pore diameter around  $8\pm1$  nm. Compared to  $TiO_{2-x}N_{xr}$  xAu-NT exhibits a significant decrease in the BET surface area. Among these composite materials, 0.05Au-NT shows the highest surface area of 213 m<sup>2</sup>g<sup>-1</sup>. The surface area decreases with increasing Au loading, and 0.30Au-



**Figure 2.** a) N<sub>2</sub> adsorption–desorption isotherms and b) BJH pore size distribution of xAu-NT composite materials. c) TEM image of 0.05Au-NT. The SAED pattern is shown in the inset. No distinct Au particles are directly observed, which indicates the good dispersion.

NT exhibits a surface area of  $157 \text{ m}^2\text{g}^{-1}$ , which indicates increasing pore blockage.

A TEM image of 0.05Au-NT is shown in Figure 2c (more TEM images can be seen in Figure S2). All of the xAu-NT particles exhibit a spherical or near-spherical shape, and a disordered mesoporous structure is observed for all xAu-NT materials. This disordered mesoporosity arises because of the intergrowth of fundamental particles, which leads to aggregates with a significant extra-framework void space. The presence of meso- and macropores is clearly visible in Figure 2 c. These assist the faster diffusion of reactants and products in heterogeneous catalysis. Selected-area electron diffraction (SAED) patterns confirm the crystalline nature of xAu-NT nanocomposites with anatase phase TiO<sub>2</sub>. TEM images show that the majority of the lattice fringes correspond to the (101) crystallographic planes of the anatase phase (d(101) = 0.352 nm). These observations are in excellent agreement with the XRD results. This disordered mesoporous structure has additional advantages owing to the small mesochannel depth of  $\leq$  10 nm; these are referred to as p3D mesopores.<sup>[14, 18, 22]</sup> This is in contrast to micron-size long mesochannels in ordered mesoporous materials.<sup>[19]</sup>

Finally, nanocrystallites in *x*Au-NT are electrically well connected with each other, and this connectivity extends up to a few micrometers (Figures 2 c and S1). As a result of the EINP nature,<sup>[14,18]</sup> the excited electron can move from one end to the other effectively and from the bulk to the surface because of the small diffusion length under light-harvesting conditions. This advantageous EINP feature associated with *x*Au-NT composite materials enhances the diffusion of charge carriers to the surface.

Unlike the reports cited in the introduction, we were unable to find any Au particles on Au-NT in our TEM studies, likely because of the similar contrasts of Au and TiO<sub>2</sub>. To explore various aspects of Au, Z-contrast image analysis was performed by using a FEI-TITAN microscope operated at 300 kV. A representative Z-contrast image of 0.10Au-NT at low magnification is

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

## CHEMCATCHEM FULL PAPERS



**Figure 3.** a) Z-contrast image of 0.10Au-NT at low magnification. b) High-resolution Z-contrast image of the nanoparticle shown within the white square shown in a). EDX spectrum recorded c) from the Au nanoparticle shown in b) and d) on the  $TiO_2$  matrix.

shown in Figure 3a, in which small bright regions indicate the possibility of the accumulation of higher-atomic-number elements than the TiO<sub>2</sub> matrix. On average, the particle size varies from 5-21 nm (Figure 3 a). The high-resolution Z-contrast image of the bright region within the white square shown in Figure 3a is shown in Figure 3b, in which the lattice spacing ( $\approx$ 0.2 nm) matches the projected distance between the Au (001) planes. The energy-dispersive X-ray (EDX) spectrum recorded from the same particle confirms that it is an Au nanoparticle embedded in a matrix that contains Ti and O (Figure 3 c). The EDX spectrum of a TiO<sub>2</sub> matrix region proves that the matrix does not contain any Au (Figure 3d). If we consider all of the results presented in Figure 3, it can be stated that Au nanoparticles were grown within a  $\text{TiO}_2$  matrix and that Au (001) and TiO<sub>2</sub> (101) planes make p-n heterojunctions, which are expected to help charge separation and hence its better utilization. Notably, the Au particles are isolated with a minimum average interparticle distance of 200 nm.

Raman spectroscopy is a versatile tool to determine the structural features of the composites. Raman spectra for all of the xAu-NT composite materials are shown in Figure 4a. All six Raman-active fundamental modes are observed at 145 (E<sub>g</sub>), 198 (E<sub>g</sub>), 398 (B<sub>1g</sub>), 516 (A<sub>1g</sub>+B<sub>1g</sub>), and 640 cm<sup>-1</sup> (E<sub>g</sub>) for the anatase phase.<sup>[38]</sup> The Raman-active E<sub>g</sub> mode of TiO<sub>2</sub> at 145 cm<sup>-1</sup> exhibits a systematic blueshift to 154 cm<sup>-1</sup> upon nanocomposite formation with Au. Furthermore, the full width at half maximum (FWHM) measured for E<sub>g</sub> (as well as other features) changes from 15.1 cm<sup>-1</sup> on N-TiO<sub>2</sub> to 25.2 cm<sup>-1</sup> on 0.1Au-NT,



**Figure 4.** a) Raman spectra of xAu-NT composite materials. The Raman-active  $E_g$  mode on N-TiO<sub>2</sub> at 145 cm<sup>-1</sup> shows a blueshift to 154 cm<sup>-1</sup> with increased line broadening and asymmetry and decreased intensity with increasing Au content. b) PL spectra for xAu-NT materials. The Au content is given for material identification. The dotted lines are a guide to the eye.

which indicates line broadening. This line broadening is accompanied with asymmetry for all of the *x*Au-NT composites, which is particularly evident for the  $E_g$  feature at 640 cm<sup>-1</sup>. The anatase (101) facet is the most abundant plane (Figures 1 a and 2 c), which is corrugated with alternating rows of five-coordinate Ti (likely Ti<sup>3+</sup>) and bridging oxygen at the edges of the corrugation.<sup>[39]</sup> This makes the (101) crystallographic facet ideal to interact with the deposited Au clusters through charge transfer, which leads to a blueshift in the Raman spectrum.<sup>[39]</sup> Indeed, this electronic interaction on a polar surface is likely to assist fast electron transfer.

The photoluminescence (PL) emission spectra of Degussa P25 (P25) and xAu-NT nanocomposites are shown in Figure 4b. All of the xAu-NT composites and P25 show peaks at 419, 442, and 470 nm. An emission peak as a result of the band-gap transition appears at 380 nm for all materials (not shown).<sup>[40]</sup> The emission band at 419 nm is attributed to the free exciton emission of TiO2.[41] The appearance of a shoulder around 470 nm is because of the surface state, such as Ti<sup>4+</sup>-OH.<sup>[42]</sup> The emission feature at 440 nm originates from the charge-transfer transition from  $Ti^{3+}$  to oxygen anions in a  $[TiO_6]^{8-}$  complex<sup>[43]</sup> present in the material. These three emission features show the lowest intensity for P25. N-TiO<sub>2</sub> shows a significant increase in the intensity of all the features, compared to P25. Upon the deposition of Au on N-TiO<sub>2</sub>, the intensity of all emission features increases, and the maximum intensity is observed with 0.05Au-NT. In particular, the intensity of the feature at 442 nm increases more significantly than other features, which suggests a better interaction of Au with NT through the unsaturated (101) facet. These observations reiterate the presence of pn heterojunctions in the xAu-NT nanocomposites, which help the electron injection into the CB of TiO<sub>2</sub>. On further Au loading, the intensity of all of the emission features starts to decrease. Nonetheless, xAu-TiO<sub>2</sub> exhibits higher intensity emission features than P25 and N-TiO<sub>2</sub>, which underscores the energy transfer from nano-Au to the CB of TiO<sub>2</sub>. Indeed this is the critical observation that highlights the electronic interaction between nano-Au and TiO<sub>2</sub>. The maximum intensity emission fea-

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

tures are observed for 0.05Au-NT, which indicates that the lifetime of the charge carriers is likely to be longer and hence the possibility of electron injection from nano-Au to the CB of TiO<sub>2</sub> is significantly high. Indeed, the lifetime measurements fully support these conclusions (vide infra). The surface plasmon state energy (1.65-2.5 eV) measured from UV/Vis absorption spectroscopy (Figure 1 b) indicates the production of energetic electrons ( $\approx$  3.3 eV) because of PL excitation at  $\lambda =$  375 nm. This ensures the injection of electrons from the surface plasmon states of Au to the CB of TiO<sub>2</sub> under visible-light irradiation as well as under the PL measurement conditions. The  $E_{\rm F}$ of Au and  $CB_{Min}$  of TiO<sub>2</sub> appear at around 0 and -0.5 eV, respectively, versus the normal hydrogen electrode (NHE).<sup>[2, 3, 28]</sup> Electron injection from the surface plasmon states of Au to the CB of TiO<sub>2</sub> is definitely possible and in accordance with the above energy levels. On increasing the Au content > 0.1, the emission features decreased in intensity, which is attributed to the larger size or agglomeration of Au particles and hence the possibility of lower electron injection from Au to TiO<sub>2</sub>. Larger Au particles, observed by XRD (Figure 1a), decrease the interaction with the  $TiO_{2-x}N_x$  lattice, and thereby the electronic interaction also decreases. Indeed, the aggregation of Au particles at x = 0.3 re-exposes the TiO<sub>2-x</sub>N<sub>x</sub> surface sites, and hence the PL emission intensity decreases dramatically. An optimum quantity of Au around x = 0.05 in the xAu-NT composite materials maximizes the interaction between TiO<sub>2</sub> and the Au clusters.

To know more about the nature of xAu-NT, X-ray photoelectron spectroscopy (XPS) studies were performed by using a custom-built high-pressure XPS instrument.<sup>[44]</sup> An interesting observation was made from the Ti (and other elements) corelevel results (Figure 5 a). As-prepared xAu-NT nanocomposites show three features for the Ti2p core level (thin traces in Figure 5 a); this is in contrast to the typical two core-level spinorbit doublets that result from Ti2p<sub>3/2</sub> and  $2p_{1/2}$  as observed



**Figure 5.** a) XPS core-level spectra recorded for the Ti 2p core level for NT and xAu-NT (thin traces) with a low-energy electron flood gun (bold traces). The low-energy electron flood gun was employed to neutralize the nonuniform static-charge build-up on xAu-NT. b) N 1s core-level results from NT and xAu-NT, and the inset shows the Au 4f core-level results from 0.05Au-NT.

for NT and TiO<sub>2</sub>.<sup>[11, 14]</sup> A glance at the Ti 2p core-level spectra obtained from xAu-NT indicates a possible nonuniform staticcharge build-up upon photoelectron emission. Nonuniform static-charge build-up occurs because of the presence of differentially conducting areas on the surface layers, especially because of the deposition of a small amount of Au on TiO<sub>2</sub>. A low-energy electron flood gun was employed to neutralize the build-up of static charge.<sup>[44]</sup> With charge neutralization, the XPS data show typical Ti2p features expected for any TiO<sub>2</sub> material; however, broad core-level peaks are observed for xAu-NT (bold traces in Figure 5a), which indicate the presence of mixed valent Ti ions. Indeed, these observations highlight the following electronic aspects of xAu-NT. 1) The feature observed at a low binding energy (BE), after static-charge neutralization, at around 457 eV corresponds to the Ti<sup>3+</sup> oxidation state on xAu-NT. 2) Even without charge neutralization, the above Ti<sup>3+</sup> feature was observed at 457 eV (thin traces), demonstrating the conducting nature of part of the xAu-NT material, which is attributed to the electronic interaction of nano-Au with TiO<sub>2</sub> through p-n heterojunctions. The observation of the conducting nature of part of the xAu-NT underscores the equilibration of Fermi levels and the electronic integration of Au with NT. 3) The Ti<sup>3+</sup> oxidation state is observed at the correct BE, even without charge neutralization, which suggests that Ti<sup>3+</sup> is generated upon the deposition of Au clusters. Indeed, the above points not only suggest an electronic interaction between Au and  $TiO_2$  in Au-NT but also the polarized nature of the Au-TiO<sub>2</sub> interface, which helps to separate electrons from electron-hole pairs. Small and uniformly sized Au clusters are likely to increase the interactions between Au and TiO<sub>2</sub>, which is likely to increase the electronic integration to a higher level and is worth exploring further.

The N1s core level appears at  $398.2 \pm 0.1$  eV (Figure 5b). Compared to NT, there is a marginal increase in the broadening observed with the N1s core level of *x*Au-NT. The Au4f core

level was recorded, and the result is shown for 0.05Au-NT in the inset of Figure 5 b. The N/Ti atomic ratio was  $0.29\pm0.03$  for xAu-NT. Although the signal-to-noise ratio is very poor, the presence of Au is confirmed. Approximately 70 min was required to obtain this data with repeated scans. The Au4f<sub>7/2</sub> core level appears at 84.2 eV, which suggests the metallic nature of Au.

To evaluate the efficacy of these Au-NT nanocomposites, the photocatalytic WSR was performed under simulated sunlight in an aqueous methanol solution. The H<sub>2</sub> evolution by using 0.05Au-NT nanocomposite continuously for 15 h with evacuation after every 5 h is shown in Figure 6a. A steady rate of H<sub>2</sub> evolution was observed for at least five of such cycles with very similar activity, which indicates the photostability of the nanocomposites. CO<sub>2</sub> was also produced along with H<sub>2</sub>, which was confirmed by GC (not shown). The molar ratio of H<sub>2</sub>/CO<sub>2</sub> is close to  $2.92 \pm 0.1$ , which suggests a general mechanism of one molecule each of CH<sub>3</sub>OH and H<sub>2</sub>O led to three molecules of H<sub>2</sub> and one molecule of CO<sub>2</sub> on TiO<sub>2</sub> sur-

## CHEMCATCHEM FULL PAPERS



**Figure 6.** Photocatalytic H<sub>2</sub> evolution activity of a) 0.05Au-NT for 15 h and b) xAu-NT nanocomposites in visible light with aqueous methanol solution. The amount of H<sub>2</sub> evolution reported is with 100 mg of catalyst. The dotted lines in a) indicate evacuation after every 5 h.

faces.<sup>[5]</sup> A H<sub>2</sub>/CO<sub>2</sub> ratio of 3 was maintained even if the methanol content varied between 5 and 25%, which indicates that the general mechanism holds well. The photocatalytic H<sub>2</sub> evolution activity of all of the xAu-NT nanocomposites is shown in Figure 6b, and 0.05Au-NT shows the highest H<sub>2</sub> evolution rate. Approximately 150 µmol H<sub>2</sub> h<sup>-1</sup> is generated with 100 mg of 0.05Au-NT. Pure TiO<sub>2-x</sub>N<sub>x</sub> shows the lowest activity towards H<sub>2</sub> generation (14 µmol h<sup>-1</sup>) under similar conditions. A half to one order of magnitude increase in H<sub>2</sub> production is observed with xAu-NT composites compared to TiO<sub>2-x</sub>N<sub>x</sub>, which demonstrates the critical role of nano-Au clusters in solar-light harvesting. The high rate of H<sub>2</sub> production is attributed to the electronic integration of nano-Au clusters with the disordered mesoporous TiO<sub>2-x</sub>N<sub>x</sub> framework.

Charge-carrier lifetime measurements were performed to explore the electron injection mechanism. We analyzed the emission decay of xAu-NT (x = 0.05and 0.1) and  $TiO_{2-x}N_{x}$ , and the results are shown in Figure 7. Initially, the materials were excited with a 375 nm light-emitting diode (LED) source, and the emission decay was collected at 440 nm with 5000 counts. The emission decay was best fitted by a biexponential decay for all of the materials. The first fast decay is a result of radiative and Auger recombination processes; this is followed by a slow decay, which accounts for the energy-transfer mechanism. The lifetime of TiO<sub>2-x</sub>N<sub>x</sub>, before Au is loaded, was  $\tau_1 = 1.76$  ps ( $\alpha_1 = 1$ ) and  $\tau_2 = 925$  ps ( $\alpha_2 = 0$ ). The major contribution is from the  $\tau_{1}$  species with a lifetime of 1.76 ps. Upon the introduction of nano-Au on TiO<sub>2</sub> (0.05Au-NT), the lifetime of the TiO<sub>2</sub> species increases to  $\tau_1 = 21.1 \text{ ps}$  ( $\alpha_1 = 0.17$ ) and  $\tau_2 = 11.4 \text{ ps}$ ( $\alpha_2 = 0.83$ ). An order of magnitude increase in the lifetime of  $\tau_1$  from NT (1.76 ps) to Au-NT (21.1 ps) underscores the importance of Au deposition on NT. This result corroborates the PL results, in which the emis-



**Figure 7.** Emission decay of xAu-NT and  $\text{TiO}_{2-x}N_x$  deposited as thin films on a glass substrate. The excitation and monitored emission wavelength are 375 and 440 nm, respectively. A kinetic fit was obtained by using biexponential decay, and the results are given in the text.

sion intensity from TiO<sub>2</sub> features increased manifold upon the introduction of nano-Au into the TiO<sub>2</sub> matrix. These observations demonstrate the energy transfer from nano-Au to TiO<sub>2</sub> in an effective manner. This is probably the first report to show such a long lifetime in a Au-TiO<sub>2</sub> system.

Photo-electrochemical (PEC) measurements were preformed under UV light with xAu-NT nanocomposites, and the results are shown in Figure 8a. Compared to P25 and  $TiO_{2-x}N_x$ , xAu-



**Figure 8.** a) The photocurrent generated upon UV illumination is shown to demonstrate the fourfold increase in photocurrent density with xAu-NT nanocomposites than that achieved without Au clusters. b) Chronoamperometry measurements made at 0.5 V with xAu-NT compared with TiO<sub>2</sub>.

NT displays a fourfold increase in photocurrent generation. An increase in the photocurrent under illumination at positive potentials is typical of n-type conductivity. Careful analysis of the PEC data revealed that the increase in the PEC amplitude is the maximum for 0.05Au-NT of these materials. This corroborates well with the lifetime and PL measurements as well as  $H_2$  production data.

Chronoamperometry measurements were performed to explore the photocurrent generation at different voltages, and a representative measurement made at 0.5 V is shown in Figure 8b. The photocurrent generation with 0.05Au-NT is approximately five times higher than that with  $TiO_2$  (P25), which highlights the increase in photon-to-current generation because of many factors, such as the decrease of defects and the diffusion of electrons to nano-Au clusters through the mesoporous  $TiO_2$  framework.

## Conclusions

We successfully synthesized visible-light-active mesoporous nano-Au-Ti $O_{2-x}N_x$  composites by using a simple combustion synthesis method (CSM). The solution combustion synthesis at 400 °C employed to prepare the nano-Au on N-doped mesoporous TiO<sub>2</sub> (xAu-NT) nanocomposites is predominantly a kinetically controlled process because of the short time of actual combustion under a high flux of ammonia as a result of sudden urea decomposition. A greater number of visible-light photons could be harvested by the surface plasmon resonance of Au clusters (than  $TiO_{2-x}N_x$ ), and charge-carrier mobility is enhanced because of the disordered mesoporosity along with electrically interconnected nanocrystallites of  $TiO_{2-x}N_x$ . This aspect was further enhanced by preparing well-dispersed Au particles with p-n heterojunctions, which act as charge-separation centers. In contrast to the 2 ps lifetime reported for charge carriers in nano-Au in the literature, we observed a much longer lifetime (21.1 ps) with our xAu-NT nanocomposites. This helps the electron injection from Au to the conduction band of TiO<sub>2</sub>. The electronic integration of nano-Au with TiO<sub>2</sub> was supported by X-ray photoelectron spectroscopy, photoluminescence spectroscopy, lifetime measurements, and Raman spectroscopy. As (001) nano-Au clusters bind to the (101) TiO<sub>2</sub> facets, a polarized pathway is available through p-n heterojunctions for charge separation and utilization. In addition, the presence of disordered mesoporosity greatly reduces the diffusion length of the charge carriers, and electrically interconnected nanoparticles aid fast charge conduction. These added advantages as a result of the pseudo-three-dimensional nature of the mesopores help to utilize the charge carriers efficiently for photocatalysis. The water splitting reaction under visible

light with 0.05Au-NT generates H<sub>2</sub> at 1.5 mmol h<sup>-1</sup> g<sup>-1</sup> catalyst, which is an order of magnitude higher than that of TiO<sub>2-x</sub>N<sub>x</sub>. Notably, a comparison of the lifetime of charge carriers and H<sub>2</sub> generation under visible light varies linearly between 0.05Au-NT and TiO<sub>2-x</sub>N<sub>x</sub>.

We would like to emphasize that the significantly higher lifetime of charge carriers observed in the present study, in comparison to other reports, is partially attributed to the material preparation by the SCM method. Indeed, the different preparation procedures adopted by different groups<sup>[25–29,45]</sup> could be a reason for controversial conclusions about the electron injection mechanism. This is highly relevant as the surface of a nanocomposite, especially the Au–TiO<sub>2</sub> interface, plays a major role in the optical properties, and the nature of the surface and interface depends on the method of preparation. Indeed, two different preparation methods would lead to significantly different surface characteristics. Nonetheless, different preparation methods could also lead to different electronic integration and hence different characteristics and capabilities.

## **Experimental Section**

#### Synthesis of xAu-NT materials

We employed SCM that involves a simple synthesis protocol and requires a short reaction time (<10 min) and cheap starting materials. All the chemicals employed were of analytical grade and used without further purification. Titanium nitrate (Sigma-Aldrich) as the Ti precursor, gold(III) chloride (Sigma-Aldrich) as the Au precursor, and urea (Merck) as the fuel were used. The required quantity of aqueous titanyl nitrate, gold chloride, and urea were put into a 250 mL beaker and introduced into a muffle furnace preheated at 400 °C. Water evaporation takes place in the first few minutes, followed by a smoldering-type combustion that occurs in the next 1-2 min. Immediately after the combustion process was completed, the xAu-NT materials were removed from the furnace. A series of xAu-NT composite materials were prepared by changing the amount of Au from 0 to 0.3 at% with a fixed urea/Ti<sup>4+</sup> ratio of 10. In xAu-NT, x stands for nominal amount of Au [at%]. We employed urea as fuel to avoid any carbon impurities so that no further calcination is required. During the combustion process, the in situ generation of NH<sub>3</sub> occurs as a result of urea decomposition, and this acts as a N source as well as a reduction atmosphere to reduce Au<sup>3+</sup> to Au clusters. Au-NT nanocomposites have been subjected to detailed characterization and photocatalytic WSR measurements.

#### Characterization

PXRD data of  $TiO_{2-x}N_x$  and xAu-NT materials were collected by using a PANalytical X'pert Pro dual goniometer X-ray diffractometer. A proportional counter detector was used for low-angle experiments. The data were collected with a step size of  $0.02^\circ$  and a scan rate of 0.5° min<sup>-1</sup>. The sample was rotated throughout the scan to obtain better counting statistics. The radiation used was  $CuK_{\alpha}$  (1.5418 Å) with a Ni filter, and the data collection was performed by using a flat holder in Bragg–Brentango geometry (0.2°). EDX analysis and SEM measurements were performed by using a SEM system equipped with an EDX attachment (FEI, Model Quanta 200 3D). EDX spectra were recorded in the spot-profile mode by focusing the electron beam onto specific regions of the sample. Calibration of the experiment for N estimation was measured with several mixtures of GaN and alumina powder mainly to ensure the reliability of the N estimation. N<sub>2</sub> adsorption-desorption isotherms for the materials were recorded by using a Quantachrome autosorb automated gas sorption system (NOVA 1200). The BET equation was used to calculate the surface area from the adsorption branch. The pore size distribution was calculated by analyzing the adsorption branch of the N<sub>2</sub> sorption isotherm by using

<sup>© 2014</sup> Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim

the BJH method. A FEI TECNAI 3010 electron microscope operating at 300 kV (Cs = 0.6 mm, resolution 1.7 Å) was employed for TEM measurements of the Au-NT materials. Samples were crushed and dispersed in isopropanol by sonication before deposition onto a holey carbon grid. A FEI-TITAN microscope operated at 300 kV equipped with an FEG source, a Cs (spherical aberration coefficient) corrector for condenser lens systems, and a high-angle annular dark-field (HAADF) detector was used to perform scanning transmission electron microscopy (STEM) experiments. The semiconvergence angle of the electron probe incident to the specimen and camera length were maintained 17.8 mrad and 128 mm, respectively, during the experiments, and all images were recorded with a HAADF detector. All EDX data were measured in spot mode for 180 s, keeping the other experimental parameters the same as for the high-resolution Z-contrast imaging, which was acquired for a dwell time of 20  $\mu s.$  The specimen for STEM experiments was prepared by dispersion of the material (0.10 Au-NT) in water and placing a drop of the dispersion on a Cu TEM grid covered with a carbon film, which was then dried.

Diffuse reflectance UV/Vis measurements were performed by using a spectrophotometer (Shimadzu, Model UV-2550) with spectralgrade BaSO<sub>4</sub> as the reference material. Raman spectra were recorded by using a Horiba JY LabRAM HR 800 Raman spectrometer coupled with a microscope in the reflectance mode with a 633 nm excitation laser source and a spectral resolution of 0.3 cm<sup>-1</sup>. PL measurements were performed by using a Horiba Jobin Yuon Fluorolog 3 spectrophotometer equipped with a 450 W Xe lamp at RT under the excitation at 280 nm. The conditions were fixed as far as possible to compare the PL signals directly. The XPS measurements were performed by using a custom-built ambient-pressure XPS system from Prevac, Poland, equipped with a VG Scienta SAX 100 emission controller monochromator using an  $AIK_{\alpha}$  anode (1486.6 eV) in transmission lens mode. The photoelectron energy was analyzed by using a VG Scienta R3000 differentially pumped analyzer. The spectra were recorded at a pass energy of 50 eV.

Fluorescence lifetime measurements were performed by using a Horiba Jobin Yvon Fluorolog 3 spectrophotometer equipped with a 450 W Xe lamp. Fluorescence lifetime decays were collected by using a time-correlated single photon counting (TCSPC) setup from IBH Horiba Jobin Yvon (USA) equipped with a 375 nm diode laser (IBH, UK, NanoLED-375 L,  $\lambda_{max}$ =375 nm) that has an FWHM of 89 ps as a sample excitation source.

The PEC properties of the Au/NT materials were measured by linear sweep voltammetry (LSV) by using an Autolab PGSTAT30 (Eco-Chemie) instrument in a conventional three-electrode test cell with Ag/AgCl as the reference electrode in 1 M NaOH solution under ambient conditions. To prepare the working electrode, the F-doped tin oxide (FTO) plates were washed thoroughly with acetone and isopropanol, and the catalyst was slurry made by dispersing catalyst (5 mg) in isopropanol (1 mL), which was drop-casted on the electrode surface and dried at RT overnight. This electrode was used as the working electrode for all of the electrochemical studies. A 400 W medium-pressure Hg vapor UV lamp was used.

The photocatalytic activity was measured for  $H_2O$  splitting under an AM 1.5 source. The reaction was performed under ambient conditions by using a Borosil photoreactor of 100 mL capacity equipped with a port for the withdrawal of gas samples at regular intervals. For each experiment, fresh catalyst (100 mg) was dispersed in water (64 mL) and methanol (16 mL) to serve as the sacrificial reagent. A 125 W simulated white-light source or a Newport solar simulator with an AM 1.5 filter was used as the irradiation source. The experiments were conducted at around pH 7. The  $H_2$  evolved was sampled and analyzed periodically by using a Chemito 8610 GC with a porapak-Q column and a thermal conductivity detector at 353 K.

#### Acknowledgements

We thank Dr. K. Sreekumar for help in PEC measurements. We acknowledge help from Drs. Jayakannan and Partha Hazra, IISER, Pune to conduct lifetime measurements at nano- and picosecond levels and follow-up discussions. K.S., S.R.A., and K.R. thank CSIR, New Delhi for senior research fellowships. Financial support from the TAPSUN programme under NWP0056 by CSIR, New Delhi is gratefully acknowledged. Part of the work is supported by CSISR under CSC-0404.

**Keywords:** heterogeneous catalysis • hydrogen • mesoporous materials • photochemistry • water splitting

- [1] S. S. K. Ma, K. Maeda, R. Abe, K. Domen, Energy Environ. Sci. 2012, 5, 8390-8397.
- [2] A. Kudo, Int. J. Hydrogen Energy 2007, 32, 2673-2678.
- [3] R. M. Navarro, M. C. Alvarez Galvan, J. A. Villoria de La Mano, S. M. Al-Zahrani, J. L. G. Fierro, *Energy Environ. Sci.* 2010, 3, 1865–1882.
- [4] K. A. Connelly, H. Idriss, Green Chem. 2012, 14, 260-280.
- [5] M. Bowker, Green Chem. 2011, 13, 2235-2246.
- [6] A. Fujishima, T. N. Rao, D. A. Tryk, J. Photochem. Photobiol. C 2000, 1, 1– 21.
- [7] M. Anpo, M. Takeuchi, J. Catal. 2003, 216, 505-516.
- [8] W. J. Youngblood, S-H. A. Lee, K. Maeda, T. E. Mallouk, Acc. Chem. Res. 2009, 42, 1966–1973.
- [9] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, Science 2001, 293, 269–271.
- [10] S. Sato, Chem. Phys. Lett. 1986, 123, 126-128.
- [11] a) M. Sathish, B. Viswanathan, R. P. Viswanath, C. S. Gopinath, *Chem. Mater.* **2005**, *17*, 6349–6353; b) M. Sathish, R. P. Viswanath, C. S. Gopiath, *J. Nanosci. Nanotechnol.* **2009**, *9*, 423–432.
- [12] A. Pandikumar, K. Sivaranjani, C. S. Gopinath, R. Ramaraj, *RSC Adv.* 2013, 3, 13390-13398.
- [13] C. S. Gopinath, J. Phys. Chem. B 2006, 110, 7079-7080.
- [14] K. Sivaranjani, C. S. Gopinath, J. Mater. Chem. 2011, 21, 2639-2647.
- [15] X. Chen, S. S. Mao, *Chem. Rev.* 2007, 107, 2891–2959.
  [16] T. M. Horikawa, M. Katoh, T. Tomida, *Microporous Mesoporous Mater*.
- 2008, 110, 397–404. [17] X. Chen, T. Yu, X. Fan, H. Zhang, Z. Li, J. Ye, Z. Zou, *Appl. Surf. Sci.* 2007, 253, 8500.
- [18] K. Sivaranjani, S. Agarkar, S. B. Ogale, C. S. Gopinath, J. Phys. Chem. C 2012, 116, 2581–2587.
- [19] N. Maity, P. R. Rajamohanan, S. Ganapathy, C. S. Gopinath, S. Bhaduri, G. K. Lairi, J. Phys. Chem. C 2008, 112, 9428–9433.
- [20] P. Maity, C. S. Gopinath, S. Bhaduri, G. K. Lahiri, Green Chem. 2009, 11, 554-561.
- [21] S. Basu, H. Paul, C. S. Gopinath, S. Bhaduri, G. K. Lahiri, J. Catal. 2005, 229, 298-302.
- [22] T. Mathew, K. Sivaranjani, E. S. Gnanakumar, Y. Yamada, T. Kobayashi, C. S. Gopinath, J. Mater. Chem. 2012, 22, 13484–13493.
- [23] S. Linic, P. Christopher, D. B. Ingram, Nat. Mater. 2011, 10, 911-921.
- [24] P. Christopher, H. Xin, S. Linic, Nat. Chem. 2011, 3, 467-472.
- [25] G. R. Bamwenda, S. Tsubota, T. Nakamura, M. Haruta, J. Photochem. Photobiol. 1995, 89, 177–189.
- [26] M. Murdoch, G. I. N. Waterhouse, M. A. Nadeem, J. B. Metson, M. A. Keane, R. F. Howe, J. Llorca, H. Idriss, *Nat. Chem.* 2011, *3*, 489–492.
- [27] V. Subramanian, E. E. Wolf, P. V. Kamat, J. Am. Chem. Soc. 2004, 126, 4943–4950.
- [28] Z. Liu, W. Hou, P. Pavaskar, M. Aykol, S. B. Cronin, Nano Lett. 2011, 11, 1111-1116.

# CHEMCATCHEM FULL PAPERS

- [29] Z. W. Seh, S. Liu, M. Low, S.-Y. Zhang, Z. Liu, A. Mlayah, M.-Y. Han, Adv. Mater. 2012, 24, 2310-2314.
- [30] B. Naik, K. M. Parida, C. S. Gopinath, J. Phys. Chem. C 2010, 114, 19473– 19482.
- [31] a) M. Mapa, C. S. Gopinath, *Chem. Mater.* 2009, 21, 351–359; b) M. Mapa, S. RajaAmbal, C. S. Gopinath, *Trans. Mater. Res. Soc. Jpn.* 2013, 38, 145–158.
- [32] M. Mapa, K. S. Thushara, B. Saha, P. Chakraborty, C. M. Janet, R. P. Viswanath, C. Madhavan Nair, K. V. G. K. Murti, C. S. Gopinath, *Chem. Mater.* 2009, 21, 2973–2979.
- [33] M. Mapa, K. Sivaranjani, D. S. Bhange, B. Saha, P. Chakraborty, A. K. Viswanath, C. S. Gopinath, *Chem. Mater.* 2010, 22, 565 – 578.
- [34] K. Sivaranjani, A. Verma, C. S. Gopinath, Green Chem. 2012, 14, 461– 471.
- [35] a) A. C. Sunil Sekhar, K. Sivaranjani, C. S. Gopinath, C. P. Vinod, *Catal. Today* **2012**, *198*, 92–97; b) A. C. Sunil Sekhar, C. J. Meera, K. V. Ziyad, C. S. Gopinath, C. P. Vinod, *Catal. Sci. Technol.* **2013**, *3*, 1190–1193.
- [36] S. Link, M. A. El-Sayed, J. Phys. Chem. B 1999, 103, 8410-8426.
- [37] Y. Tian, T. Tatsuma, J. Am. Chem. Soc. 2005, 127, 7632-7637.

- [38] T. Ohsaka, F. Izumi, Y. Fujiki, J. Raman Spectrosc. 1978, 7, 321-324.
- [39] A. Fujishima, X. Zhang, D. A. Tryk, Surf. Sci. Rep. 2008, 63, 515-582.
- [40] Y. Li, N.-H. Lee, D.-S. Hwang, J. S. Song, E. G. Lee, S.-J. Kim, Langmuir 2004, 20, 10838–10844.
- [41] K. Nagaveni, M. S. Hegde, G. Madras, J. Phys. Chem. B 2004, 108, 20204– 20212.
- [42] K. M. Parida, N. Sahu, A. K. Tripathi, V. S. Kamble, *Environ. Sci. Technol.* 2010, 44, 4155-4160.
- [43] J. C. Yu, J. Yu, W. Ho, Z. Jiang, L. Zhang, Chem. Mater. 2002, 14, 3808– 3816.
- [44] K. Roy, C. P. Vinod, C. S. Gopinath, J. Phys. Chem. C 2013, 117, 4717– 4726.
- [45] V. Subramanian, E. E. Wolf, P. V. Kamat, J. Phys. Chem. B 2003, 107, 7479-7485.

Received: August 26, 2013 Revised: November 7, 2013 Published online on January 21, 2014