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## Introduction

TiO<sub>2</sub> is a widely studied material in photocatalytic water splitting due to its abundance, environmental friendliness, and stability.<sup>1-3</sup> However, TiO<sub>2</sub> only generates H<sub>2</sub> in pure water at a low rate due to the fast recombination of electron-hole pairs, and has a fast backward reaction, in addition to its ability to absorb only the UV spectrum.4 Co-catalyst loading such as Pt deposition on TiO<sub>2</sub> has been proven to increase H<sub>2</sub> production from solar water splitting by preventing the recombination of electron-hole pairs.5-7 However, Pt and other various rare and expensive noble metal co-catalysts (like Au and Pd) limit the scale of implementation for extensive water splitting, and thus other cost-effective co-catalysts have been explored. Copper oxide as a co-catalyst has been studied by several groups and has been shown to improve the  $H_2$  production rate by  $\sim 30$  to 129 fold compared to pure TiO2,8-13 achieving a rate of 5.133 mmol g<sup>-1</sup> h<sup>-1</sup> using a Hg lamp in 5% vol methanol in water,<sup>9</sup> and 2.061 mmol  $g^{-1}$  h<sup>-1</sup> in 0.1 M aqueous glycerol with an

# Harvesting broadband absorption of the solar spectrum for enhanced photocatalytic $H_2$ generation<sup>+</sup>

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Absorption of the solar spectrum in the visible and near infrared region is highly desirable to improve photocatalytic H<sub>2</sub> generation. Traditionally, this can be fulfilled by designing photocatalyst materials with narrower band gaps, or with upconversion capabilities. However, such materials often pose challenges such as in synthesis, structural defects, and stability which may lead to adverse photocatalytic performance. This paper focuses on broadband utilization of the solar spectrum for enhanced photocatalysis solar H<sub>2</sub> production where the spectrum not utilized by the photocatalysts is absorbed and converted to heat energy. This approach delves into harvesting the broadband spectrum for synergistic photocatalysis and thermal heat generation, with minimal photocatalyst material manipulation. The profound impact of temperature on photocatalysis was manifested in a drastic increase of H<sub>2</sub> production by a maximum of 40-fold. The apparent quantum yield was also calculated to reach 66.9% using an ultraviolet LED light source. Outdoor testing verifies the potential of broad spectrum operation under natural sunlight as well as the convenience and simplicity of various reactor designs for practical photocatalysis applications.

apparent quantum yield (AQY) of 13.4% using a 365 nm LED.<sup>11</sup> Other earth abundant co-catalysts such as Ni were also explored. Ni-loaded TiO<sub>2</sub> produced H<sub>2</sub> at a rate of 2.547 mmol g<sup>-1</sup> h<sup>-1</sup> with an AQY of 8.1% using a 365 nm UV LED.<sup>14</sup> In comparison, an AQY of 70% was measured for a Pt-loaded TiO<sub>2</sub> photocatalyst using a black lamp (365 nm) in 1 M aqueous glycerol,<sup>15</sup> while a graphene based Au-loaded TiO<sub>2</sub> photocatalyst produced 0.296 mmol g<sup>-1</sup> h<sup>-1</sup> of H<sub>2</sub>, with an AQY of 4.1% using a 420 nm LED in ethanol (25% vol)–water.<sup>16</sup> Using earth abundant co-catalysts allows for economical and effective catalyst material development for solar water splitting, with performance that can be compared to noble metal co-catalyst loading.

To better utilize solar energy, research has been focused on developing semiconductor photocatalysts that can harvest a wider spectrum of solar radiation to increase the absorption of useful photons for conversion to H<sub>2</sub>. However, most of the studies are focused on the development of visible-light-induced photocatalysts, with visible light irradiation (400-750 nm) accounting for 43% of the incoming solar energy. In the case of TiO<sub>2</sub>, doping with metal cations and/or anions to decrease the band gap is often carried out.4,5,17-22 However, doping often leads to poorer performances as defects and traps are introduced, causing unwanted recombination of photogenerated electron-hole pairs. For example, black TiO<sub>2</sub> has been synthesized by hydrogenation of TiO<sub>2</sub> nanoparticles under high temperature and pressure. This created disorder in TiO2 nanoparticles causing a narrower band gap and extending the absorption to the visible-near infrared range. A H<sub>2</sub> production



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#### Paper

rate of 10 mmol  $g^{-1} h^{-1}$  was achieved with a solar simulator in 50% vol methanol in water.23 Narrow band gap semiconductors like metal oxynitrides, nitrides, sulphides or phosphides have also been explored as an effort to harness more of the solar spectrum, but they tend to be unstable, undergoing photocorrosion in the presence of visible light. These materials oxidize during the water splitting process, and thus degrade over time.<sup>24-26</sup> Pt<sub>3</sub>Co-loaded CdS was shown to have a H<sub>2</sub> production rate of 15.89 mmol  $g^{-1} h^{-1}$  using a Xe lamp with a 420 nm cutoff filter, in a 10% vol aqueous lactic acid solution.<sup>27</sup> ZnS-based solid solutions are efficient and low-toxic visiblelight driven photocatalysts, and Yu et al. have synthesized Cu2+modified  $Zn_xCd_{1-x}S$  with a high H<sub>2</sub> production rate of 4.639 mmol  $g^{-1}$  h<sup>-1</sup>, and an AQY of 20.9% at a visible wavelength of 420 nm, in a solution of Na<sub>2</sub>S/Na<sub>2</sub>SO<sub>3</sub> sacrificial reagent to suppress photocorrosion.<sup>28</sup> Wang et al. have also synthesized ZnO(a)ZnS-Bi<sub>2</sub>S<sub>3</sub> core-shell nanorods anchored on reduced graphene oxide, with a H<sub>2</sub> production rate of 0.310 mmol  $g^{-1}$  h<sup>-1</sup> in a solution of 5% glycerol under 1000 W m<sup>-2</sup> Xe lamp illumination.29

Even if UV to visible light can be fully harvested, the utilization of solar energy is still limited to 51%. Most importantly, harvesting of full visible light radiation using a photocatalyst material is not achievable since the near infrared (750-2500 nm) region, which accounts for 38.6% of solar energy, remains unutilized due to the water splitting nature which requires photocatalysts to have a minimum band gap of 1.5-2.0 eV, taking the overpotentials into account.30 Subsequently, the photocatalyst search is extended to nearinfrared light photocatalysts which are limited mainly to upconversion luminescence of rare earth materials.<sup>31,32</sup> Upon near-infrared excitation, rare earth materials generate upconverted emission peaks ranging from near-infrared to UV. Though the upconversion crystal exploits the near infrared solar spectrum, the absorption profile consists of discrete wavelengths, rather than a band of wavelengths. Furthermore, the upconversion intensity is low and often requires a laser to excite.

It can be seen that utilization of the broadband solar spectrum for photocatalysis remains a significant challenge, especially in the near infrared region which has insufficient energy to carry out the photogeneration of H<sub>2</sub> from water splitting. Utilizing the visible and near infrared portion of the solar spectrum to enhance solar H<sub>2</sub> production with minimal effort and nominal material manipulation is the focus of this work. Specifically, the unabsorbed solar spectrum is used for heat generation to increase the temperature of the photocatalysis system, which has explicitly shown to prolong the lifetime of the photogenerated carriers and hence drastically improve the rate of H<sub>2</sub> production. To date, we have not seen any studies that specifically exploit sunlight for this purpose of heat generation to synergistically improve photocatalytic hydrogen production. Thus, simple prototypes were constructed to demonstrate the proof-of-concept harvesting of broadband solar energy for photon and heat conversions to enable practical and efficient solar-energy driven photocatalysis.

## Results and discussion

The SEM images in Fig. 1(a) and the inset depict TiO<sub>2</sub> nanotubes with a uniform cylindrical structure of length  $\sim$ 200 nm and diameter  $\sim 10$  nm. The TEM images in Fig. 1(b) show that the TiO<sub>2</sub> nanotube structure can be seen clearly with the darker edges and the lighter contrast in the center of the tube. Welldispersed and uniform CuO nanoparticles are seen loaded on the surface of the TiO<sub>2</sub> nanotubes, having a diameter of a few nanometers. The inset of Fig. 1(b) shows the high resolution TEM diffraction fringe pattern of one of the CuO nanoparticles, with a lattice spacing of 2.31 Å corresponding to the (111) plane of CuO. Fig. 1(c) shows the XRD patterns of the TiO<sub>2</sub> nanotubes as well as for TiO<sub>2</sub> nanoparticles, after Cu(NO<sub>3</sub>)<sub>2</sub> addition. The XRD peaks of nanoparticles correspond to both TiO<sub>2</sub> anatase and rutile phases, while the TiO<sub>2</sub> nanotubes contain only the TiO<sub>2</sub> anatase phase. The presence of CuO diffraction peaks indicates the formation of the CuO-TiO<sub>2</sub> composite.



Fig. 1 (a) SEM and (b) TEM of  $TiO_2$  nanotubes loaded with CuO nanoparticles. (b, inset) HRTEM of a CuO nanoparticle with the corresponding (111) plane of CuO. (c) XRD pattern of CuO loaded NPs and NTs. (d) UV-vis absorption spectra of nanoparticles and nanotubes, with and without CuO nanoparticles, (top) before and (below) after UV illumination and (e) nitrogen adsorption/desorption isotherm of nanotubes with (inset) BJH pore size distribution.

UV-vis spectra of nanoparticle and nanotube samples with and without CuO loading are shown in Fig. 1(d). They are measured before and after a period of 10 min UV illumination. It is observed that nanoparticles show an absorption edge at around 400 nm, while the nanotube absorption edges are seen around 380 nm. This is attributed to nanotubes having a pure anatase TiO<sub>2</sub> phase of band gap 3.2-3.3 eV, compared to the nanoparticles which are a mixture of rutile (smaller bandgap) and anatase phases. In general, there is a slight increase in absorption after UV illumination for all samples. This corresponds to the samples turning slightly grey due to the oxygen vacancies33-36 which reverted back to white colour on contact with air/oxygen. The CuO-loaded samples turned purplish-grey upon UV illumination which corresponded to a local maximum in the absorption spectra at  $\sim$ 580 nm, as well as an increase in absorption across the wavelength range. The presence of the specific absorption peak and the change in color are attributed to the reduction of the CuO by the transfer of electrons from the TiO<sub>2</sub> conduction band to the adsorbed CuO nanoparticles (Fig. S1<sup>†</sup>).<sup>9,12,37,38</sup>

The Brunauer–Emmett–Teller (BET) specific surface area and pore distribution were determined using nitrogen isotherm adsorption and desorption. The nitrogen adsorption/desorption curve (Fig. 1(e) and S2†) displayed H3 hysteresis loops, suggesting the presence of mesopores. With calculations based on desorption branches using the BET and Barrett–Joyner– Halenda model, the determined specific surface area of nanoparticles is 48.7 m<sup>2</sup> g<sup>-1</sup> and 51.8 m<sup>2</sup> g<sup>-1</sup>, while the specific area of NT is 154.4 m<sup>2</sup> g<sup>-1</sup> and 110.7 m<sup>2</sup> g<sup>-1</sup> before and after CuO loading, respectively. The pore radius is measured to be ~13–14 nm for nanoparticles and ~9 nm for the nanotube samples regardless of CuO loading. The higher specific areas of nanotubes imply more active surface sites for the photogeneration to take place, beneficial for the photocatalysis.

In order to optimize the photocatalytic H<sub>2</sub> production, CuO loading of different weight percentages (0-5 wt%) onto TiO<sub>2</sub> nanoparticles (using commercial P25 as a standard reference) and nanotubes was carried out (Fig. 2(a) and (b)). It can be observed that the CuO loading has a substantial effect on the photocatalytic properties, as such even the lowest CuO loading of 1% shows significant improvement in H<sub>2</sub> generation performance by around 37 and 40-fold for nanoparticle and nanotube samples, respectively. Notably, the improvement in H<sub>2</sub> production is higher for nanotubes possibly due to their higher specific surface as determined from the BET. It is also noted that 3% CuO loading has consistently showed the best photocatalytic performance for both nanoparticles and nanotubes. Photocatalytic H<sub>2</sub> production enhancement of  $\sim$ 54-fold has been attained for both samples, with a rate of 4.10 mmol  $g^{-1}$  h<sup>-1</sup> and 5.40 mmol  $g^{-1} h^{-1}$  for CuO-loaded nanoparticles and nanotubes, respectively. This is comparable to other studies performed on CuO-TiO2.9-12,39

It is postulated that the loaded CuO nanoparticles will reduce to  $Cu_2O$  or Cu nanoparticles by accepting photogenerated electrons generated by UV light irradiation in TiO<sub>2</sub>.<sup>10</sup> The reduced CuO nanoparticle co-catalyst introduces active sites for H<sub>2</sub> evolution such that electrons generated in TiO<sub>2</sub> can be easily transferred to the co-catalyst, thus functioning as effective trapping centers.<sup>35</sup> Hence the co-catalyst nanoparticles loaded on the  $\text{TiO}_2$  photocatalyst are well-suited for charge separation as after the electron–hole pair generation, the electron is transferred into the conduction band of the co-catalyst, which is below that of the photocatalyst, effectively inhibiting recombination.<sup>9,11–13,37,38</sup> However, a higher loading of CuO nanoparticles >3% is seen to decrease the rate of H<sub>2</sub> generation, possibly due to excessive loading which leads to particle agglomeration, consequently shielding the photosensitive  $\text{TiO}_2$  surfaces. It is also suggested that overloading of the CuO co-catalyst may absorb the photons, hence reducing the photoexcitation capacity of  $\text{TiO}_2$ .<sup>38</sup>

We also examined the heat absorbing effect of CuO-loading under full spectrum illumination. NT and CuO–NT photocatalysts were each put in 10 ml of (20% vol) glycerol solution in a 25 ml quartz reactor, which was placed under Xe lamp illumination at 1000 W m<sup>-2</sup>, equivalent to 1 sun intensity. The photocatalysts would absorb heat from the direct illumination of the Xe lamp and cause the temperature to rise. The reactors were first placed in an ice water bath to ensure that the initial temperatures were the same. Later, we observed that the CuO– NT photocatalysts had a faster increase in temperature, as well as reached a higher final temperature after 30 min (Fig. S3†). This can be associated with the darker color of the photocatalysts from the CuO nanoparticles as evidenced by the UV-vis spectrum, which allowed for a greater absorbance of the incoming light and converted a portion of it to low-grade heat.

Photocatalytic H<sub>2</sub> production under UV illumination was also performed at various temperatures with glycerol as the sacrificial reagent, to study the effect of temperature on photocatalysis. Glycerol was chosen as the sacrificial agent in this case as the boiling point of a water-glycerol solution is above 100 °C, which is higher than a methanol-water mixture (methanol boiling point  $\sim$ 64.7 °C). Furthermore, glycerol is a byproduct of biodiesel available in large quantities and treated as a waste material.<sup>40-42</sup> It is observed that increasing the photocatalysis temperature from 25 to 90 °C boosted the rate of H<sub>2</sub> production of the pure TiO<sub>2</sub> nanoparticles and nanotubes up to 20 and 40-fold, respectively (Fig. 2(c) and (d) and Table S1<sup>†</sup>). The CuO loaded TiO<sub>2</sub> samples also showed an improvement in the H<sub>2</sub> production of 5 and 7-fold corresponding to the nanoparticle and nanotube samples. On the whole, a remarkable improvement in photocatalytic  $H_2$  production of ~300 to 350-fold is observed for the pristine TiO2 samples after co-catalyst loading and operation at elevated photocatalysis temperature.

Some possible reaction pathways for the photocatalytic production of  $H_2$  from glycerol have been studied and proposed in the literature. Panagiotopoulou *et al.* have examined the photocatalysis of glycerol using both pure TiO<sub>2</sub> and Pt/TiO<sub>2</sub>, and have proposed several reaction pathways based on the intermediates formed.<sup>43</sup> Some of the intermediates that are present in the liquid state include acetol, acetaldehyde, methanol and ethanol, and the intermediates are present regardless of the photocatalyst. The benefit of the Pt co-catalyst, as discussed before, is that it improves electron-hole pair separation as well as promotes the rate-limiting half reaction of  $H_2$  evolution.



Fig. 2 Top row, NP photocatalysts: (a)  $H_2$  evolution rate with different wt% CuO loading at room temperature. (c)  $H_2$  evolution rate with and without CuO loading at different temperatures. (e)  $H_2$  evolution rate at different light intensities. (g) Amount of  $H_2$  evolved for the cyclic stability test under UV LED irradiation at 90 °C, measured for 4 cycles. Bottom row, NT photocatalysts: (b, d, f, and h) the same as the top row.

### $2H^+ + 2e^- \rightarrow H_2$

The variation of  $H_2$  production with the intensity of UV illumination was also investigated (Fig. 2(e) and (f)). It was observed that the  $H_2$  production rate had a linear relationship with the intensity of light shone on the photocatalysts for the four temperatures tested. This shows that light concentration up to the measured intensity does not affect the rate of  $H_2$  production, and thus suggests the possibility of the use of solar concentrators to increase the temperature of the reactor.

Even though the performance of the photocatalysts is usually reported in mol  $g^{-1}$  h<sup>-1</sup> of hydrogen generation rate, it is dependent on various factors such as type and intensity of light source, illumination area, and type of reactor. Using the apparent quantum yield (AQY) metric to determine the photocatalytic performance of the samples gives us a more consistent standard as the H<sub>2</sub> production capabilities of the samples are measured with respect to the input power of the illumination source. This metric is defined as the ratio of H<sub>2</sub> molecules generated to the incident power for a given wavelength of irradiation as follows:<sup>11,13</sup>

$$AQY = \frac{\text{output of } H_2 \text{ per second}}{\text{input power}}$$
$$= \frac{\text{no. of } H_2 \text{ generated per second } \times 2}{\text{no. of incident photons per second}}$$

From the equation, the light to  $H_2$  conversion efficiency was calculated to be 66.9% for the 3% CuO-loaded nanotube sample at 90 °C at the highest intensity, which is much higher than the

10.3% efficiency calculated for the same sample at 25  $^{\circ}$ C. This suggests the considerable roles of temperature and co-catalyst-loading in the remarkable increase of the photocatalytic efficiency.

Fig. 2(g) and (h) show the photocatalytic cyclic stability testing for nanoparticle and nanotube samples as well as the 3% CuO-loaded counterparts, over a period of 4 hours of continuous testing under UV illumination for 4 cycles at 90 °C. From the figures, it can be seen that the initial H<sub>2</sub> evolution is approximately in a linear rate and tapered off towards the end of the 4 hours. It is postulated that the byproducts such as acetaldehyde and acetic acid are formed from the sacrificial reagents during the photocatalytic process slowed down the rate of reaction.44-47 The same trend was also seen for pure TiO2 samples, albeit more obvious after a longer period of photocatalysis. However, the rate of H2 evolution was restored once the photocatalysts were regenerated (details in the Experimental section). Fig. S4<sup>†</sup> shows the initial H<sub>2</sub> evolution rate for each of the samples over the 4 cycles, and it can be seen that the rates were fairly constant throughout the tests. The results were also consistent with those that were measured during the single run at 90 °C tests (Fig. 2(c) and (d)).

Photocatalytic cyclic stability testing was also performed under simulated solar irradiation by means of a Xe lamp. Xe arc lamps have been widely used as an illumination source for solar simulators as even the unfiltered emission spectrum matches closely to that of natural sunlight. Also a Xe lamp would be able to provide consistent, reproducible measurements of photocatalytic activities which would be challenging under the illumination of sunlight where cloud cover and outdoor temperatures and activities would affect the measurements.

Transient photovoltage measurements have been used routinely to find the pseudo-first-order recombination rate constant which gives an indication of the carrier lifetimes. This small perturbation method used in photochemical electrochemical water splitting has shown that trap limited transport and recombination of electron mechanisms correlate well with those for dye sensitized solar cells, as well as in good agreement between the photovoltage and electron density measured by transient absorption spectroscopy.48,49 The pristine TiO2 nanoparticles and nanotubes were measured at different temperatures to examine the effect of temperature on the electron lifetimes (Fig. 3(a) and (b)). The exponential increase and decay are consistent with the exponential distribution of trap states below the TiO<sub>2</sub> conduction band, termed the multiple trapping model, while the time constant for the exponential decays gives the effective electron lifetimes.49 Both samples consistently showed longer lifetimes of photogenerated electrons with increasing temperature at varying light intensities. This suggests that the higher temperature leads to an observed increased lifetime of the photogenerated carriers, hence suggesting that the recombination rate is reduced, substantially improving the H<sub>2</sub> generation rate as observed earlier.

Photocurrent measurements were carried out to investigate the effect of glycerol on the photocatalysts at different temperatures (Fig. 3(c)). A potential bias of 0.5 V was set up between two electrically isolated regions of FTO with a continuous layer of  $TiO_2$  residing on top to generate a photocurrent through the  $TiO_2$ film. Almost no dark current was observed in the deionized water without glycerol indicating that no dark reaction has occurred. When the light was switched on some photocurrent  $\sim$ 2.5–6.5  $\mu$ A was observed, an indication of water splitting taking place. Glycerol was then added to the deionized water and the photocurrent was observed to increase to  $\sim$ 14–26 µA. Glycerol is a hole scavenger which serves to remove the photogenerated holes in the TiO<sub>2</sub> film.<sup>11</sup> This leads to a higher concentration of electrons remaining in the conduction band of TiO2 resulting in a higher conductivity and photocurrent. The photocurrent increased with higher temperatures, which we postulate was due to the better hole scavenging effect of glycerol. This observation links back to the TPV results of a higher electron lifetime, as a lower rate of recombination would naturally infer a longer lifetime for the photogenerated electrons.

Simple prototypes for outdoor testing were constructed to demonstrate a proof-of-concept for broadband spectrum operation under natural sunlight, as well as the simplicity of this concept for practical photocatalytic applications. The first test was performed with a parabolic reflector focusing sunlight onto a borosilicate round-bottomed flask, filled with 3% CuO-NT photocatalysts in glycerol-water solution (Fig. 4(a)). A slow initial  $H_2$  evolution rate of 12.1 mmol  $g^{-1} h^{-1}$  was observed after the first 10 min due to the gradual heating up of the water containing



Fig. 3 TPV measurements of (a) NPs and (b) NTs at varying temperatures; and (c) photocurrent measurements of a NT film showing the effect of glycerol at different temperatures.



Fig. 4 (a)  $H_2$  evolution under solar irradiation with a 30 cm diameter concentrator and (b) corresponding  $H_2$  production (solid marker) and temperature (open marker), (c) model of the quartz reactor in insulation foam for direct solar irradiation (no concentrator); (d) corresponding  $H_2$  production (solid marker) and temperature (open marker), with and without insulation.

sacrificial agent from room temperature (22 °C) (Fig. 4(b)). However, once the solution reached the maximum temperature of ~93 °C at 40 min, the highest H<sub>2</sub> generation rate was recorded between the 40 to 50 min marks where the evolution rate reached 105 mmol g<sup>-1</sup> h<sup>-1</sup>. The overall H<sub>2</sub> evolution measured for such simple photoreactor design was a high rate of ~65 mmol g<sup>-1</sup> h<sup>-1</sup>. However, such a simple reactor without insulation has the drawback of not retaining the temperature of the solution when the light irradiance fluctuates.

With this in mind, the second reactor was designed with the comparison done on the effect of insulation on the reactors. Two cylindrical quartz reactors were placed concurrently under the sun without any light concentration effect. One was placed in a box with insulation foam all around, leaving only a gap on top for light to shine through an acrylic window (Fig. 4(c)). The other was placed in the open, without any form of insulation. From Fig. 4(d), it is observed that the uninsulated quartz reactor performed better for the first two readings, as the uninsulated reactor heated up faster than the one in the insulation box. The reactor in the insulation box took 45 min to reach the temperature of 40 °C after which the H<sub>2</sub> generated from the insulated reactor began to exceed that of the uninsulated reactor. The maximum temperature attainable for the uninsulated reactor is higher than the insulated one as it reached  $\sim$ 50 °C. As the photocatalytic reaction continued, it is apparent that the insulated reactor steadily produced more H<sub>2</sub> than the uninsulated counterpart, due to heat absorption and retention through the black insulation foam. In general, the reactors have a higher

temperature than the ambient temperature of 31 °C due to the absorption of radiation through the solution and photocatalysts. The reactors had an initial H<sub>2</sub> evolution rate of ~1.22– 1.26 mmol g<sup>-1</sup> h<sup>-1</sup> within the first 20 min and subsequently reached 4.83 and 6.84 mmol g<sup>-1</sup> h<sup>-1</sup> for the uninsulated and insulated reactors, respectively. These outdoor tests clearly demonstrated that temperature has a crucial effect on increasing the rate of H<sub>2</sub> production, both from comparing the initial room temperature and elevated temperature rates, as well as comparing the insulated and uninsulated reactor rates.

## Conclusion

This work demonstrates the utilization of the broadband solar spectrum to increase the  $H_2$  evolution rate of a photocatalytic system, by converting the unused portion of the solar spectrum to heat. Increasing the temperature of photocatalysis has been shown to correlate with an increase in the electron lifetime in TPV measurements that is beneficial for the photocatalytic reaction. Furthermore, the presence of the CuO co-catalyst also reduces the electron-hole recombination by separating the photogenerated electron from the hole. CuO also contributed to a greater absorbance of the full spectrum of light and converted a portion of it to low grade heat. On the whole, a remarkable improvement in photocatalytic  $H_2$  production up to 350-fold was measured for the pristine TiO<sub>2</sub> nanotubes with the double-effect of co-catalyst loading and operating at elevated photocatalysis temperature. An AQY of 66.9% was achieved under

## Experimental

#### Synthesis of TiO<sub>2</sub> nanotube-CuO composite

TiO<sub>2</sub> nanotube synthesis was adapted from an established hydrothermal synthesis process.<sup>50</sup> 1 g of P25 (Degussa) was added into 35 ml of 10 M NaOH and heated at 130 °C for 16 h in an autoclave. The product was washed with 0.1 M HCl until the pH reached ~1 and subsequently rinsed to a pH of 5–6. The suspension obtained was dried at 60 °C and then annealed at 450 °C for 2 h. CuO loading was performed by wet impregnation. Different concentrations of Cu(NO<sub>3</sub>)<sub>2</sub> (aq.) were mixed with TiO<sub>2</sub> nanotubes (NTs) or P25 nanoparticles (NPs). The mixture was then sonicated for 30 min and stirred for 2 h to ensure even mixing. Then, the solution was dried at 60 °C and annealed at 350 °C for 5 h.

#### Materials characterization

Scanning electron microscopy (SEM) optical characterization was carried out using a JEOL FEG JSM 7001F operating at 15 kV. The structural properties were analyzed using a transmission electron microscope (TEM, Phillips FEG CM300) operating at 200 kV. X-ray diffraction (XRD, Philips X-ray diffractometer equipped with graphite-monochromated Cu K $\alpha$  radiation at  $\lambda = 1.541$  Å) measurements were used to identify the crystal structures. UV-visible absorption spectra were obtained using a Shimadzu UV-3600 UV-vis spectrophotometer. Specific surface areas were calculated by Brunauer–Emmett–Teller (BET) analysis conducted using a Quantachrome Nova 1200 with N<sub>2</sub> as the adsorbate at liquid nitrogen temperature.

#### Photocatalyst performance measurements

H<sub>2</sub> evolution measurements were conducted using 10 mg of photocatalysts in 10 ml of water with glycerol sacrificial reagent (20% vol) in a 25 ml quartz reactor with a light emitting diode (LED) of 365 nm as the illumination source. All LED intensities were measured with a Coherent PowerMax-USB PM3 sensor. The sealed quartz reactor was purged with Ar for 10 min. A water bath was used to control the temperature as required. The H<sub>2</sub> gas concentration was measured by using a gas chromatogram (GC) (Shimadzu, GC 2014AT). For the heat absorbance test, the same quartz reactors were used with the same amount of photocatalysts (NT and CuO-NT) and electrolyte. The reactors were purged with Ar and photocatalysts were exposed to UV to allow the reduction of CuO-NTs. The quartz reactors were then immersed in an ice water bath for 30 min, and the temperature of the reagents in the quartz reactors was measured to be 0 °C  $(\pm 0.2 \ ^{\circ}\text{C})$  upon starting the test by using a thermometer inserted into the reactor. The quartz reactors were placed in front of a

300 W Xe lamp with an intensity of 1000 W  $m^{-2}$  (Perkin Elmer, PE300BFA). The ambient temperature was kept constant at 28.0 °C ( $\pm$ 0.2 °C), and the temperature of the reagents was measured every 30 s for 30 min. For the cyclic stability test performed using a UV LED, 10 mg of photocatalysts were used for the photocatalytic reaction for 4 h in a 90.0  $^{\circ}$ C (±1.0  $^{\circ}$ C) water bath. They were then centrifuged down, washed with deionized water and dried overnight at 120 °C. The dried powders were exposed to UV light (Novascan UV surface decontamination system) for 5 min to remove any organic residue. The photocatalysts were then used for the stability test for 4 consecutive hours for 4 cycles, by the same washing procedure stated above. Similarly for the cyclic stability test performed under simulated solar irradiation, the quartz reactors with CuO-NPs or CuO-NTs were placed in front of a 300 W Xe lamp with an intensity of 1000 W  $m^{-2}$ . The reactors were allowed to heat up naturally in air without the use of a water bath. The washing procedure in between cycles is the same as above.

Outdoor measurements were done on 16 Feb 2015, 12 to 1 pm, maximum solar intensity 950 W m<sup>-2</sup>, ambient temperature 33 °C with a parabolic concentrator (30 cm diameter) onto a borosilicate round bottom flask containing 25 mg of 3% CuO-NT photocatalyst in 50 ml of water with glycerol (20% vol) (Fig. 4(a)). Another outdoor measurement with solar insulation was done on 13 Jan 2015, 1 to 3 pm, maximum solar intensity 1020 W m<sup>-2</sup>, ambient temperature 31 °C concurrently using 2 separate quartz reactors. One was placed in an insulation box surrounded by ArmorFlex insulation (Fig. 4(c)) with an acrylic window (3 mm thick) while the other reactor was placed in the open without insulation. Both reactors contained 10 mg of 3% CuO-NT photocatalyst in 10 ml of water with glycerol (20% vol). Both quartz reactors were placed perpendicular to the sun's rays, and the positions were adjusted every 15 min. Similarly, all reactors were purged before H2 measurements were carried out with the GC at regular intervals.

#### Transient photovoltage (TPV) measurements

Slurries were prepared by mixing 1 g TiO<sub>2</sub> powders in 10 g of  $\alpha$ terpineol and 0.5 g of ethyl cellulose dissolved in ethanol. TPV samples were prepared by spin coating the slurry on fluorine doped tin oxide (FTO) substrates of size  $3 \times 5 \text{ cm}^2$  (QZ hybrid supplies, <10  $\Omega$  per sq.) and annealed at 450 °C for 2 h. The transient photovoltage measurements were performed using the Parstat 4000, with a 2 electrode configuration using the photoanode prepared on FTO and a Pt foil counter electrode immersed in a solution of 0.1 M Na<sub>2</sub>SO<sub>4</sub> with 20% vol glycerol. The electrolyte was purged with Ar to remove any dissolved gas before the experiments and in between measurements. The illumination source was a LED (365 nm) connected to a function generator (Agilent 35522B) generating a square wave at 5 different amplitudes (from 100-300 mV) for various light intensities. The whole cell was placed on a hotplate stirrer to maintain the temperature and the ionic transport of the products. Signals were filtered for 50 Hz noise and the photovoltage increase and decay time constants were determined by fitting single exponentials.

#### Photocurrent measurements

A TiO<sub>2</sub> film was prepared using the NT slurry onto a FTO substrate similarly to the above procedure. Part of the FTO was removed through the centre so that the substrate has 2 isolated conducting regions, prior to spin coating. The prepared sample was then immersed into deionized water purged with argon and the photocurrent was measured using a 2 electrode configuration with a 0.5 V potential between them. The LED was then switched on at the 60 s mark, and 1.0 ml of a 10% vol glycerol solution added at the 120 s mark. The LED was switched off after another 60 s. This was done at 4 different temperatures.

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