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# Efficient Solar Light Photoreduction of CO<sub>2</sub> to Hydrocarbon Fuels via Magnesiumthermally Reduced TiO<sub>2</sub> Photocatalyst

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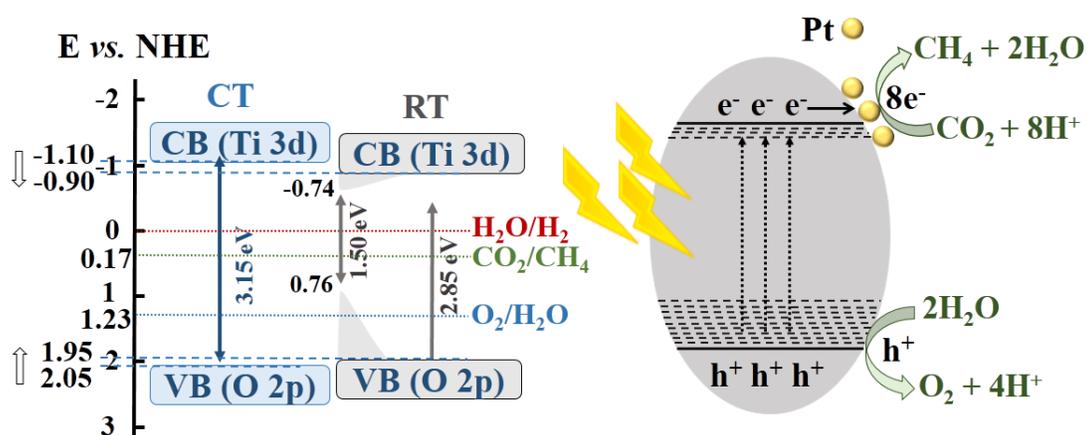
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## Graphical Abstract

Reduced TiO<sub>2</sub> is prepared using a new technique, magnesiothermic reduction under 5% H<sub>2</sub>/Ar and employed for CO<sub>2</sub> photoreduction application. The synergistic effects arising from magnesiothermic reduction for reduced TiO<sub>2</sub> photocatalyst offers improved light absorption, immense stability and well-matched CO<sub>2</sub>/CH<sub>4</sub> band edge positions. The magnesiothermally reduced TiO<sub>2</sub> with Pt cocatalyst exhibited a significantly elevated CH<sub>4</sub> yield over its counterparts; reduced TiO<sub>2</sub> control samples and un-reduced TiO<sub>2</sub>. Further <sup>13</sup>CO<sub>2</sub> isotopic experiments confirms CH<sub>4</sub> generation mainly from CO<sub>2</sub>, the original source of carbon.



## Highlights

- Reduced TiO<sub>2</sub> photocatalyst is synthesized via magnesiothermic synthesis approach.
- The photocatalytic activity is investigated for CO<sub>2</sub>/H<sub>2</sub>O<sub>(g)</sub> mixture conversion to CH<sub>4</sub>.
- Pt co-catalyst is photodeposited & optimized for efficient charge separation.
- Reduced TiO<sub>2</sub> exhibited threefold increase in CH<sub>4</sub> production rate over pure TiO<sub>2</sub>.
- Improved performance is attributed to enhanced light absorption, efficient charge separation, and well band edge alignment.

**Abstract**

Elevated atmospheric CO<sub>2</sub> levels are recognized as a key driver of global warming. Making use of sunlight to photoreduce CO<sub>2</sub>, in turn fabricating hydrocarbon fuels compatible with the current energy infrastructure, is a compelling strategy to minimize atmospheric CO<sub>2</sub> concentrations. However, practical application of such a photocatalytic system requires significant efforts for improved photoreduction performance and product selectivity. Herein, we investigate the performance of our newly developed reduced TiO<sub>2</sub>, prepared by a reduction process using Mg in 5 % H<sub>2</sub>/Ar, for photoconversion of CO<sub>2</sub> and water vapor to hydrocarbons, primarily CH<sub>4</sub>. Using Pt nanoparticles as a co-catalyst, under simulated solar light irradiation the reduced anatase TiO<sub>2</sub> exhibits a relatively stable performance with a threefold increase in the rate of CH<sub>4</sub> production (1640.58 ppm·g<sup>-1</sup>·h<sup>-1</sup>, 1.13 μmol·g<sup>-1</sup>·h<sup>-1</sup>) as compared to anatase nanoparticles (546.98 ppm·g<sup>-1</sup>·h<sup>-1</sup>, 0.38 μmol·g<sup>-1</sup>·h<sup>-1</sup>). The improved photocatalytic performance is attributed to enhanced light absorption, suitable band edge alignment with respect to the CO<sub>2</sub>/CH<sub>4</sub> redox potential, and efficient separation of photogenerated charges. Our results suggest that the Pt-sensitized reduced TiO<sub>2</sub> can serve as an efficient photocatalyst for solar light CO<sub>2</sub> photoreduction.

**Keywords:** Reduced TiO<sub>2</sub>, Magnesiothermic reduction, Visible light absorption, CO<sub>2</sub> photoreduction, Stable performance.

## 1. Introduction

Increased atmospheric carbon dioxide (CO<sub>2</sub>) concentrations, primarily due to the combustion of fossil fuels, is one of the preeminent obstacles faced by global society [1,2]. In this regard, numerous approaches have been investigated to control and normalize atmospheric CO<sub>2</sub> concentrations [3]. One of the most effective ways is to use sunlight-activated catalysis (photocatalysis) to transform CO<sub>2</sub> and water vapor into hydrocarbon fuels and chemicals, such as methane, ethane, methanol, carbon monoxide, and formic acid [4-6]. CO<sub>2</sub> photoreduction, *i.e.* “artificial photosynthesis,” [4] provides a viable means for turning sunlight into a readily transportable fuel compatible with the current energy infrastructure.

To date, various photocatalytic materials have been investigated for their utility in CO<sub>2</sub> photoreduction, including ZnO [7], ZnGa<sub>2</sub>O<sub>4</sub> [8], Ga<sub>2</sub>O<sub>3</sub> [9], BiVO<sub>4</sub> [10], g-C<sub>3</sub>N<sub>4</sub> [11], Si nanocrystals [12], GO [13] and TiO<sub>2</sub> [14]. Among them, TiO<sub>2</sub> is a widely investigated photocatalyst that possesses several comparative advantages including excellent chemical stability, nontoxicity, corrosion resistance, abundant availability and low cost [15]. However the photocatalytic performance of TiO<sub>2</sub> is limited due to its relatively wider band gap (~ 3.2 eV for anatase), which limits light absorption to UV wavelengths comprising only 3-5 % of terrestrial sunlight energy [15]. Several strategies have been investigated to enhance the solar-spectrum absorption of TiO<sub>2</sub>, including metal and non-metal doping [16,17], coupling of low band gap materials [18,19], and dye-sensitization [20]. Co-catalyst metals such as Pt, Ag, Nb, Au, and Cu act as electron traps, or sinks, facilitating separation of photoexcited charges, in turn leading to improved photocatalytic performance [16].

Recently, Mao and co-workers reported hydrogenated TiO<sub>2</sub> nanocrystals [21], black in color, with a highly disordered surface layer resulting in enhanced light absorption with, in turn,

improved photocatalytic activity for methylene blue degradation and hydrogen production from methanol-water. Subsequently, several studies have been done for the development of hydrogenated or reduced TiO<sub>2</sub> via manipulation and influence of various reaction parameters (temperature, pressure, gas composition *etc.*), synthesis methodologies, and initial TiO<sub>2</sub> precursors [22-25]. It is generally accepted that reduction of TiO<sub>2</sub> generates a large number of surface defects, Ti<sup>3+</sup> ions, and oxygen vacancies, which are mainly responsible for the improved light absorption that, in turn, leading to higher photocatalytic performance [22-25]. While the utilization of the absorbed visible light resulting from these samples has proven limited, the hypothesis of those working in the field is that a controlled synthetic approach may improve the visible light activity [26,27]. To that end, we recently reported a new approach for fabrication of a defect-induced TiO<sub>2</sub> photocatalyst that involves magnesiothermic reduction in 5 % H<sub>2</sub>/Ar followed by acid washing [28,29]. The reduced TiO<sub>2</sub> exhibits better activity for visible light hydrogen production, by water photoelectrolysis, than that previously reported for black TiO<sub>2</sub> [28]. In terms of CO<sub>2</sub> photoreduction, until now there exist but few studies employing hydrogenated/reduced TiO<sub>2</sub> systems, with results suggesting the oxygen vacancies and surface defects acting as electron donors can promote charge transport and CO<sub>2</sub> activation [30-33].

Herein we investigate the simulated solar light-driven CO<sub>2</sub> photoreduction with water vapor on reduced TiO<sub>2</sub> (RT) nanoparticles synthesized by controlled magnesiothermic reduction of commercially available anatase TiO<sub>2</sub> (CT) nanoparticles. Interestingly, the band edge positions of RT are found in good alignment with the CO<sub>2</sub>/CH<sub>4</sub> redox potential, and hence CH<sub>4</sub> is produced as a dominant product with minor amounts of ethane and higher alkanes. Platinum (Pt), an electron transferring co-catalyst, is photodeposited onto the reduced TiO<sub>2</sub> surface for efficient separation of photogenerated charges. Optimization of Pt deposition is accomplished by preparing a series of

Pt deposited RT samples in which the weight percent of Pt precursor is varied. The aforementioned requirements of broad-spectrum light absorption, efficient charge transfer, and well-aligned band edges are all achieved with the described photocatalyst system.

## 2. Experimental Methods

### 2.1 Synthesis of reduced $TiO_2$ (RT)

The RT used in the present study was synthesized by magnesiothermic reduction in the presence of 5 %  $H_2/Ar$  [28]. In a typical procedure, 1.6 g (20 mmol) of commercial nano- $TiO_2$  (Anatase nanoparticles purchased from Sigma-Aldrich, USA) were well-mixed with 240 mg (10 mmol) of Mg powder ( $\geq 99$  %, Sigma-Aldrich) and heated to 650 °C (ramp 2 °C $\cdot$ min $^{-1}$ ) for 5 h under 5%  $H_2/Ar$  in a tube furnace. After cool down, the sample was collected and washed with dilute HCl (ACS reagent, 37.0 %, Sigma-Aldrich) to remove the Mg species. The Mg and  $Cl^-$  free RT sample was obtained after copious washing with DI water, and then dried in a hot air oven overnight. The removal of Mg and  $Cl^-$  was confirmed using X-ray photoelectron spectroscopy (XPS), see Fig. S1; the absence of  $Cl^-$  was further confirmed by the  $AgNO_3$  solution test. A 1:0.5 molar ratio of  $TiO_2$  and Mg was selected, as it was previously observed this ratio produced the optimal photocatalyst for hydrogen production by water photoelectrolysis [28,29].

Different control samples were prepared such as: (i) CT with Mg only annealed under Ar gas named as RT(Mg); (ii) CT annealed under Ar only named as CT(Ar); and (iii) CT annealed under 5 %  $Ar/H_2$  named as RT( $H_2$ ). All control samples were synthesized under conditions similar to those of the RT samples.

## 2.2 Synthesis of Pt sensitized reduced TiO<sub>2</sub> (Pt-x-RT)

Pt co-catalyst nanoparticles were deposited onto RT using photodeposition [34]. A series of Pt-x-RT samples were prepared, where  $x = 0.5, 0.9, 1.0, 1.2,$  and  $2.0$  represents the theoretically calculated weight percent (wt. %) of Pt with respect to a fixed amount of RT (100 mg). The desired amount of H<sub>2</sub>PtCl<sub>6</sub>·6H<sub>2</sub>O (ACS reagent,  $\geq 37.50$  %, Sigma-Aldrich) was added to 25 ml of methanol (20 vol. %)-water solvent containing 100 mg of RT. After continuous stirring for 1 h in a closed system, the well-dispersed solution was irradiated using 300 W xenon arc lamp (Newport) with a 6.0 cm long IR water filter for 2 h. Finally, the Pt sensitized RT sample was thoroughly washed with deionized (DI) water and dried under vacuum at 90 °C for 12 h. Pt (1.0 wt. %) was also photodeposited on all control samples with similar procedure and tested for CO<sub>2</sub> photoreduction experiment.

## 2.3 Characterization techniques

Sample crystallinity was determined from X-ray diffraction (XRD) patterns, recorded using an X-ray diffractometer (Panalytical, Empyrean) operated at 40 kV and 30 mA with Cu K $\alpha$  radiation ( $\lambda = 1.54$  Å) as an X-ray source, scanned with a step degree of 0.02° and duration time of 0.05 s in the range of  $2\theta = 20$ -60°. Crystallite size of the RT and CT samples was calculated using the Scherrer equation. The light absorption of powder samples was analyzed by UV-visible diffuse reflectance spectroscopy (UV-vis DRS), using a Cary series (Cary 5000) UV-visible-near IR spectrophotometer (Agilent Technologies) with a diffuse reflection accessory in the range of 300-700 nm. Photoluminescence (PL) spectra were measured using Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) with an excitation wavelength of  $\lambda_{\text{ex}} = 300$  nm. PL measurement samples were prepared by dispersing powder samples in ethanol with a concentration of 0.5 mg·ml<sup>-1</sup>. Transmission electron microscopy (TEM) images were obtained using a FE-TEM

(Hitachi HF-3300). Samples for TEM analysis were prepared by dispersing powder samples ( $0.05 \text{ mg}\cdot\text{ml}^{-1}$ ) in ethanol followed by sonication of the mixture for few minutes, with one drop of the suspension dropped onto a Ni TEM grid and allowed to dry overnight. ImageJ software was used to estimate the Pt nanoparticle size distribution and average particle size ( $d_{\text{avg}}$ ) from the HR-TEM images. The surface composition, oxidation states and valence band for pure CT, RT and Pt (1.0 wt. %) sensitized RT (Pt-1.0-RT) were determined by X-ray photoelectron spectroscopy (XPS, Thermo Scientific, ESCALAB 250Xi) using Al  $K\alpha$  line (148606 eV) as the X-ray source. Curve fitting of the XPS spectra was performed using the Gaussian method and all XPS peaks were calibrated against the reference peak of carbon C 1s appearing at Binding energy = 284.6 eV (Fig. S2). Electron paramagnetic resonance (EPR) spectra of samples CT and RT were recorded using a continuous wave X-band spectrometer (JEOL, JES-FA200), by applying a 9185.041 MHz, 0.998 mW microwave signal at  $-163.5 \text{ }^\circ\text{C}$ . A Micromeritics ASAP 2020 apparatus was used to measure the  $\text{N}_2$  sorption isotherms at  $-196 \text{ }^\circ\text{C}$ , to investigate surface area and pore size of all samples; prior to measurement, all samples were extensively degassed at  $200 \text{ }^\circ\text{C}$  to 20 mTorr for 300 minutes. The Brunauer-Emmett-Teller (BET) equation was used to calculate the surface areas for all samples in the relative pressure ( $P/P_0$ ) range of 0.05 to 0.30. Pore size was obtained by applying the Barrett-Joyner-Halenda (BJH) equation to the desorption isotherms.

To examine possible coverage of the photocatalyst surface by intermediate species generated during the photocatalytic reactions, BET surface area and  $\text{CO}_2$ -Temperature Programmed Desorption (TPD) analyses were carried out employing representative sample Pt-1.0-RT after the 3<sup>rd</sup> cycle of a stability test, and the same sample after thermo-vacuum treatment. BET specifications were similar to those mentioned above, but to preclude high-temperature removal of sought intermediate species, a degassing temperature of  $50^\circ\text{C}$  was used (20 mTorr for

300 minutes). CO<sub>2</sub>-TPD profiles were measured using an AutoChem II Chemisorption analyzer (RS232 Status, Micromeritics); samples (30 mg) were treated under He gas flow (50 ml·min<sup>-1</sup>) at 50 °C (1 h) followed by cooling to ambient temperature, after which CO<sub>2</sub> gas (5% in He) was allowed to flow (50 ml·min<sup>-1</sup>) through the samples for CO<sub>2</sub> adsorption (30 minutes). TPD analysis was performed under He gas flow (50 ml·min<sup>-1</sup>) by heating the sample to 500 °C with a rate of 20 °C·min<sup>-1</sup>.

#### *2.4 Band gap and band edge estimation*

Band gap ( $E_g$ ) values were estimated using Tauc plots [35]. The KM function  $(\alpha h\nu)^2$ , where  $\alpha$  is the absorption coefficient,  $h$  is Planck constant, and  $\nu$  is frequency, was plotted against band gap energy ( $E = h\nu = hc/\lambda$ ). Band gaps were determined by extrapolating the linear portions of the curves to  $y = 0$ . Values for the upper edge of the valence band were obtained from valence band XPS which is aligned *vs.* NHE. The conduction band minimum was thus obtained by subtracting the band gap value from the valence band maximum.

#### *2.5 CO<sub>2</sub> photoreduction*

Using a gas phase reactor, the prepared materials were investigated for their ability to promote photoconversion of CO<sub>2</sub> and water vapor into CH<sub>4</sub>, see Fig. S3. Following the procedure reported earlier [36], 70 mg of photocatalyst was loaded into a stainless steel photoreactor (Volume = 15.4 cm<sup>3</sup>) with a quartz window. CO<sub>2</sub> (1000 ppm in He) was allowed to pass through a water bubbler forming a mixture of CO<sub>2</sub> and water vapor. Prior to photoreduction experiments the reactor was repeatedly, 5x, purged with CO<sub>2</sub> gas (1000 ppm in He) and vacuum to remove gaseous

impurities. The photoreactor was illuminated with 1 sun simulated sunlight using a 100 W xenon solar simulator (Oriel, LCS-100) equipped with an AM 1.5G filter. After 1 h of continuous illumination, a sample of 500  $\mu\text{l}$  was taken from photoreactor, using an argon-purged syringe, and injected into the gas chromatography (GC) unit (Shimadzu GC-2014, Restek RT-Q-Bond column, ID = 0.53 mm, length = 30 m) equipped with a flame ionization detector (FID). The hour normalized rate of  $\text{CH}_4$  formation is calculated by:

$$\text{CH}_4 \text{ production rate} = \frac{\text{amount of CH}_4 \text{ evolved (ppm)}}{\text{photocatalyst amount (g)} \cdot \text{hour (h)}}$$

At least three freshly-prepared samples of each material composition were tested under similar experimental conditions. The average of the three measurements, with their standard deviation indicated by error bars, is reported as the  $\text{CH}_4$  evolution rate. Photocatalyst stability was tested by passing the same Pt-1.0-RT sample through up to seven  $\text{CO}_2$  photoreduction cycles. After each  $\text{CO}_2$  photoreduction cycle the photoreactor was purged, five times, with  $\text{CO}_2$  gas (1000 ppm in He) and vacuum, then finally refilled with  $\text{CO}_2/\text{H}_2\text{O}_{(\text{g})}$  vapor and illuminated for 1 h. To investigate the origin of the carbon intrinsic to the  $\text{CH}_4$  evolution a control test was performed by illuminating sample Pt-1.0-RT in an  $\text{Ar}/\text{H}_2\text{O}_{(\text{g})}$  atmosphere.

### 2.6 $^{13}\text{CO}_2$ isotopic experiment

$^{13}\text{CO}_2$  isotopic experiments were performed to confirm  $\text{CO}_2$  as the original source of carbon.  $^{13}\text{CO}_2$  ( $^{13}\text{C}$  99.0 %), was purchased from Aldrich and diluted in pure He gas (99.999 %) to

give  $^{13}\text{CO}_2$  with final concentration of 1000 ppm in He. The gas was then passed through a bubbler forming a mixture of  $^{13}\text{CO}_2/\text{H}_2\text{O}_{(\text{g})}$  which was introduced into the photoreactor, argon purged, loaded with Pt-1.0-RT photocatalyst (70 mg) and then illuminated.

### 3. Results and discussion

#### 3.1 Crystalline Structure

Fig. 1 displays powder X-ray diffraction (XRD) patterns of pure CT, RT and Pt-x-RT samples. All samples exhibit a main diffraction peak of anatase (A) at a  $2\theta$  value of  $25.2^\circ$  corresponding to  $d_{101}$ , along with other respective minor peaks [37], suggesting no transformation or appearance of any new phase during the reduction process. A Pt peak corresponding to  $d_{111}$  is only observed in sample Pt-2.0-RT, at  $2\theta = 39.67^\circ$  [38]. The Pt peaks are quite faint in the other Pt-x-RT samples, due possibly to the high dispersion of Pt nanoparticles or simply the low concentration. Hence further analysis was conducted to confirm the presence of Pt in these samples, as discussed later. High-resolution transmission electron microscopy (HR-TEM) images for CT and RT samples are shown in Fig. S4. HR-TEM images indicate a particle size within the range of 20-25 nm, with an interplanar spacing of 0.35 nm corresponding to the  $d_{101}$  plane of anatase  $\text{TiO}_2$  [37]. Average crystallite size was calculated for both RT and CT samples using the Scherrer equation, see Fig. S5; a value of 12.9 nm was determined for CT, and 15.4 nm for RT, an increase in size presumably due to the heat of the magnesiothermic reduction process.

STEM elemental mapping and an HR-TEM image for a representative Pt-1.0-RT sample are presented in Fig. 2. The HR-TEM images (Fig. 2e and f) clearly demonstrate deposition of

well-defined Pt nanoparticles 2-3 nm in diameter, as estimated using ImageJ software, on the RT sample surface with an interplanar  $d_{111}$  spacing of 0.22 nm [37]. The STEM-EDS elemental mapping (Fig. 2a-d) further supports the presence of homogeneously distributed Pt in the Pt-1.0-RT sample.

### 3.2 Surface analysis

Fig. 3a presents the high resolution XPS of region Ti 2p for both CT and RT samples, both of which exhibit the corresponding peaks for Ti 2p<sub>3/2</sub> and Ti 2p<sub>1/2</sub>, with pure CT exhibiting the respective Ti 2p peaks located at 458.38 eV and 464.02 eV [39]. As compared to CT, a slight peak shifting ( $\sim 0.13$  eV) towards lower binding energy is observed for RT with peak broadening indicating the presence of Ti<sup>3+</sup> in RT [22,30]. Further, the Ti 2p<sub>3/2</sub> peak of the RT samples shows a peak tail at lower binding energy, see Fig. 3b, with increased area ( $\sim 6$  % of 2p<sub>3/2</sub> peak area) as compared to CT ( $\sim 2$  % of 2p<sub>3/2</sub> peak area) that can be attributed to Ti<sup>3+</sup> [22,30]. The O 1s XPS spectra (Fig. 3c) of CT shows a main peak located at 529.59 eV, corresponding to Ti-O-Ti from the lattice, while the shoulder peak appearing at 530.68 eV can be assigned to non-lattice oxygen [28,40]. However, O 1s XPS spectra of RT (Fig. 3d) also shows a shift of the O 1s peaks to lower binding energies indicating the presence of Ti<sup>3+</sup> [21]. As compared to sample CT, the peak appearing at the relatively higher binding energy (for non-lattice oxygen) of the RT sample possesses a larger area, as trait associated with more oxygen vacancies [28].

Sample Pt-1.0-RT (Fig. S6) exhibits similar XPS peaks for Ti 2p and O 1s as the RT sample, with the additional peak of Pt 4f (Fig. S6c), a consequence of the Pt nanoparticles. The Pt 4f spectrum can be fitted into four peaks with the main peaks appearing at 70.21 eV and 73.55 eV

corresponding to the metallic Pt(0) state [41]. The Pt 4f XPS spectra for various Pt-x-RT samples (Fig. S7) demonstrates, as expected, an increase in Pt signal magnitude with increased Pt wt. %, see Table S1.

### 3.3 Electron paramagnetic resonance (EPR) analysis

The EPR spectra for pure CT and RT are shown in Fig. S8. The EPR spectra of sample CT shows no absorption, while the RT sample exhibits a significant and intense absorption at  $g = 1.975$ , with a shoulder peak appearing at approximately  $g = 1.99$ , traits that are assigned to the presence of  $Ti^{3+}$  ions [42,43]. In addition to these peaks, another small shoulder peak is observed at  $g = 2.002$ , which can be associated to the presence of  $O^-$  species, possibly generated via interaction of  $O_2$  with  $Ti^{3+}$  surface ions [44].

### 3.4 Optical properties

As compared to pure CT, see Fig. 4, the RT sample exhibits a slight red shift in the absorption peak, with increased absorption in the visible region (Fig. 4a). Such an extension of light absorption for the RT sample suggests a narrowing of the band gap due to formation of new energy states near the top of the valence band and bottom of the conduction band, a behavior we hypothesize is due to oxygen vacancies or surface defects. A further increase in visible spectrum absorption was observed for Pt-x-RT, which can be attributed to local surface plasmon resonance (LSPR) induced by the Pt nanoparticles [45]. The LSPR effect increases with Pt loading up to 1.0 wt. %, with no significant difference observed for Pt-1.2-RT and Pt-2.0-RT. It is well known that LSPR induced visible light absorption increases with Pt

nanoparticle size and/or Pt amount [45-49]. We see as the Pt loading is increased from 0.5 to 1.0 wt. %, there is an increase of Pt content (Fig. S7 & Table S1) with perceptible increase in average Pt particle size (Fig. S10), hence both parameters contributing for increased LSPR induced light absorption. For Pt 1.2 wt. % and 2.0 wt. % loaded RT samples there is no significant difference in average Pt nanoparticle size (Fig. S10), which suggests that the slight increase in visible light absorption for Pt-2.0-RT is simply associated with increased Pt content.

Fig. 4b shows photoluminescence (PL) spectra in the 350-700 nm wavelength range. Sample CT displays an intense emission peak around 390 nm, which can be attributed to the band gap transition of anatase TiO<sub>2</sub>. Sample RT exhibits a significant decrease of this peak with the appearance of another broader peak centered at 620 nm, which can be associated with RT surface defects. PL emission intensity is proportional to the photogenerated electron and hole (e<sup>-</sup>/h<sup>+</sup>) recombination rate. The decreased intensity of the  $\lambda = 390$  nm peak for RT indicates a low e<sup>-</sup>/h<sup>+</sup> recombination rate. Moreover, when Pt is loaded on the RT sample, as seen for representative sample Pt-1.0-RT, the emission intensity of the  $\lambda = 390$  nm peak is further decreased. Such peak quenching indicates effective separation of the photoexcited electrons, with the Pt nanoparticles acting as electron sinks [50,51]. Among all the Pt-loaded RT samples, Pt-1.0-RT shows the lowest PL intensity implying optimal Pt content.

### 3.5 CO<sub>2</sub> photoreduction

The photocatalytic performance of the CT, RT, and Pt-x-RT samples was evaluated by testing them for photocatalytic conversion of CO<sub>2</sub> into hydrocarbons under AM 1.5G illumination. As discussed, photocatalytic experiments were carried out in a gas phase reactor (Fig. S3) with a mixture of CO<sub>2(g)</sub> and water vapor as reactants. Fig. 5a shows the photocatalytic CH<sub>4</sub> production rate for pure CT, RT and Pt-x-RT samples; the output species were found to be primarily methane (CH<sub>4</sub>) with minor products of ethane (C<sub>2</sub>H<sub>6</sub>) and higher alkanes (C<sub>x</sub>H<sub>y</sub>). CT produced a negligible amount of CH<sub>4</sub> without Pt sensitization, whereas RT exhibited a measurable but low CH<sub>4</sub> yield; the CH<sub>4</sub> production rate is significantly improved with Pt sensitization. In particular, Pt-1.0-RT produced CH<sub>4</sub> at a rate of 1640.58 ppm·g<sup>-1</sup>·h<sup>-1</sup> (1.13 μmol·g<sup>-1</sup>·h<sup>-1</sup>), approximately 82 times higher than that of pure RT (18.31 ppm·g<sup>-1</sup>·h<sup>-1</sup>, 0.013 μmol·g<sup>-1</sup>·h<sup>-1</sup>) and 3 times higher than that of Pt-1.0-CT (546 ppm·g<sup>-1</sup>·h<sup>-1</sup>, 0.38 μmol·g<sup>-1</sup>·h<sup>-1</sup>). The photocatalytic hydrocarbon yield, and selectivity, is reported in Table S2 for all samples. Compared to Pt-1.0-CT, sample Pt-1.0-RT yielded over a factor of two increase in turnover number (TON) and over a factor of three increase in the rate of CO<sub>2</sub> to CH<sub>4</sub> conversion, see Table S3. The increase in CH<sub>4</sub> production rate as well as photoactivity of Pt deposited RT can be understood considering: (i) improved RT visible light absorption due to a reduction in band gap and reduced recombination of photogenerated charge; and (ii) enhanced charge separation due to the Pt nanoparticles. When the Pt loading is increased from 0.5 to 1.0 wt. % the CH<sub>4</sub> production also increases, however the rate decreases for 1.2 and 2.0 wt. % Pt loaded samples. A control experiment employing Pt-1.0-RT under similar conditions in the presence of Ar/H<sub>2</sub>O(g) produced negligible amounts of hydrocarbons, suggesting no involvement of any organic impurities on the surface of the samples.

To help understand our results surface areas and pore size distributions of all Pt-x-RT samples were investigated, see Fig. S9 and Table S4; all samples possess essentially identical surface areas and pore structure. However, the HR-TEM images (Fig. S10) reveal a gradual increase in size and agglomeration of the Pt nanoparticles with loading amount. We submit that as the Pt loading was increased from 0.5 to 1.0 wt. % the amount of Pt nanoparticles was increased with good dispersion, while on further increasing the Pt loading above 1.0 wt. % the size and agglomeration of the Pt nanoparticles increased, in turn increasing the diffusion length of the separated electrons and hence increasing recombination [46]. This supposition is supported by the PL spectra (Fig. 4b), where Pt-1.2-RT and Pt-2.0-RT show higher emission peaks than the Pt-1.0-RT sample.

The stability of sample Pt-1.0-RT was investigated by repeated testing of the same sample (Fig. 5b). While similar amounts of CH<sub>4</sub> were obtained for the 1<sup>st</sup> and 2<sup>nd</sup> cycles, activity decreased sharply for the 3<sup>rd</sup> cycle. The sample was then reactivated by heating at 90 °C under vacuum for 3 h, with photocatalytic activity almost fully recovered for the 4<sup>th</sup> and 5<sup>th</sup> cycles. During the 6<sup>th</sup> cycle the activity decreased in a pattern similar to that of the 3<sup>rd</sup> cycle, hence the sample was again subjected to vacuum heat treatment, whereupon for the 7<sup>th</sup> cycle photocatalytic activity was found to be approximately 76% that of the 1<sup>st</sup> cycle. The mechanism for photocatalyst deactivation is not exactly known, however literature suggests coverage of active sites by intermediate products [52-54].

Fig. S11 shows the BET surface areas of a Pt-1.0-RT sample after the 3<sup>rd</sup> stability test cycle, and after subsequent thermo-vacuum treatment; both N<sub>2</sub> sorption curves demonstrate type IV isotherms with H3 hysteresis loops [55]. The BET surface area for the used sample (36.80 m<sup>2</sup>.g<sup>-1</sup>) is significantly less than that after thermo-vacuum treatment (44.94 m<sup>2</sup>.g<sup>-1</sup>). Such a decrease in surface area can be ascribed to coverage of the sample surface by intermediate species, in turn influencing the photocatalytic performance. Fig. S12 shows the CO<sub>2</sub>-TPD profiles for both samples; the thermo-vacuum treated sample shows greater CO<sub>2</sub> adsorption with increased intensity peaks in the region of weak basic sites (~ 100-250 °C) [56-58] that can be attributed to desorbed CO<sub>2</sub> [58,59], indicating favorable interaction of the gas with the photocatalyst surface. In contrast the used sample (after 3<sup>rd</sup> cycle) exhibits a decreased peak intensity in the weak basic sites region, indicating poor CO<sub>2</sub> absorption, with a broad hump in the medium basic sites region (~ 250-400 °C) [56,58] associated with bidentate carbonate species, possibly formed by intermediate species on the photocatalyst surface [54]. The CH<sub>4</sub> evolution rate yielded by various control samples is shown in Fig. S13. The RT samples show a superior CH<sub>4</sub> yield, with the Pt sensitized RT samples exhibiting photocatalytic performance competitive with previously reported reduced TiO<sub>2</sub> samples (Table S5).

Fig. S14, shows the gas chromatogram of the <sup>13</sup>CO<sub>2</sub> isotopic experiment employing sample Pt-1.0-RT; peaks at m/z = 45 and m/z = 17 are observed, which are associated, respectively, with <sup>13</sup>CO<sub>2</sub> and <sup>13</sup>CH<sub>4</sub>. GC-MS analysis shows the formation of <sup>13</sup>CH<sub>4</sub> from <sup>13</sup>CO<sub>2</sub>, confirming the CH<sub>4</sub> produced during the photochemical reaction predominately originates from CO<sub>2</sub>.

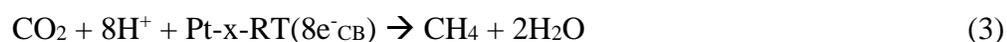
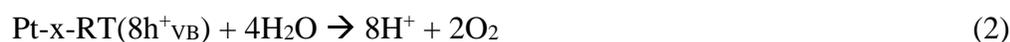
### 3.6 Mechanism for CO<sub>2</sub> photoreduction

To help understand the process by which CO<sub>2</sub> is photocatalytically converted into CH<sub>4</sub> the CT and RT band gaps, obtained using Tauc plots [35], and VB positions were analyzed, see Fig. 6. It can be clearly seen that CT exhibits a band gap of 3.15 eV, while RT shows a band gap of 2.85 eV. However, the RT Tauc plot displays an additional slope that leads to a lower band value gap of 1.50 eV, suggesting the formation of CB and VB tails due to a new density of states introduced during reduction [44]. VB XPS data indicates the top of the VB for CT is 2.05 eV (Fig. 6b), and 1.95 eV for RT (Fig. 6c) with a tail up to 0.76 eV (Fig. 6d). The band gap is narrowed via the reduction process through introduction of Ti<sup>3+</sup> and O vacancies/surface defects [21,44].

A schematic illustration of the probable energy level diagram (potential vs. NHE) and CO<sub>2</sub> photoreduction scheme can be seen in Fig. 7a, displaying the relative positions of CB and VB for CT and RT, and redox potentials for CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>O/O<sub>2</sub>. RT appears a more efficient photocatalyst for CO<sub>2</sub> photoreduction, possessing a CB minimum at -0.90 eV with a CB tail up to -0.74 eV, and a corresponding VB maximum at 1.95 eV with a VB tail up to 0.76 eV. The downward shifted CB bottom lies above the redox potential of CO<sub>2</sub>/CH<sub>4</sub> (0.17 eV), whereas the VB top lies slightly above the H<sub>2</sub>O/O<sub>2</sub> redox potential (1.23 eV) [60].

As suggested by Fig. 7b, under illumination the photogenerated e<sup>-</sup>/h<sup>+</sup> pairs are generated via band to band and sub-band gap excitations; the photoexcited electrons are injected to the CB and efficiently extracted by the Pt nanoparticles. Taking into mind proton assisted multi-electron

processes for CO<sub>2</sub> photoreduction [6,60], these photoexcited electrons can react with surface adsorbed CO<sub>2</sub> in the presence of protons (H<sup>+</sup>, produced in water oxidation) to evolve CH<sub>4</sub> as a primary product. Concurrently, the VB generated holes are involved in water oxidation, producing O<sub>2</sub> and protons (H<sup>+</sup>). The suggested reactions involved in CO<sub>2</sub> photoreduction to CH<sub>4</sub> can be summarized as follows:



#### 4. Conclusions

Reduced TiO<sub>2</sub> is prepared by a two-step method, magnesiothermic reduction in H<sub>2</sub>/Ar followed by acid washing, and investigated with respect to its utility in CO<sub>2</sub> photoreduction to CH<sub>4</sub> under simulated solar light (1 sun, AM 1.5G). The improved light absorption and suitable band edge position of reduced TiO<sub>2</sub>, sensitized with photodeposited Pt nanoparticles, results in a significant enhancement of CH<sub>4</sub> evolution. The reduced TiO<sub>2</sub> sample with 1.0 wt. % of Pt yielded a maximum photocatalytic CH<sub>4</sub> yield of 1640.58 ppm·g<sup>-1</sup>·h<sup>-1</sup> (1.13 μmol·g<sup>-1</sup>·h<sup>-1</sup>), three times higher than anatase TiO<sub>2</sub> (CT) and four times higher than commercial P25, both with a similar loading of Pt co-catalyst. We believe our material design approach offers significant opportunities for developing enhanced, high-performance photocatalytic materials.

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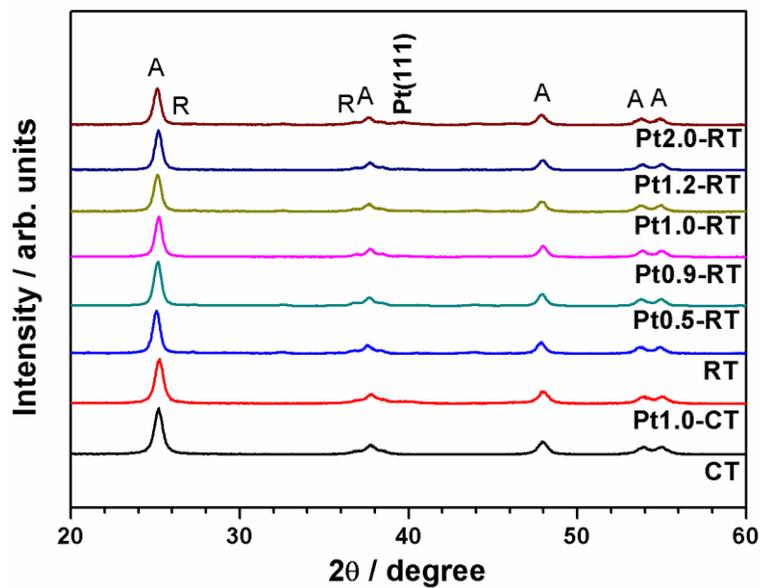
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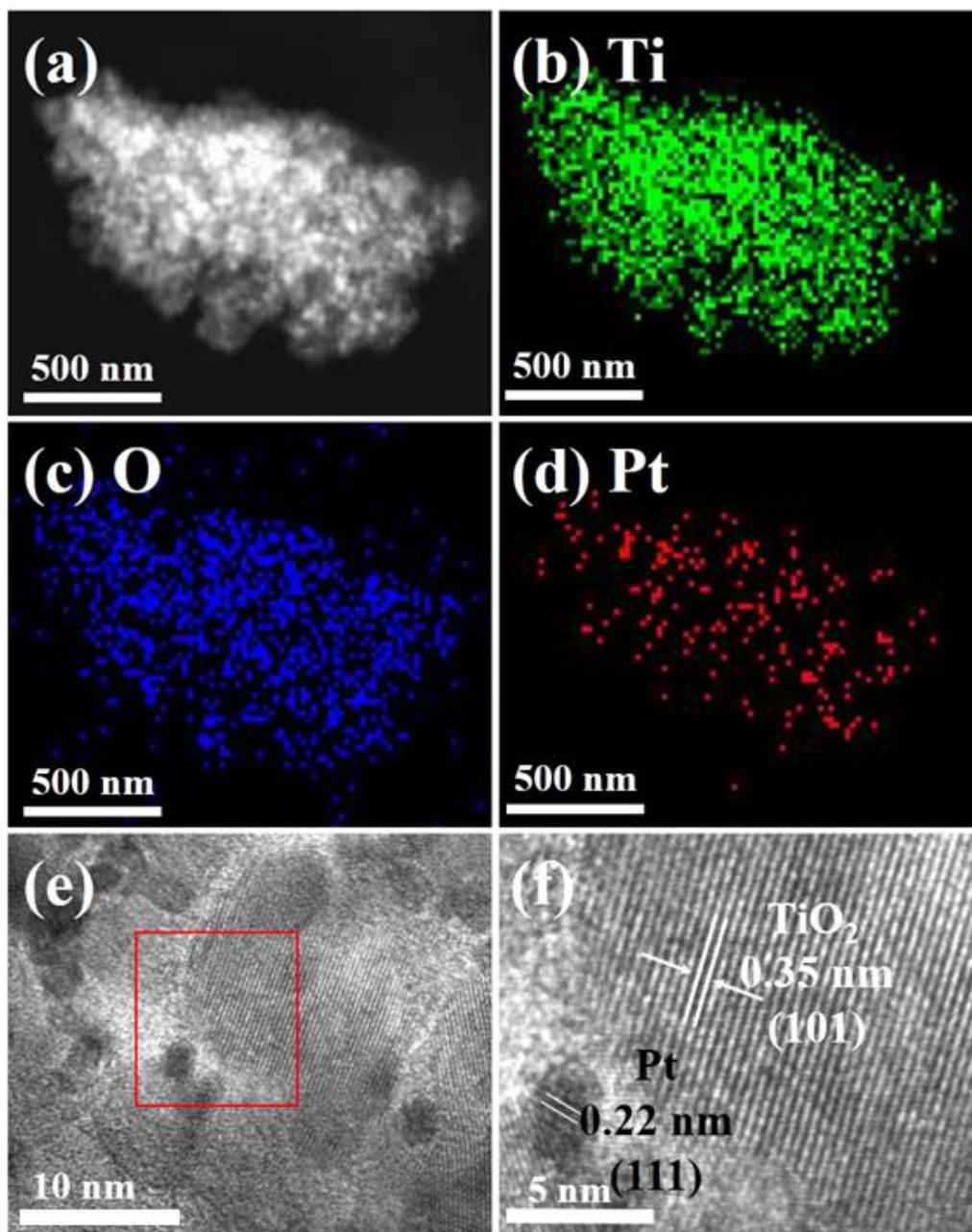
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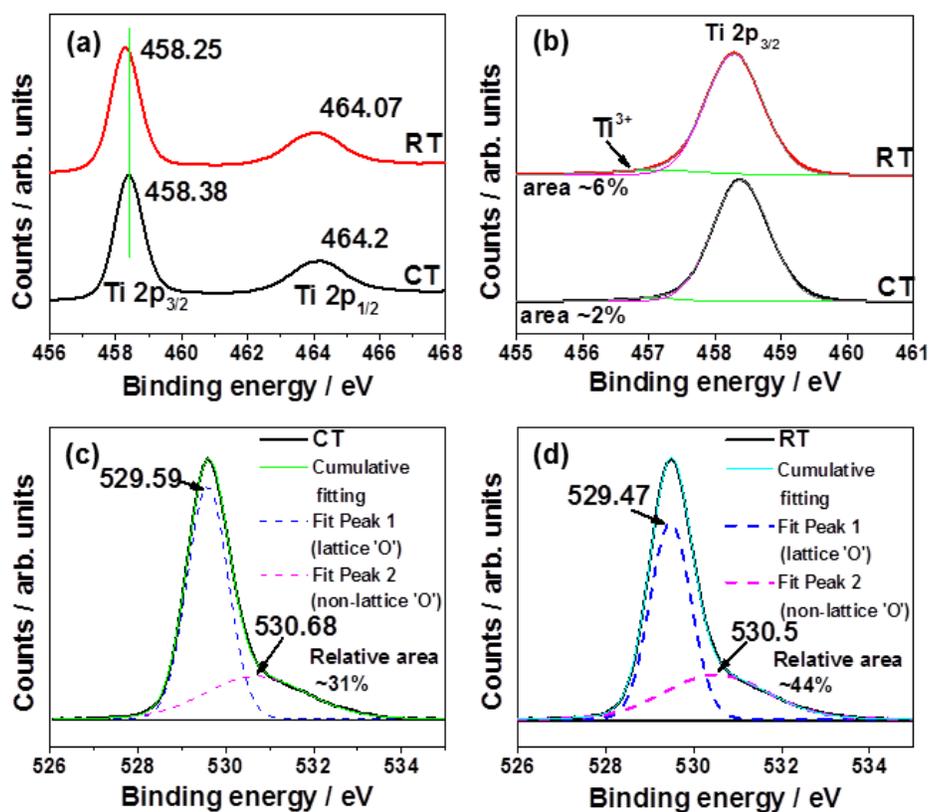
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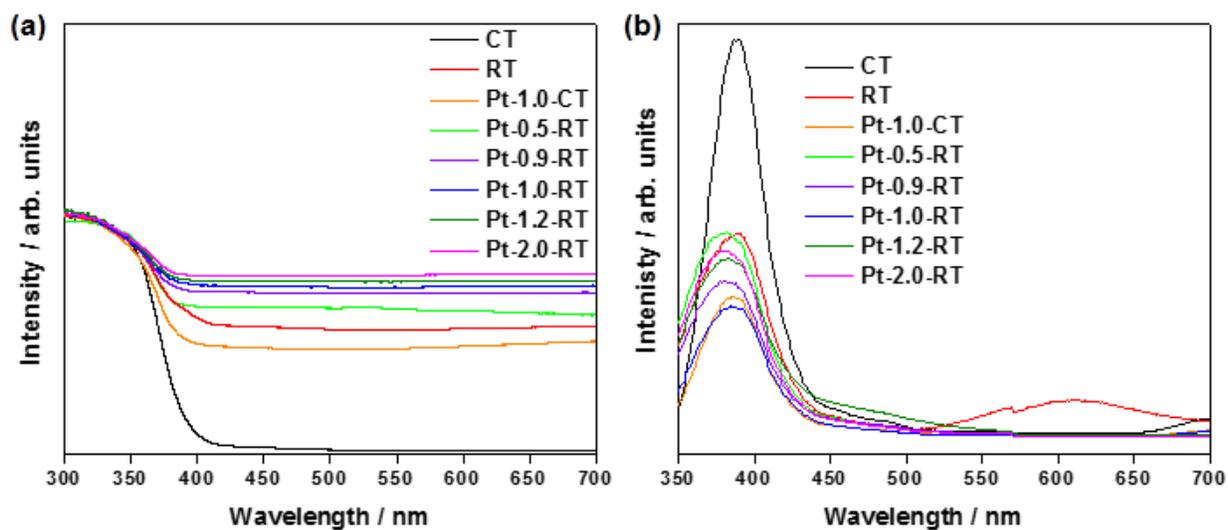
**Fig. 1.** (a) X-ray diffraction pattern for pure CT, RT and various Pt-x-RT samples (where x = 0.5, 0.9, 1.0, 1.2, and 2.0 corresponds to the theoretically calculated wt. % of Pt for photodeposition).



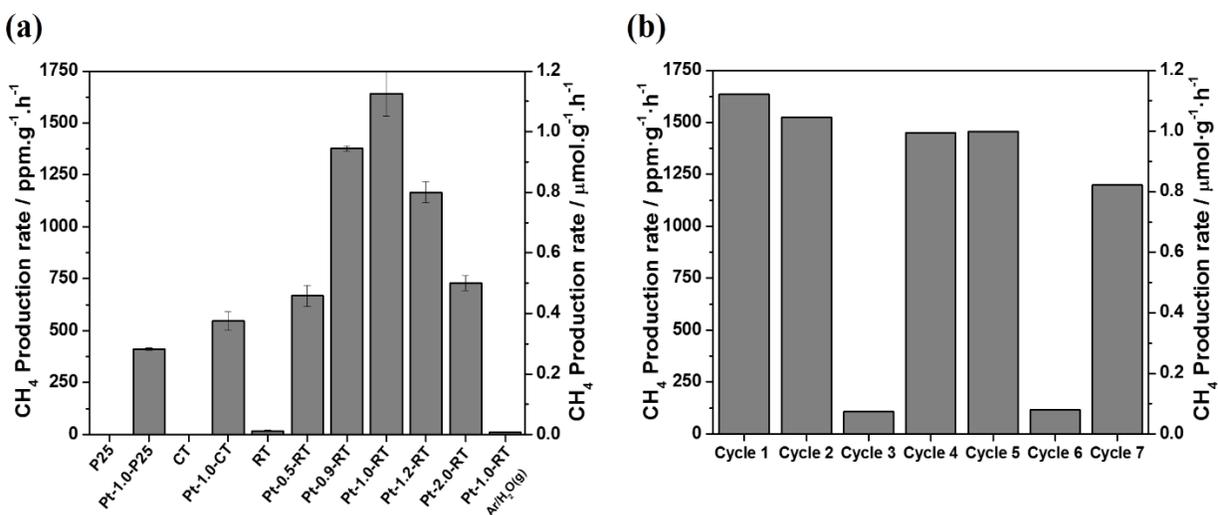
**Fig. 2.** (a) STEM image, and (b-d) STEM elemental mapping for a Pt-1.0-RT sample showing the presence of (b) Ti, (c) O, and (d) Pt. (e) HR-TEM image for Pt-1.0-RT sample with selected region (red square) showing (f) lattice fringes corresponding to Pt(111) and TiO<sub>2</sub>(101).



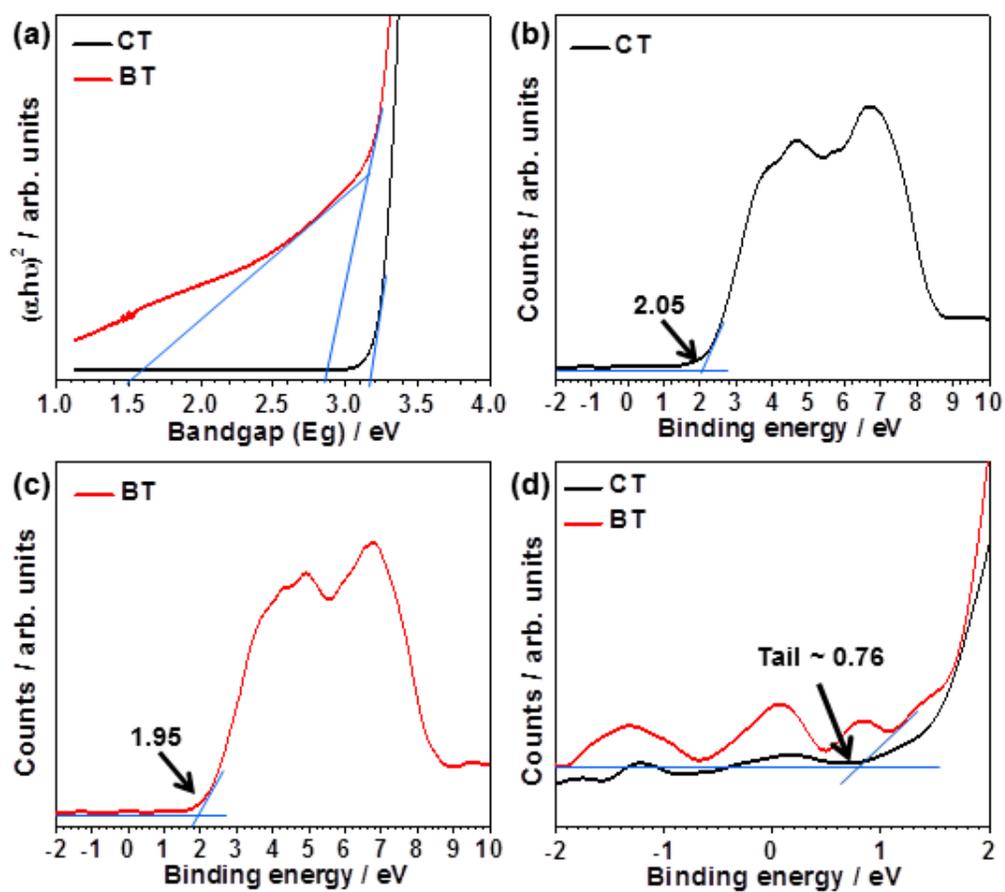
**Fig. 3.** X-ray photoelectron spectra (XPS) of pure CT and RT samples, regions: (a) Ti 2p, and (b) enlarged view of Ti 2p<sub>3/2</sub> region. Oxygen region for: (c) pure CT, and (d) RT.



**Fig. 4.** (a) UV-vis DRS, and (b) Photoluminescence (PL) spectra for pure CT, RT and various Pt-x-RT samples. RT shows visible range absorption due to inter-bandgap states. The PL band-to-band emission peak of sample Pt-1.0-RT is the most quenched, indicating the fastest electron extraction among all Pt-x-RT samples (where x = 0.5, 0.9, 1.0, 1.2, and 2.0 corresponds to theoretically calculated wt. % of Pt for photodeposition).

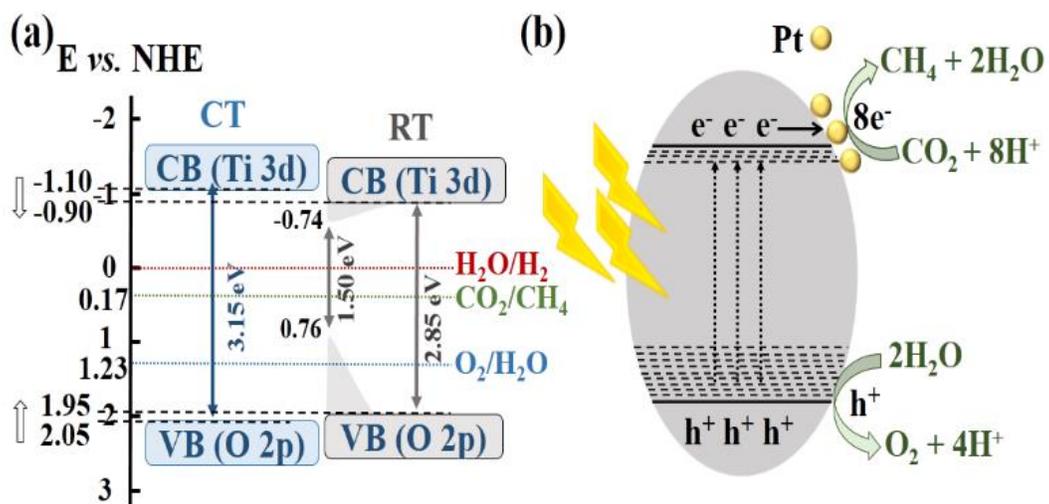


**Fig. 5.** (a) Methane production rate from P25 (Degussa), pure CT, RT, and various Pt-x-RT samples (where x = 0.5, 0.9, 1.0, 1.2 and 2.0 corresponds to theoretically calculated wt. % of Pt for photodeposition). Control test employing Pt-1.0-RT sample under Ar/H<sub>2</sub>O(g) atmosphere suggests negligible CH<sub>4</sub>. (b) Methane production rate from Pt-1.0-RT sample for seven test cycles of CO<sub>2</sub> photoreduction.



**Fig. 6.** (a) Band gap estimation using Tauc plot and (b-d) valence band XPS for pure CT and RT.

The RT shows a VB band tail up to 0.76 eV hence further shifting VB upward.



**Fig. 7.** (a) Energy level diagram (potential vs. NHE) and (b) proposed mechanism for CO<sub>2</sub> photoreduction.