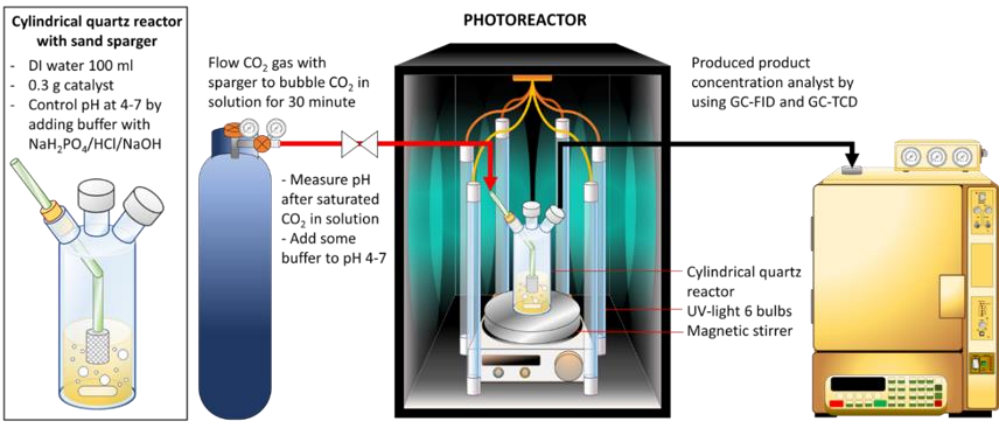
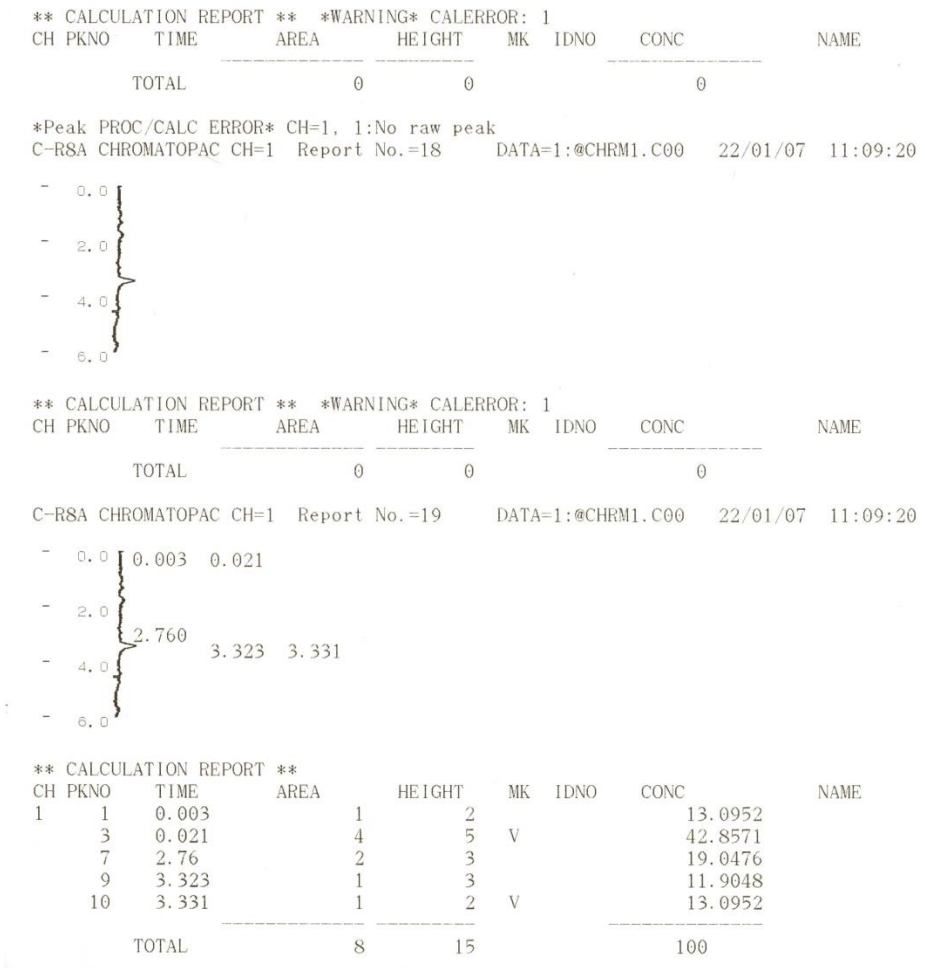


Figure S1 Photo reactor setup and CO_2 photo reduction procedure.



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** CALCULATION REPORT **  *WARNING* CALERROR: 1
CH PKNO     TIME        AREA        HEIGHT     MK   IDNO     CONC             NAME
          TOTAL                 0          0                     0

*Peak PROC/CALC ERROR* CH=1, 1:No raw peak
C-R8A CHROMATOPAC CH=1  Report No.=18     DATA=1:@CHRM1.C00    22/01/07  11:09:20
```



```
** CALCULATION REPORT **  *WARNING* CALERROR: 1
CH PKNO     TIME        AREA        HEIGHT     MK   IDNO     CONC             NAME
          TOTAL                 0          0                     0

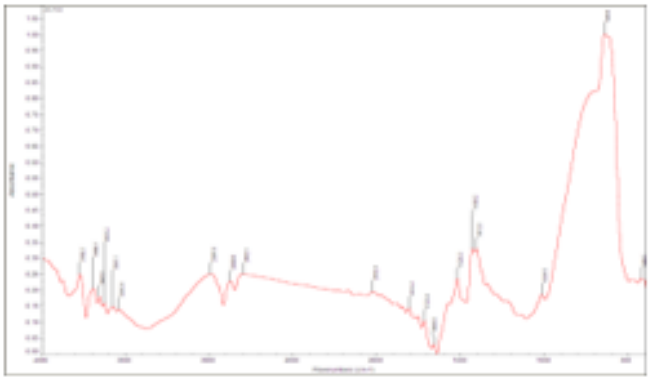
C-R8A CHROMATOPAC CH=1  Report No.=19     DATA=1:@CHRM1.C00    22/01/07  11:09:20
```

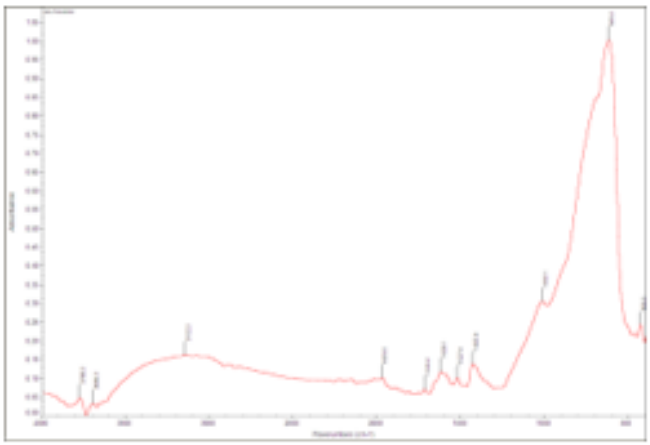


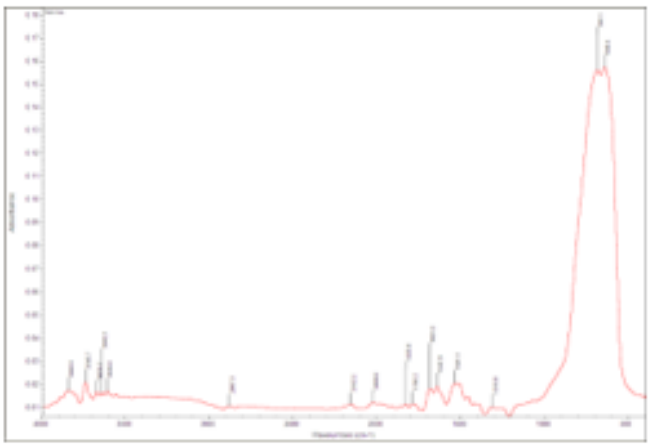
```
** CALCULATION REPORT **
CH PKNO     TIME        AREA        HEIGHT     MK   IDNO     CONC             NAME
1     1     0.003              1          2                    13.0952
      3     0.021              4          5    V               42.8571
      7     2.76               2          3                    19.0476
      9     3.323              1          3                    11.9048
     10     3.331              1          2    V               13.0952
          TOTAL                 8         15                     100
```

Figure S2 GC-FID after 3 h reaction progress. am-TiO_2-SiO_2 catalyst in water + CO_2 (reactor headspace) lamp off. Peak 9 corresponds to CH_4.

The reported concentration is equivalent to 0.03 nmol/mLH_2Ogcat: (((((0.000007*12)))/24.696) * (1/0.5)) * (150*1000/100) * (1/0.3) = 0.03; where 0.000007 * 12 = µL CH_4 from calibration curve; 24.696 = µmol CH_4 at 30°C; 0.5 = mL of sample taking from the reactor headspace; 150 = mL of headspace; 1000 = µmol to nmol; 100 = mL H_20 into the reactor; 0.3 = g cat.







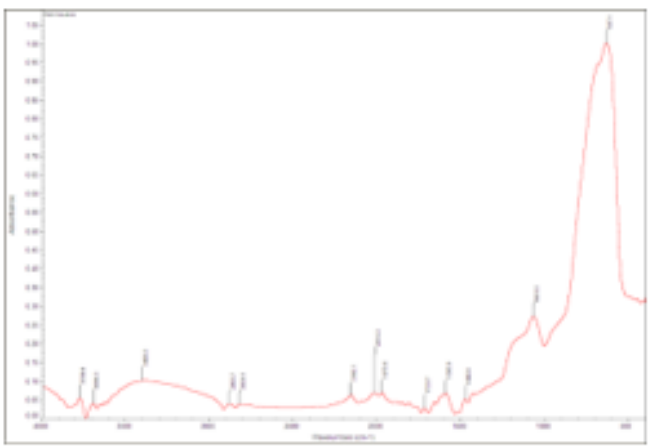


Figure S3 FT IR spectrum, top to bottom of am-P25, am-P25-SiO_2, am-TiO_2 and am-TiO_2-SiO_2·O-Si-O stretching signal at 1022-1080 cm^{-1} is present only in the -SiO_2 catalysts.

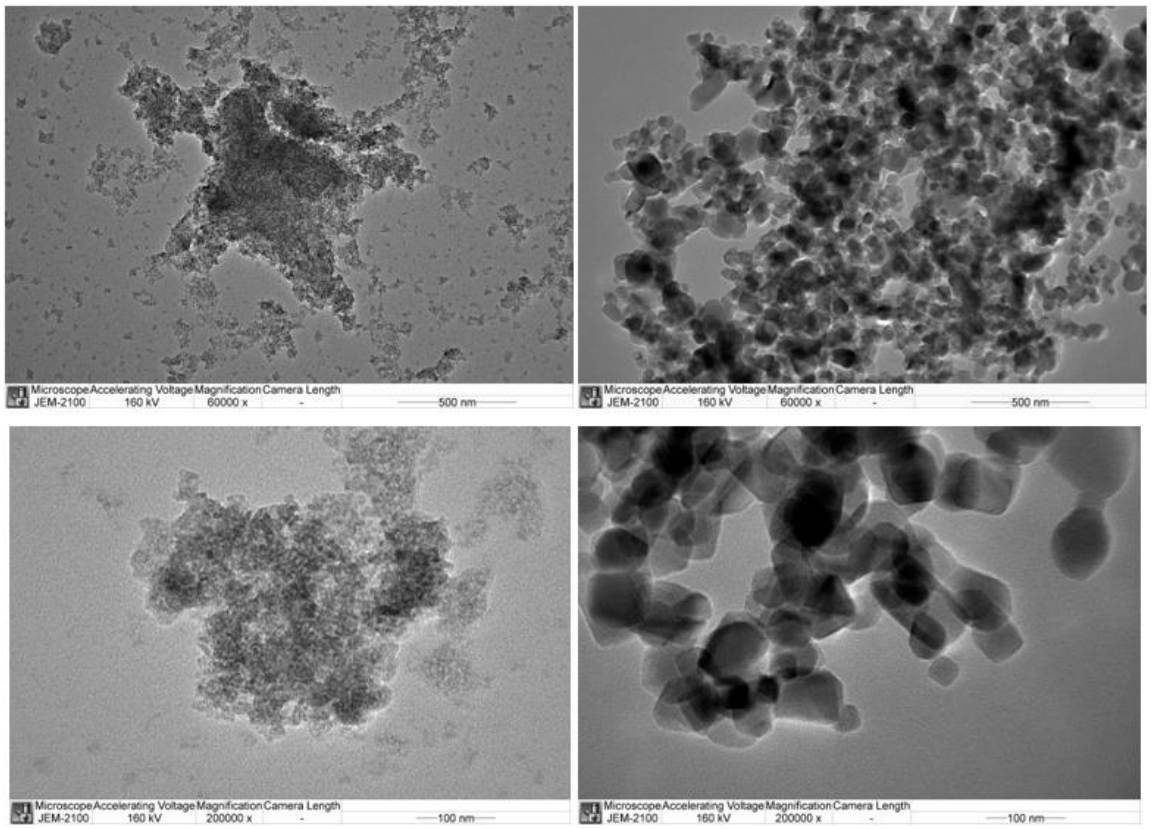


Figure S4 80000 x and 200000 x TEM images. Left: am-TiO_2-SiO_2. Right: P25-TiO_2-SiO_2.

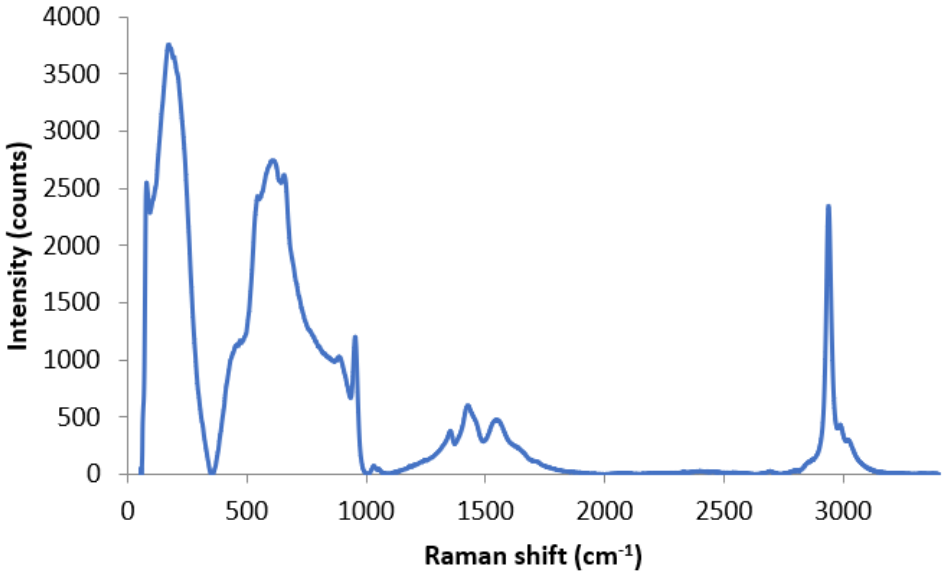


Figure S5 -am-TiO_2 Raman spectrum.

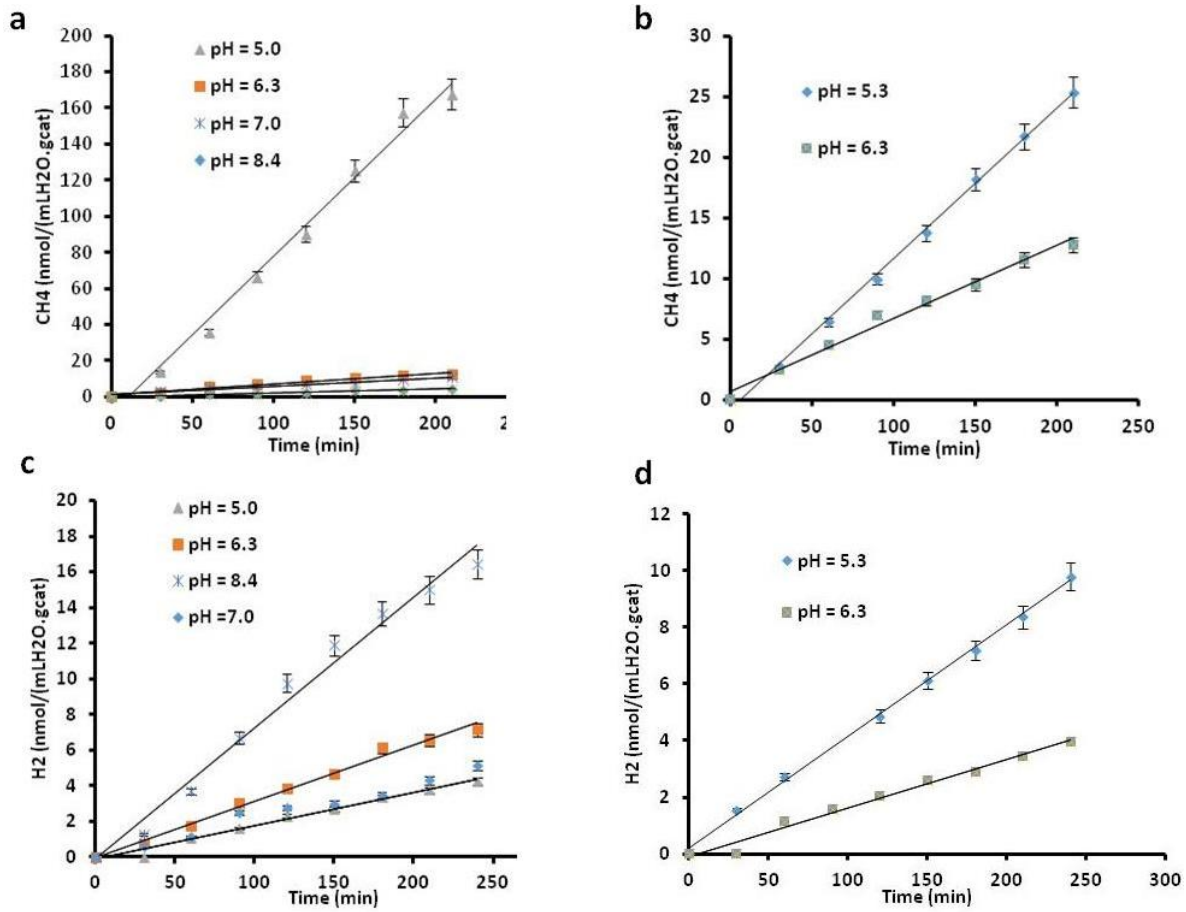


Figure S6 a and **c** Reactor headspace [CH_4] and [H_2] produced in water UV photo reduction of 100 mg of $NaHCO_3$ using 0.3 g of am-TiO_2-SiO_2 at different initial pH (without buffer); **b** and **d** Reactor headspace [CH_4] and [H_2] produced in water UV photo reduction of 100 mg of $NaHCO_3$ using 0.3 g of am-TiO_2-SiO_2 using NaH_2PO_4 buffer.

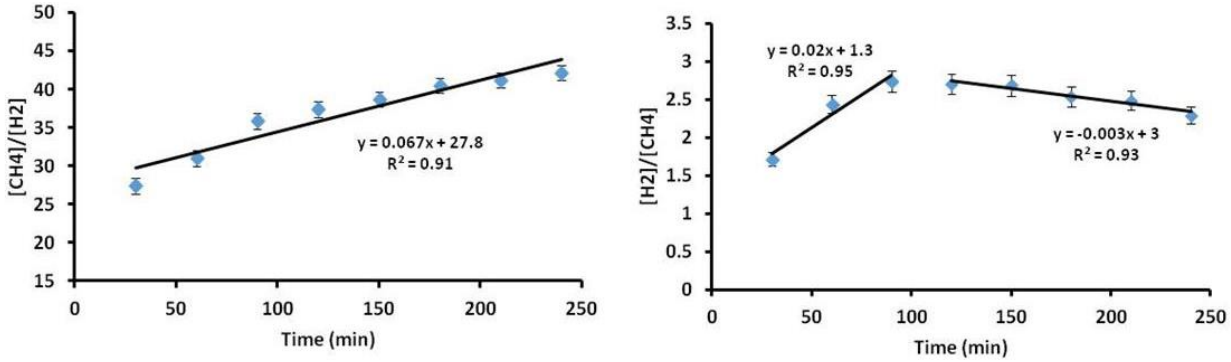


Figure S7 Left: [CH_4]/[H_2] ratio Vs. time at pH = 3. Right: [H_2]/[CH_4] ratio Vs. time at pH = 7.4.

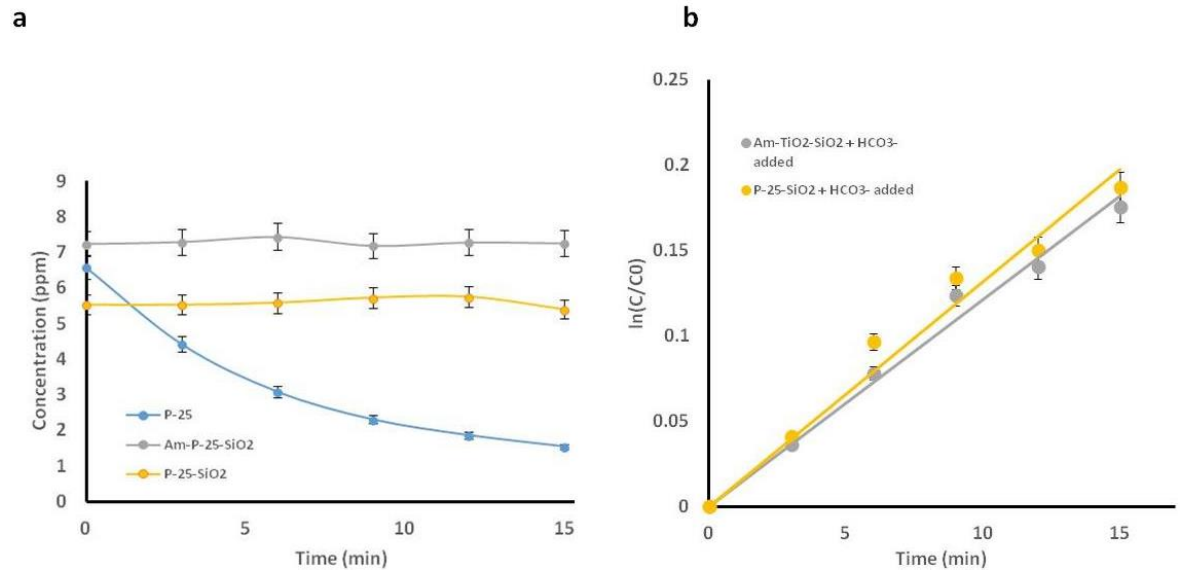


Figure S8 a 8 ppm of MB photo oxidation using silicate surface-modified TiO_2 catalysts. **b** ln (C/Co) Vs. time plot of MB UV photo oxidation using P25-SiO_2 and am-TiO_2-SiO_2 catalysts. Pseudo-first order rate constants are found from the corresponding slopes and reported in **Table 4.**

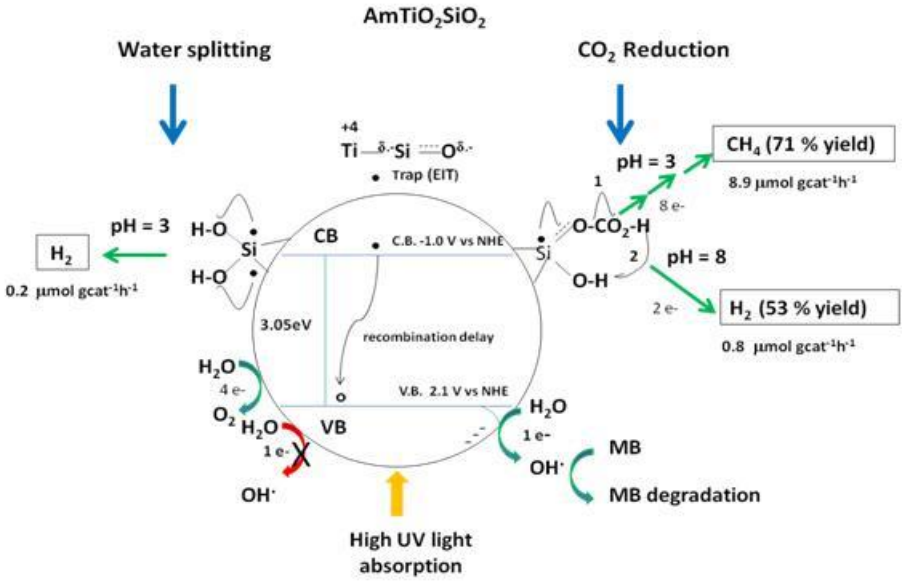


Figure S9 am-TiO_2-SiO_2 RedOx photo-activity. Si acts as an external intramolecular trap (**EIT**) promoted by the (d-p) π-bonding at the Si-O bond. e/h recombination is then reduced. CH_4 is produced 80 times faster than when P25 is used and H_2 is produced 8 times faster. Only O_2 is produced at the valence band due to its relatively low potential with a value lower than the OH/H_2O one. However, when adding HCO_3^- the negative surface charge increases promoting VB down-bending and some $OH^\cdot$ is produced that is quenched by MB.

Table S1 am-TiO_2 Vs. am-TiO_2-SiO_2 BET results.

	am-TiO_2	**am-TiO2-SiO_2**
Surface Area		
Single point surface area at p/p° = 0.200350555	253.7107 m^2/g	258.7982 m^2/g
BET Surface Area	258.8039 m^2/g	264.3750 m^2/g
Langmuir Surface Area	358.8783 m^2/g	358.8783 m^2/g
t-Plot Micropore Area	64.5905 m^2/g	59.7896 m^2/g
t-Plot External Surface Area	194.2134 m^2/g	204.5854 m^2/g
BJH Adsorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width	200.742 m^2/g	142.225 m^2/g
BJH Desorption cumulative surface area of pores between 17.000 Å and 3000.000 Å width	108.2672 m^2/g	164.3499 m^2/g
Pore Volume		
Single point adsorption total pore volume of pores less than 1235.454 Å width at p/p° = 0.984078269	0.133658 cm^3/g	0.162290 cm^3/g
Single point desorption total pore volume of pores less than 587.763 Å width at p/p° = 0.965980087	0.132743 cm^3/g	0.160996 cm^3/g
t-Plot micropore volume	0.028545 cm^3/g	0.025989 cm^3/g
BJH Adsorption cumulative volume of pores between 17.000 Å and 3000.000 Å width	0.109010 cm^3/g	0.111161 cm^3/g
BJH Desorption cumulative volume of pores between 17.000 Å and 3000.000 Å width	0.069848 cm^3/g	0.120946 cm^3/g
Pore Size		
Adsorption average pore width (4 V/A by BET)	20.6578 Å	24.5545 Å
Desorption average pore width (4 V/A by BET):	20.5164 Å	24.3587 Å
BJH Adsorption average pore width (4 V/A):	21.721 Å	31.263 Å
BJH Desorption average pore width (4 V/A):	25.806 Å	29.436 Å
Freundlich		
Qm·C	30.2841 ± 0.0921 cm^3/g STP	30.8619 ± 0.1593 cm^3/g STP
m	5.7133 ± 0.0508	5.7317 ± 0.0875