

### Supporting Figure Captions

**Figure S1.** STEM-EDS spectrum with EDS mapping of Cu, Nb and O elements for 1wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub> sample.

**Figure S2.** STEM-EDS spectrum with EDS mapping of Cu, Nb and O elements for 3wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub> sample.

**Figure S3.** STEM-EDS spectrum with EDS mapping of Cu, Nb and O elements for 5wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub> sample.

**Figure S4.** BET surface area of (A) pure Nb<sub>2</sub>O<sub>5</sub>, (B) r-Nb<sub>2</sub>O<sub>5</sub> and (C) 2wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub> nanosheets.

**Figure S5.** The amount of photocatalytic products (H<sub>2</sub>, CO & CH<sub>4</sub>) evolved during CO<sub>2</sub> reduction for of pure Nb<sub>2</sub>O<sub>5</sub>, r-Nb<sub>2</sub>O<sub>5</sub>, 1wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub>, 2wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub>, 3wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub>, 5wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub> and 2wt% Cu/Nb<sub>2</sub>O<sub>5</sub> nanosheets.

**Figure S6.** Summary of Mott-Schottky results with flat band potential and charge carrier density.

**Table TS1.** Atomic weight% of Cu, Nb and O elements obtained from STEM-EDS analysis.

**Table TS2.** The obtained CO<sub>2</sub> selectivity for Nb<sub>2</sub>O<sub>5</sub>, reduced Nb<sub>2</sub>O<sub>5</sub>, 1wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub>, 2wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub>, 3wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub>, 5wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub> and 2wt% Cu/Nb<sub>2</sub>O<sub>5</sub> nanosheets.

**Table TS3.** Photocatalytic CO<sub>2</sub> reduction performance of present nanostructures compared to the Vanadate based photocatalyst with the reported photocatalysts.

**Table TS4.** Results obtained after CO<sub>2</sub> reduction tests for 10 consecutive cycles.

**Table TS5.** Summary of TRPL results for pure Nb<sub>2</sub>O<sub>5</sub>, r-Nb<sub>2</sub>O<sub>5</sub> and 2wt% Cu/r-Nb<sub>2</sub>O<sub>5</sub> nanosheets.

### Formula for charge carrier density (N<sub>D</sub>)

$$N_D = (2/e_0\epsilon\epsilon_0)/[d(1/C^2)/dV]$$

where  $e_0$ =electron charge,  $\epsilon$  = dielectric constant of Nb<sub>2</sub>O<sub>5</sub> (77) and  $V$  = applied potential

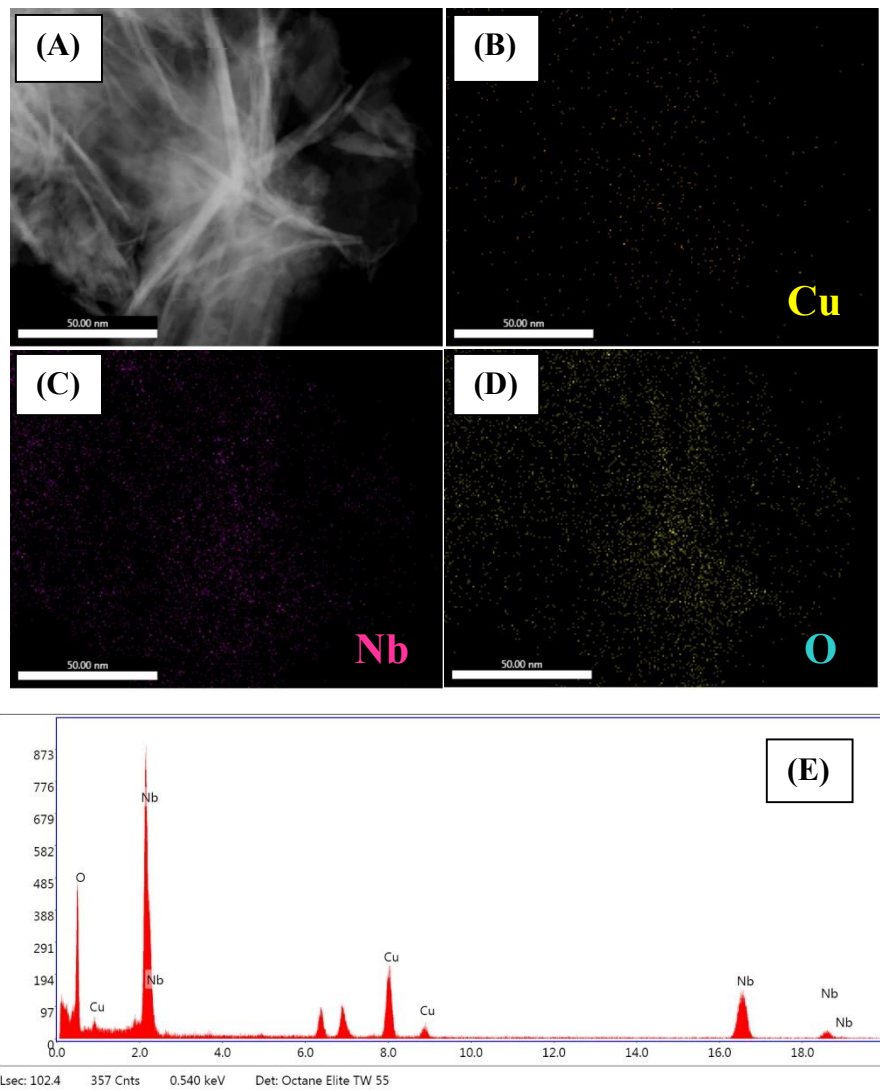


Figure S1

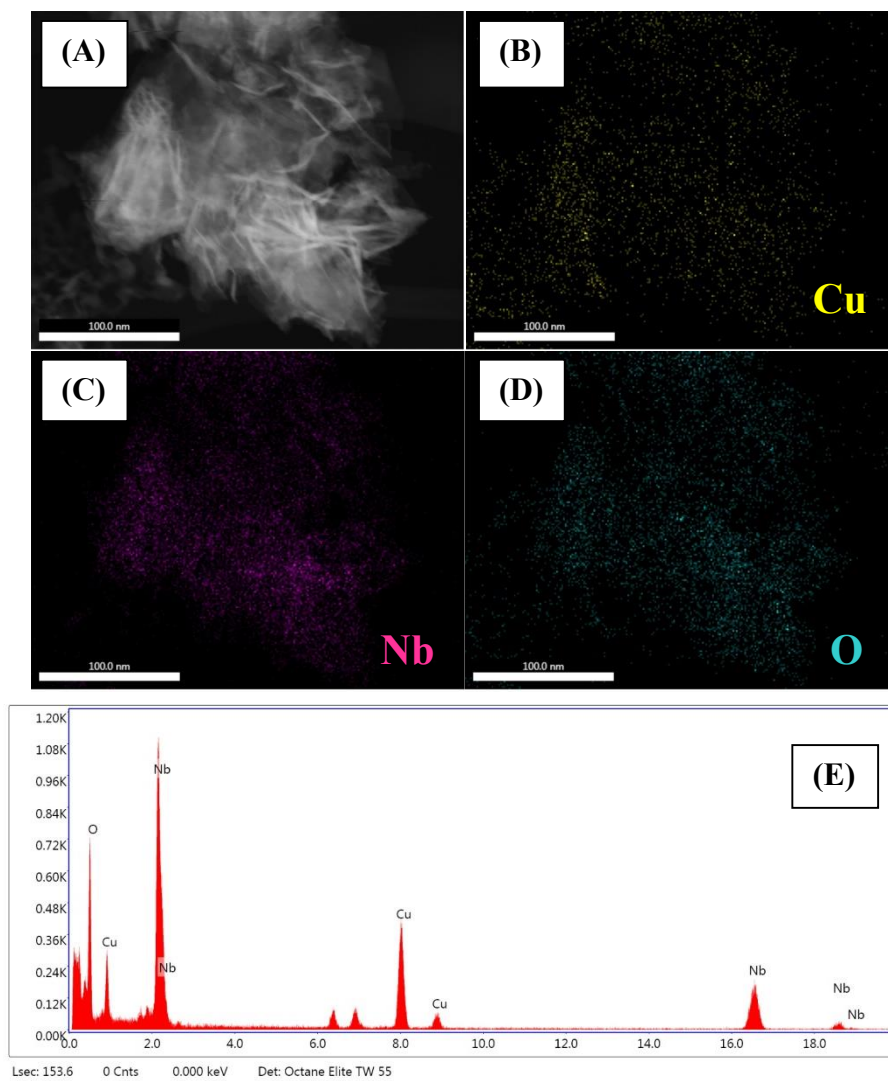


Figure S2

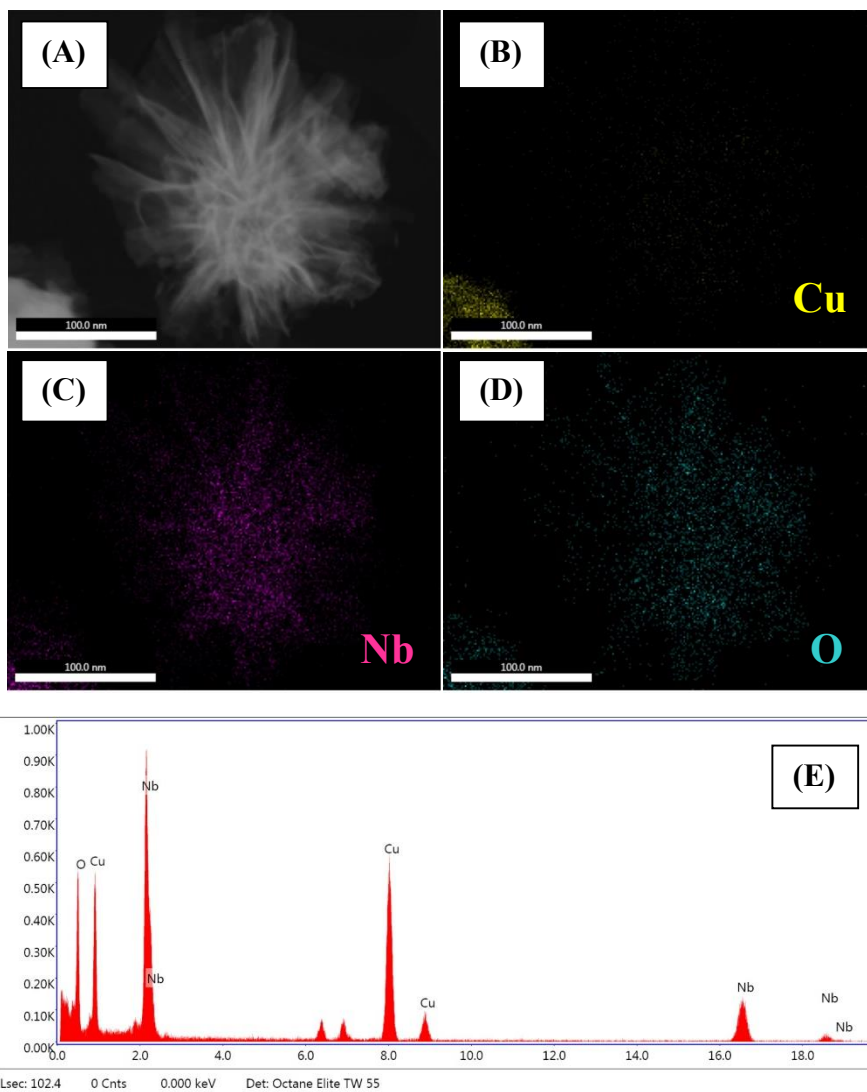


Figure S3

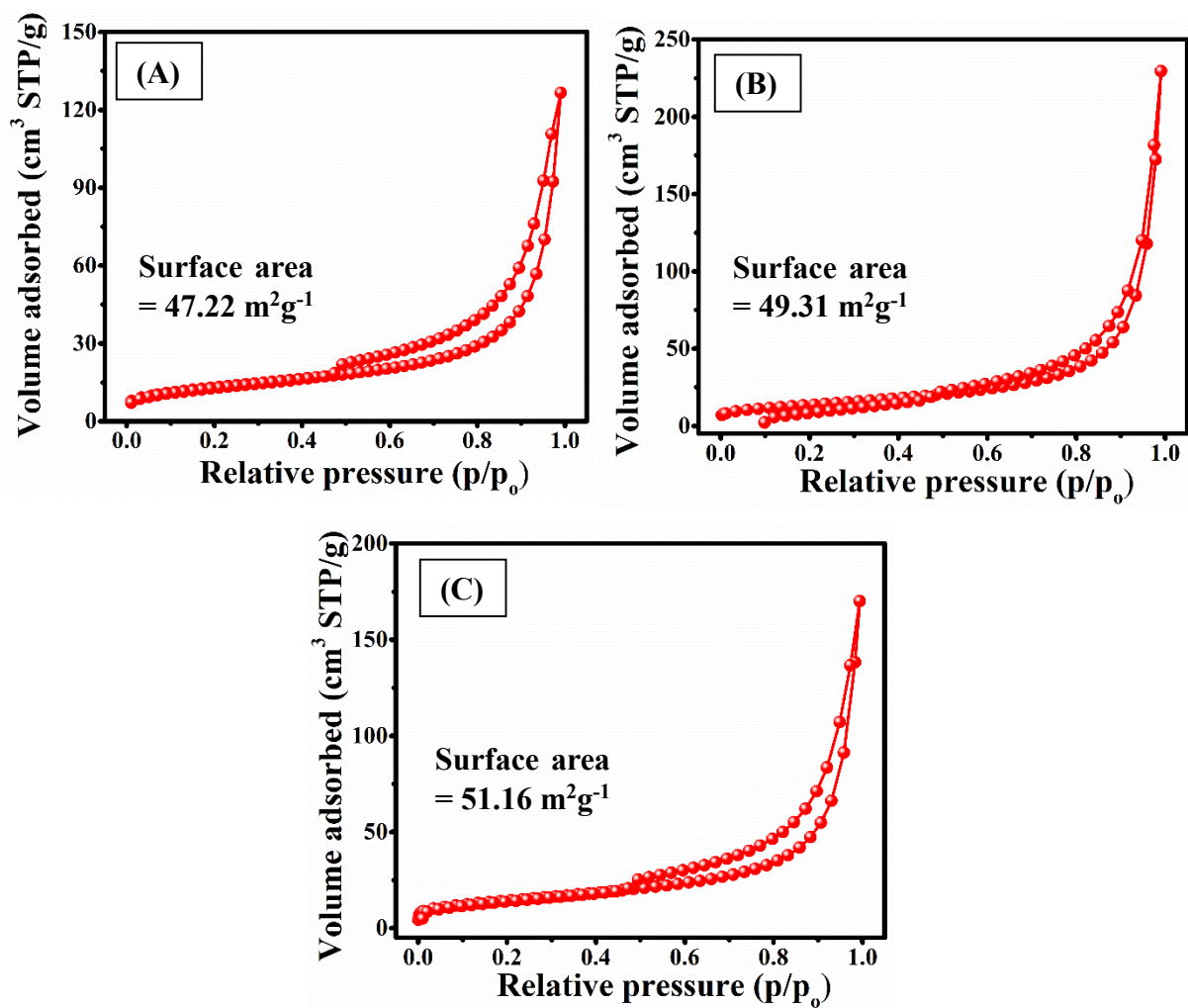


Figure S4(A to C)

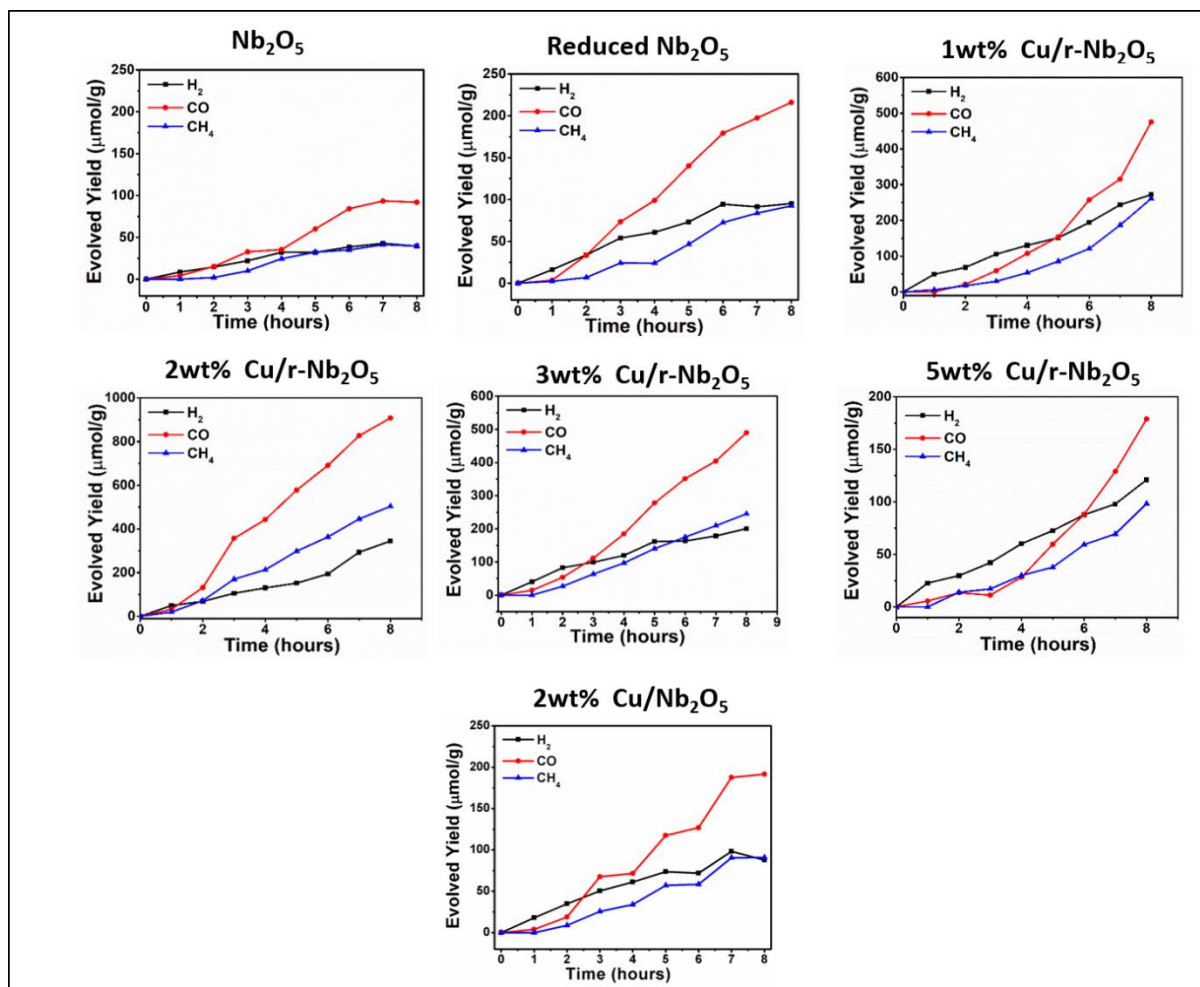


Figure S5

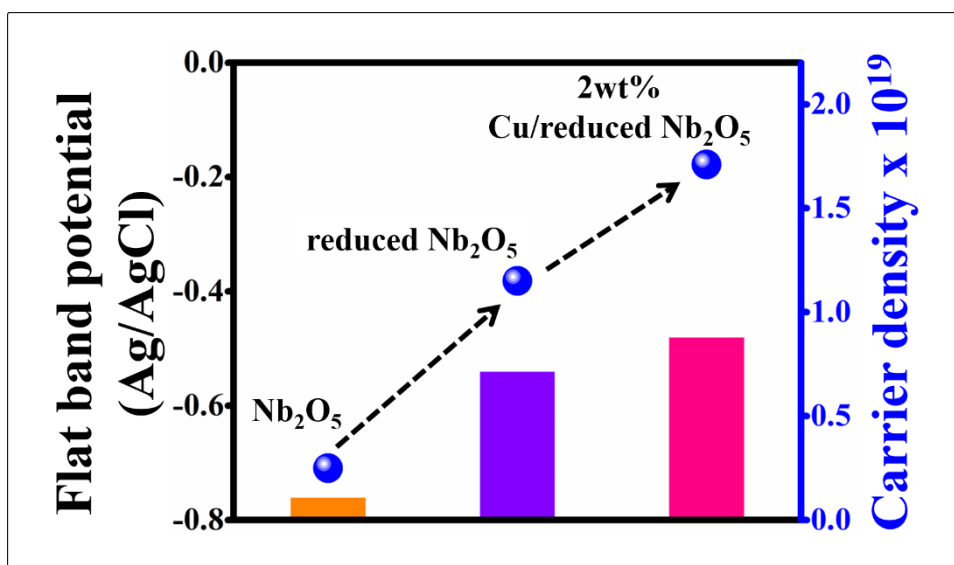


Figure S6

<b>Sample Name</b>	<b>Cu (Atomic %)</b>	<b>Nb (Atomic %)</b>	<b>O (Atomic %)</b>
Nb <sub>2</sub> O <sub>5</sub>	-	55.39	44.61
r-Nb <sub>2</sub> O <sub>5</sub>	-	73.57	26.43
1wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	0.94	56.29	42.77
2wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	1.75	58.85	39.40
3wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	6.62	49.03	44.35
5wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	15.93	46.57	37.50

**Table TS1**

<b>Sr. No.</b>	<b>Sample Name</b>	<b>H<sub>2</sub> (mmol/g)</b>	<b>CO (mmol/g)</b>	<b>CH<sub>4</sub> (mmol/g)</b>	<b>Selectivity (%) S<sub>CO2</sub></b>
1	Nb <sub>2</sub> O <sub>5</sub>	0.039	0.092	0.039	86
2	r-Nb <sub>2</sub> O <sub>5</sub>	0.095	0.216	0.092	86
3	1wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	0.272	0.475	0.261	85
4	2wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	0.344	0.908	0.504	89
5	3wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	0.201	0.490	0.245	88
6	5wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	0.121	0.179	0.098	83
7	2wt% Cu/Nb <sub>2</sub> O <sub>5</sub>	0.087	0.0192	0.091	86

**Table TS2**



Sr. No.	Catalyst Name	Products (mmol g <sup>-1</sup> )	Experimental details	Reference no.
1	0.51wt% Cu/Nb <sub>2</sub> O <sub>5</sub>	CO: 0.199, CH <sub>4</sub> : 0.419	Catalyst amount: 0.1g, 6 UV lamps of 15 W	30
2	Nb <sub>2</sub> O <sub>5</sub> /g-C <sub>3</sub> N <sub>4</sub>	CO: 0.343, CH <sub>4</sub> : 0.041	Catalyst amount: 0.03g 300 W Xe lamp	34
3	SiO <sub>2</sub> -HNb <sub>3</sub> O <sub>8</sub>	CH <sub>4</sub> : 0.004	Catalyst amount: 0.1g, 0.4 wt % Pt 350 W Xe lamp, 34.8 mW cm <sup>-2</sup>	56
4	g-C <sub>3</sub> N <sub>4</sub> /NaNbO <sub>3</sub>	CH <sub>4</sub> : 0.024	Catalyst amount: 0.05g + 0.5 wt % Pt 300-W Xe lamp, UV cutoff filter ( $\lambda > 420$ nm).	57
5	10wt% Cu/Nb <sub>2</sub> O <sub>5</sub>	CH <sub>4</sub> : 0.048, HCOOH: 0.074 CH <sub>3</sub> COOH: 0.007	Catalyst amount: 0.3g UVC lamp (OSRAM 11 W) 21.49 mW·cm <sup>-2</sup>	58
6	Nb <sub>2</sub> O <sub>5</sub> nanofibers	CO: 0.008, CH <sub>4</sub> : 0.005	Sample glass slide (2x2 cm) 18 W mercury lamp, 254 nm	59
7	Bi <sub>2</sub> O <sub>2</sub> (OH)(NO <sub>3</sub> )/Nb <sub>2</sub> O <sub>5</sub>	CO: 0.016, C <sub>2</sub> H <sub>4</sub> : 0.006	UV-C irradiation (Philips 18 W mercury)	60
8	Nb <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> :0.039; CO:0.092; CH <sub>4</sub> :0.039	Nanostructure grown on FTO substrate (4 cm x 2 cm) 300 W Xenon lamp	<b>Present work</b>
	r-Nb <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> :0.095; CO:0.216; CH <sub>4</sub> :0.092		
	2wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	H <sub>2</sub> :0.344; CO:0.908; CH <sub>4</sub> :0.503		

**Table TS3**

<b>Cycle number</b>	<b>H<sub>2</sub> (mmol/g)</b>	<b>CO (mmol/g)</b>	<b>CH<sub>4</sub> (mmol/g)</b>	<b>Selectivity (%) S<sub>CO2</sub></b>
1	0.344	0.908	0.504	89
2	0.374	0.930	0.493	88
3	0.314	0.938	0.460	89
4	0.330	0.910	0.405	88
5	0.287	0.923	0.422	90
6	0.389	0.968	0.425	87
7	0.371	0.938	0.506	89
8	0.321	0.909	0.480	89
9	0.290	0.799	0.481	90
10	0.256	0.622	0.313	88

**Table TS4**

<b>Sample Name</b>	<b><math>\tau_1</math></b>	<b><math>\tau_2</math></b>	<b>B1</b>	<b>B2</b>	<b>Average carrier life time <math>\tau</math> (ns)</b>
Nb <sub>2</sub> O <sub>5</sub>	0.10	0.35	11	3.9	0.23
r-Nb <sub>2</sub> O <sub>5</sub>	0.14	0.41	12	3.3	0.26
2wt% Cu/r-Nb <sub>2</sub> O <sub>5</sub>	0.29	3	9.7	1.1	1.75

**Table TS5**