Supplementary Information

Use of an optofluidic microreactor and Cu nanoparticles synthesized in ionic liquid and embedded in TiO_2 for an efficient photoreduction of CO_2 to methanol

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Figure S1. Schematic representation of the preparation of the light-responsive papers.

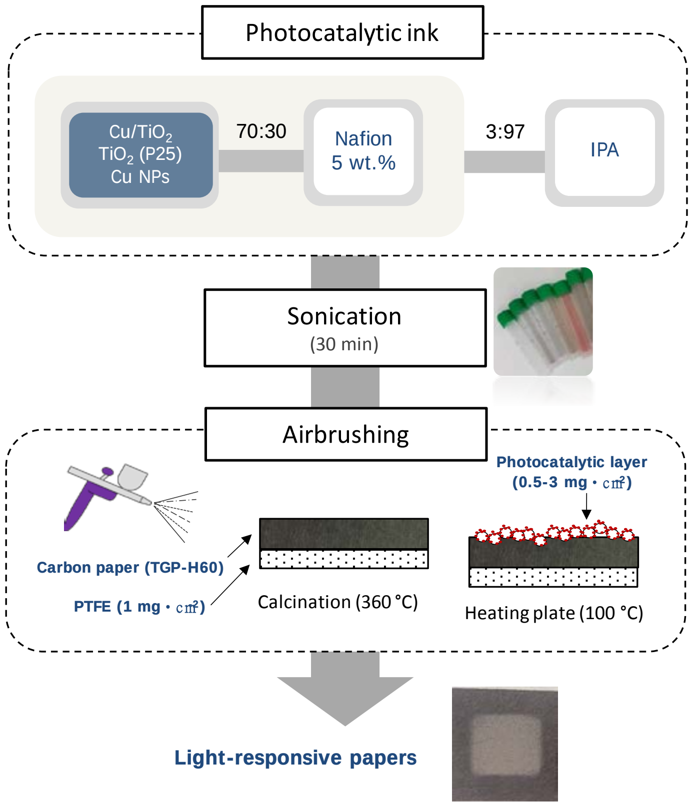


Figure S2. (a) Inner parts, and (b) images of the micro-optofluidic reactor.

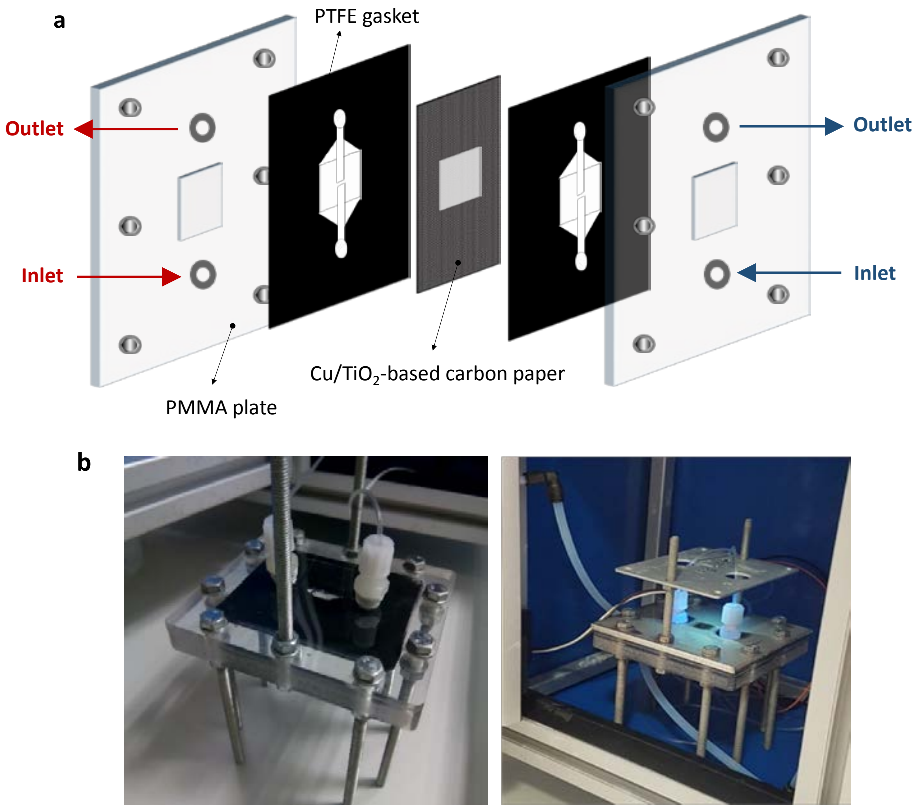


Figure S3. Raman spectra of TiO_2 and Cu/TiO_2 samples.

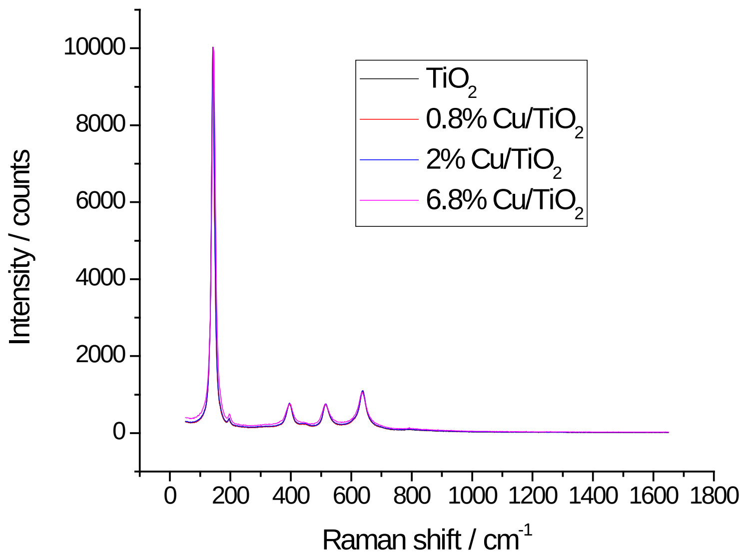
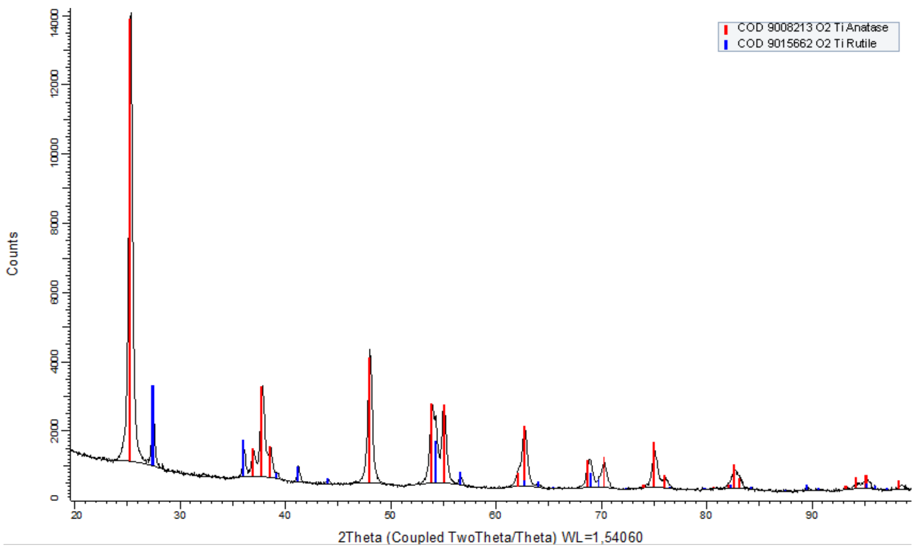


Figure S4. The X-ray powder diffraction patterns and composition of (a) 0.8% Cu/TiO_2, (b) 2% Cu/TiO_2, (c) 6.8% Cu/TiO_2 and, (d) Cu nanoparticles.

a



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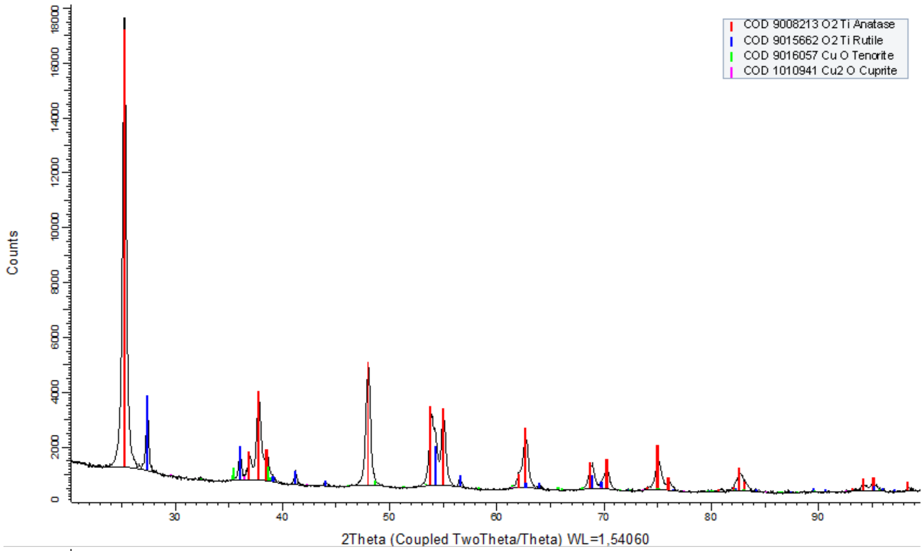
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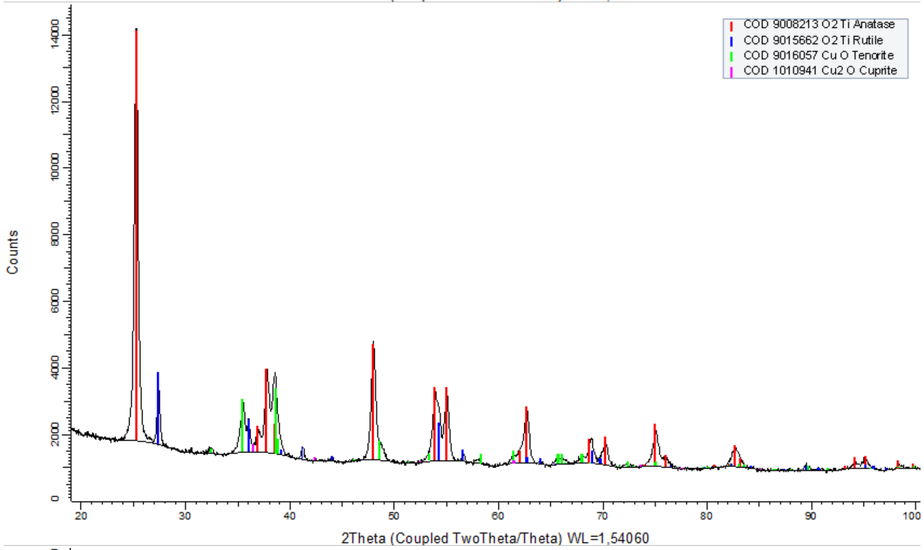
COD 9015662 O2 Ti Rutile
COD 9016057 Cu O Tenorite
COD 1010941 Cu2 O Cuprite
Counts
2Theta (Coupled TwoTheta/Theta) WL=1,54060

c


COD 9008213 O2 Ti Anatase
COD 9015662 O2 Ti Rutile
COD 9016057 Cu O Tenorite
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Counts
2Theta (Coupled TwoTheta/Theta) WL=1,54060

d

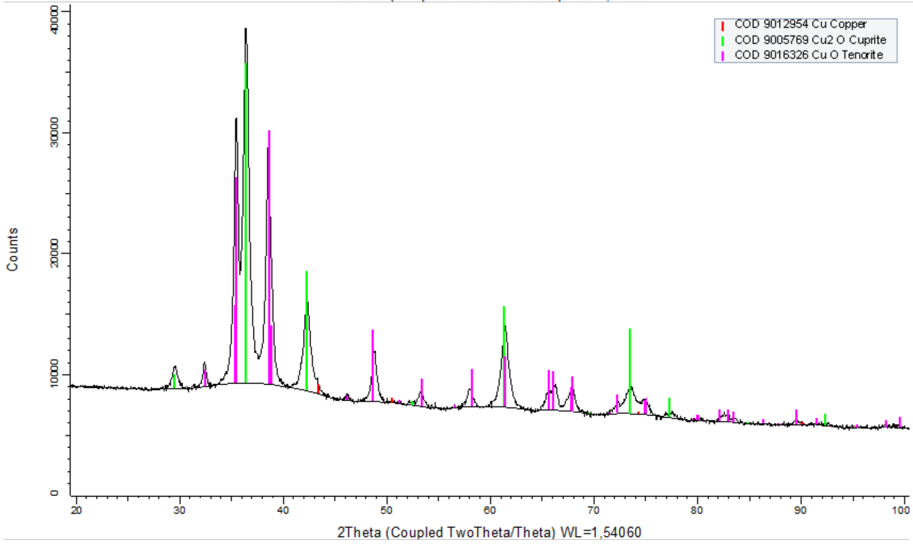
COD 9012954 Cu Copper
COD 9005769 Cu2 O Cuprite
COD 9016326 Cu O Tenorite
Counts
2Theta (Coupled TwoTheta/Theta) WL=1,54060

Table S1. Crystalline phase of Cu and Cu/TiO_2 from PXRD.

Sample	Composition (%)				
	Anatase	*Rutile*	*CuO*	*Cu_2O*	*Cu*
Cu	-	-	52	46	2
0.8% Cu/TiO_2	80	20	-	-	-
2% Cu/TiO_2	77	19	2	2	-
6.8% Cu/TiO_2	65	16	13	6	-

Figure S5. TEM image of Cu NPs.

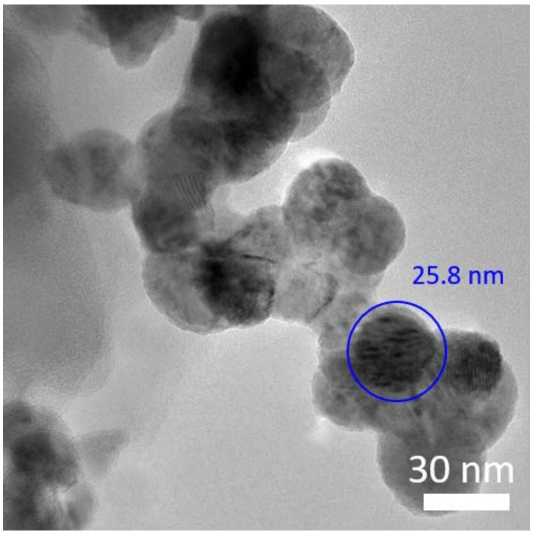

Figure S6. Scanning electron transmission microscopy (STEM) images and EDX mapping of (a) TiO_2, (b) 0.8% Cu/TiO_2, (c) 2% Cu/TiO_2 and (d) 6.8% Cu/TiO_2 and (e) Cu NPs.

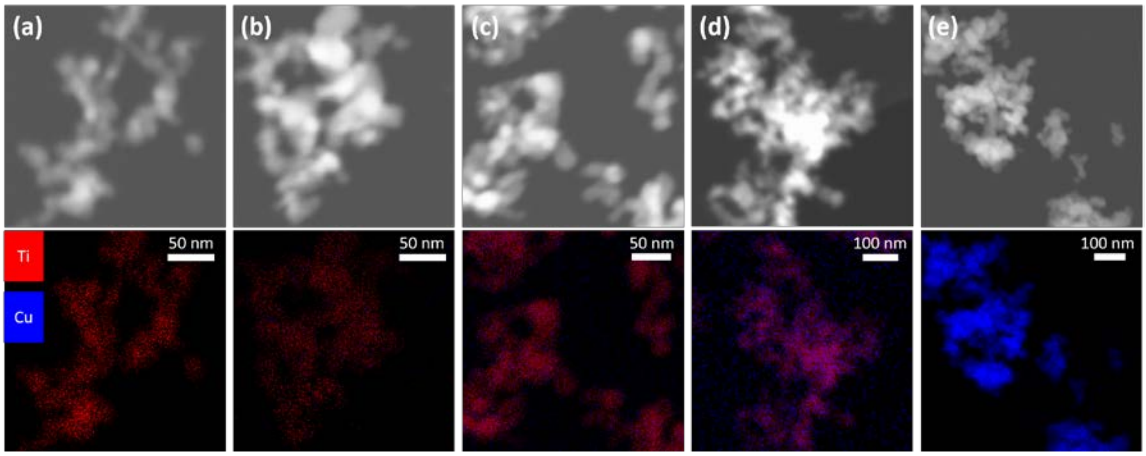

Figure S7. TEM images and EDX spectra of (a) 0.8% Cu/TiO_2, (b) 2% Cu/TiO_2 and (c) 6.8% Cu/TiO_2.

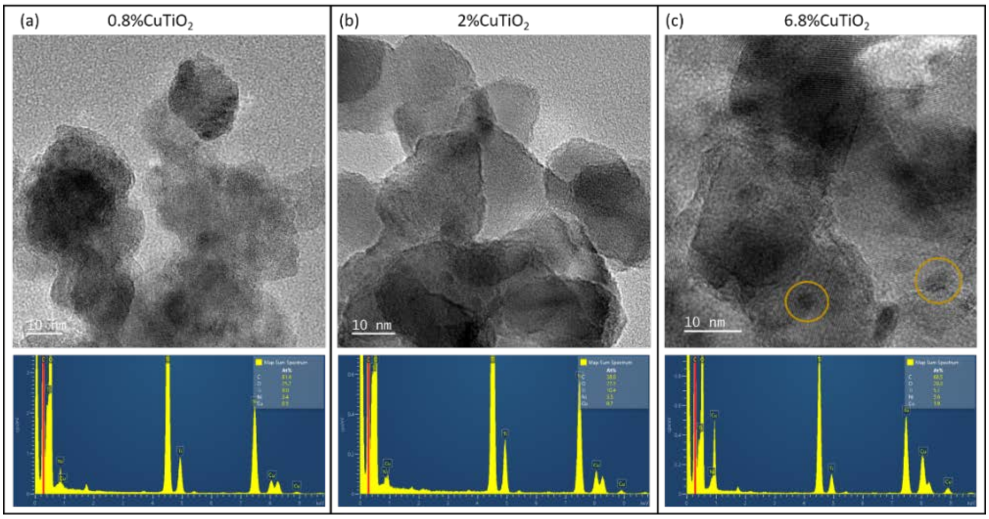

Table S2. XPS fittings for Cu 2p region. These data were extracted from Cu 2p region fittings, and they illustrate the main differences between the samples reported in this work. Therefore, slightly different values can be found in different reports depend on the fitting model applied. In this work, we used: GL(30) line shape, U2-Touguard as background type and FWHM constrain between 0.9 to 4 eV.

	Cu_2O			**CuO**		
	$2p_{3/2}$ / eV	FWHM / eV	atom%	$2p_{3/2}$ / eV	FWHM / eV	atom%
0.8 Cu/TiO_2	932.5	2.3	82.9	934.5	2.1	17.1
2%Cu/TiO_2	932.5	2.3	56.2	934.8	2.8	43.8
6.8%Cu/TiO_2	932.7	2.3	32.3	934.7	3.5	77.7

Figure S8. Cu 2p region deconvolution for (a) 0.8% Cu/TiO_2, (b) 2% Cu/TiO_2 and (c) 6.8% Cu/TiO_2. (d) Cu NPs oxidation states ratio and FWHM for fitting associate Cu^{2+} (data extract from Table S1).

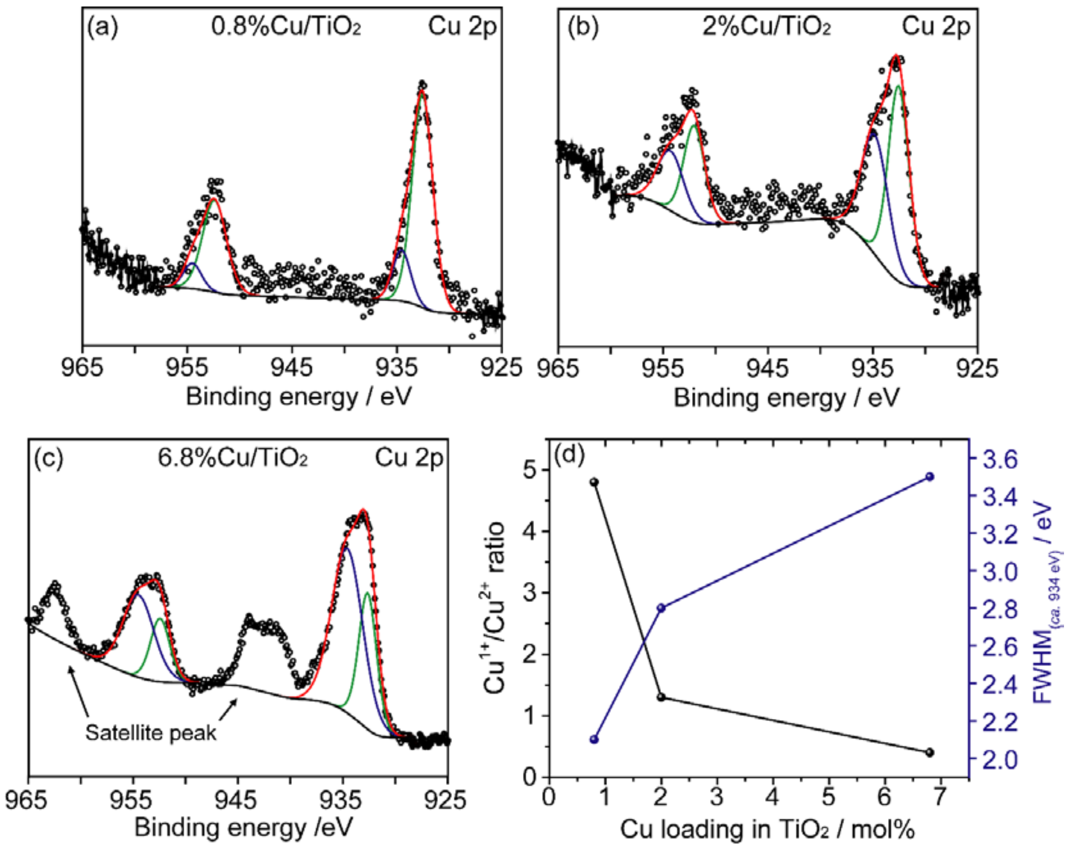

Figure S9. FTIR spectra of (a) 0.8% Cu/TiO_2, (b) 2% Cu/TiO_2 and 6.8% Cu/TiO_2.

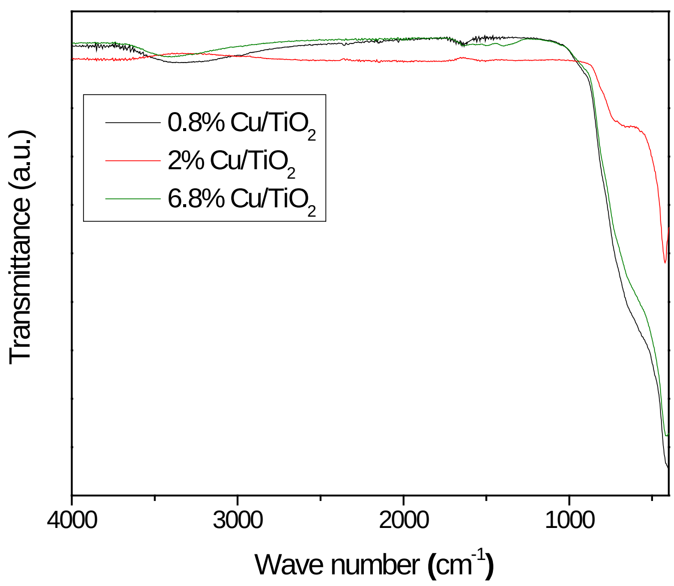

Figure S10. BET N_2-physisorption isotherms for bare TiO_2 and Cu/TiO_2 composites.

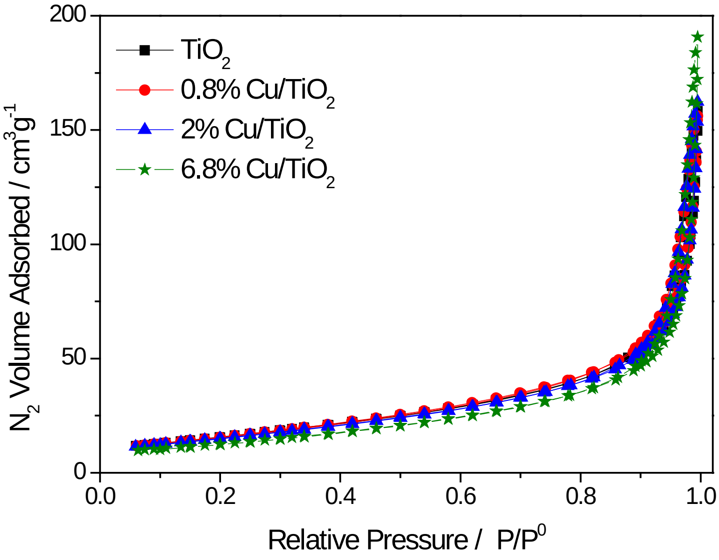

Table S3. Textural properties of bare TiO_2 and Cu/TiO_2 samples.

Sample	**SBET[a] ($m^2 \cdot g^{-1}$)**	**Vpore[a] ($cm^3 \cdot g^{-1}$)**
TiO_2	56.7	0.106
0.8%Cu/TiO_2	58.6	0.110
2%Cu/ TiO_2	56.0	0.104
6.8%Cu/ TiO_2	46.8	0.097

[a] Determined by BET multipoint method and BJH method.

Table S4. Summary of literature reports on the photocatalytic synthesis of CH_3OH from at Cu containing TiO_2 photocatalysts.

Photocatalyst	Light source	Reaction media/ Reactor configuration	*r* (μmol·g^{-1}·h^{-1})	AQY (%)	Other products	Ref.,year
Cu2.5	UV 1200 mW LED (365 nm, 5 mW·cm^{-2})	0.5 M $KHCO_3$/OFM[a]	167.5	3.7	HCOOH, C_2H_5OH	This work, 2020
	UV 1200 mW LED (365 nm, 10 mW·cm^{-2})	0.5 M $KHCO_3$/OFM (two compartments)	230.3	2.5		
	Vis 1200 mW LED (450 nm, 5 mW·cm^{-2})	0.5 M $KHCO_3$/OFM	36.7	0.7		
	Vis 1200 mW LED (450 nm, 10 mW·cm^{-2})	0.5 M $KHCO_3$/OFM (two-compartment)	43.1	0.4		
2 wt% Cu/TiO_2	UV 20 W lamp	0.1 M $NaHCO_3$/ Pyrex closed chamber	12.4	-	-	[1], 2019
Fe-N-TiO_2/CPO-Cu-27	Vis 70 W Hg lamp (350-600 nm, 85 mW·cm^{-2})	H_2O vapor / Continuous flow Pyrex vessel	2.2	-	CH_4	[2], 2019
Cu porphyrin/Ti-MCM-48	UV-Vis 500W Xe lamp (33 mW·cm^{-2})	0.1 M NaOH-Na_2SO_3/Quartz glass reactor (inside irradiation)	49.5	-	-	[3], 2018
2 wt% Cu/TiO_2	UV-A 8 W lamp (350 nm, 0.12 mW·cm^{-2})	0.2 M KOH/Gas recirculation quartz reactor	19.7	-	CH_4, C_2H_4, C_3H_6O	[4], 2018
	Vis 20 W LED (0.02 μW·cm^{-2})	ACN[b]-TEOA[c]/ Gas recirculation quartz reactor	352.9	-	CH_4, C_2H_4	
0.5 wt% Cu/TiO_2	UV Hg lamp (365 nm)	ACN[b]- BZA[d]/-	64.1	-	HCOOH, HCHO, CH_4	[5], 2018
3 wt% Cu-C/TiO_2 NPs	UV lamp (254-365 nm)	Seawater/Batch pyrex annular reactor	577	-	-	[6], 2018
	Natural sunlight		188	-	-	
TiO_2/$CuInS_2$ (3.1 mol%) core-shell NFs[e]	Vis 350W Solar Xe arc lamp	2 M H_2SO_4/Pyrex reactor	0.86	-	CH_4	[7], 2018
3 wt% Cu-C/TiO_2 NPs[f]	UV lamp (365 nm, 120 mW·cm^{-2})	0.2 M NaOH/Stirred Pyrex annular reactor	518.6	-	-	[8], 2017
	Natural sunlight		177	-	-	
3 wt% Cu g-C_3N_4/TiO_2	Vis 500 W Xe lamp	1 M NaOH/Pyrex glass reactor	429	-	HCOOH	[9], 2017
	UV Hg lamp (254 nm, 5.4 mW·cm^{-2})		102.3	-	HCOOH	
1.5 wt% CuO-TiO_2 NRs[g]	UV LED (365 nm)	H_2O/OFM	36.2	-	C_2H_5OH	[10], 2017
1 wt% Cu-In_2O_3/TiO_2	UV 500 W Hg lamp (365 nm, 25 mW·cm^{-2})	H_2O-H_2/Batch photoreactor	68	-	CH_4	[11], 2016
$CuFe_2O_4$/TiO_2	Vis 500 W Xe lamp (24 mW·cm^{-2})	0.07 M KOH/Continuous-flow reactor	81.4	-	-	[12], 2016
3 wt%CuO/TiO_2	UV 500 W Hg lamp (365 nm, 4.2 mW·cm^{-2})	0.2 M $KHCO_3$-0.1 M Na_2SO_3/Quartz reactor	2.1	-	C_2H_5OH	[13], 2016
Pt/$CuAlGaO_4$-Pt/$SrTiO_3$:Rh (1:1)	Vis 300 W Sunlight Xe lamp (90 mW·cm^{-2})	2 mM $FeCl_2$/Twin photoreactor	0.5	0.002	-	[14], 2015
$CuFe_2O_4$/TiO_2	Vis 500 W Xe lamp (320-400 nm, 24 mW·cm^{-2})	0.07 M KOH-Na_2S/Continuous-flow quartz reactor	24.4	-	-	[15], 2015

Cu-TiO_2/ZSM-5	UV 14 W lamp (254 nm, 0.97 mW·cm^{-2})	0.1 M $NaHCO_3$/Inside illumination	50.1	-	-	[16], 2015
0.5 wt% Cu/TiO_2 monoliths	UV 200 W Hg lamp (33.42 mW·cm^{-2})	H_2O vapor/Cylindrical Pyrex glass reactor	1	-	C_2H_4O, C_2H_5OH	[17], 2014
	Vis 500W halogen lamp (68.35 mW·cm^{-2})		0.06	-		
1 wt% Cu/TiO_2 NPs	UV 18 W Hg lamp (254 nm)	0.2 M NaOH/Quartz reactor	0.3	-	CO, HCHO, CH_4	[18], 2014
1 wt% CuTiO_2/SiO_2	UV 400 W Hg lamp	H_2O/Pyrex batch gas solid reactor	0.003	-	CH_4, C_2H_4O, C_3H_6O	[19], 2013
Cu/TiO_2/mol. sieve	UV 250 W Hg lamp	0.2 N NaOH/Quartz reactor (external irradiation)	0.7	-	CH_4 $C_2H_2O_4$, $C_2H_4O_2$	[20], 2011
2 wt% Cu-Ce/TiO_2	UV 125 W lamp (365 nm)	0.2 M NaOH/Quartz reactor high-pressure reactor	11.3	-	-	[21], 2011
2 wt% Cu/ TiO_2/SBA-15	UV 400 W halide lamp (365 nm)	0.1 N NaOH/Quartz cell (inner irradiation)	627	-	-	[22], 2009
3 wt% CuO/TiO_2	UV tubular lamp (365 nm, 2.45 mW·cm^{-2})	1 M $KHCO_3$/Pyrex stainless steel vessel	450	-	HCOOH	[23], 2009
1.2 wt% Cu/TiO_2	UV Hg lamp (365 nm, 1.6 mW·cm^{-2}	H_2O/Optical fiber quartz reactor	0.45		-	[24], 2005
3 wt%CuO/TiO_2	UV 10 W lamp (415-700 nm, 2.45 mW·cm^{-2})	1 M $KHCO_3$/Quartz cell	442.5	19.23	-	[25], 2005
1.2 wt% Cu/TiO_2	UV Hg lamp (365 nm, 16 W·cm^{-2})	H_2O/Optical-fiber photo reactor	0.45	-	-	[26], 2005
2 wt% Cu/TiO_2	UV-C Hg lamp (254 nm)	0.2 N NaOH/Cylindrical quartz reactor	20	-	-	[27], 2004
2 wt% Cu/TiO_2	UV 8 W Hg lamp (>254 nm)	0.2 N NaOH/Cylindrical quartz reactor	40	-	-	[28], 2004
Fe-0.03wt% Cu-K/DAY[h])-Pt/$K_2Ti_6O_{13}$ (1:1)	Concentrated sunlight (62 mW·cm^{-2})	H_2O/Optical quartz tube cell	4.83	-	HCOOH, HCHO, CH_4, C_2H_5OH	[29], 2003
2.0 wt% Cu/TiO_2 NPs[f]	UV 8W Hg lamp (254 nm)	0.2 N NaOH/Quartz reactor (inner-irradiated)	19.6	10.02	-	[30], 2002
Cu/TiO_2 rutile	UV 75 W Hg lamp (>280 nm)	H_2O/Quartz cell	0.0024	-	CO, CH_4	[31], 1995
3 wt% Cu/TiO_2	Vis 500 W Xe lamp	0.01 M $KHCO_3$/Cylindral pyrex cell	1.32	-	CO, HCHO, HCOOH	[32], 1992

[a] Optofluidic microreactor; [b] Acetonitrile; [c] Triethanolamine; [d] Benzylamine; [e] Nanofibers; [f] Nanoparticles; [g] Nanorods; [h] Dealuminized Y-type zeolite.

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