Electronic Supplementary Material (ESI) for Environmental Science: Nano.

Supporting Information

Optimization of process variables for the concurrent removal of aliphatic and aromatic volatile organic compounds over copper impregnated titanium dioxide photocatalyst

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1. Reagents and chemicals

TiO_2 (P25) powder (particle size = 21 nm) and copper (II) nitrate hemi(pentahydrate) were procured from Sigma Aldrich (United States of America (USA)). 5,5-Dimethyl-1-pyrroline N-Oxide (DMPO) spin trapper was purchased from Tokyo Chemical Industry (TCI) Co. Ltd. Analytical grade reagents of target VOCs were purchased from Sigma-Aldrich (USA) and were used without further purification. Gas cylinders of air containing 21% O_2 and balance N_2 (99.999%), hydrogen (H_2, 99.999%), and nitrogen (N_2, 99.999%) were procured from Union Gas Co., Ltd. (Yongin, Republic of Korea).

Table S1. Information on the target VOCs.

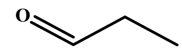
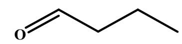
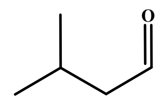
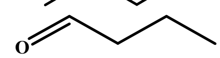
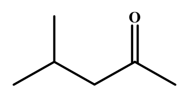
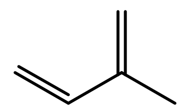
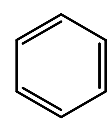
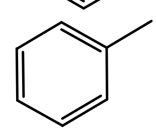
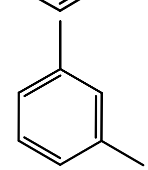
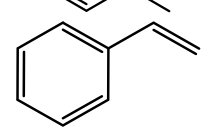
Order	Full name	Short name	Molecular weight (g·mol^{-1})	Chemical formula	Density (g·cm^{-3})	Boiling point (°C)	Chemical structure
(a) Aliphatic VOCs							
1	Propionaldehyde	PA	58.1	C_3H_6O	0.81	49	
2	Butyraldehyde	BA	72.1	C_4H_8O	0.81	74.8	
3	Isovaleraldehyde	IA	86	$C_5H_{10}O$	0.81	92	
4	Valeraldehyde	VA	86.1	$C_5H_{10}O$	0.81	103	
5	Methyl isobutyl ketone	MIBK	100.2	$C_6H_{12}O$	0.80	116	
6	Acrylonitrile	AN	53.1	C_3H_3N	0.81	77	
7	Isoprene	IP	68.1	C_5H_8	0.68	34.1	
(b) Aromatic VOCs							
8	Benzene	B	78.1	C_6H_6	0.81	80.1	
9	Toluene	T	92.1	C_7H_8	0.87	110.6	
10	m-Xylene	X	106	C_8H_{10}	0.86	139	
11	Styrene	S	104	C_8H_8	0.91	145	

Table S2. Method for the preparation of the liquid and gaseous (1 ppm each) primary standards mixture of 11 volatile organic compounds (VOCs).

Order	**VOC**	**Purity (%)**	**Density (g/mL)**	**Volume of each VOC in the LPS (µL)**	**Dilution factor**	**Conc. (%)**	**Conc. (ng/µL)**	**Gaseous working standard (GWS) concentration (2.5 µL LPS in a 50 L bag)**
1	PA	97.0	0.81	100.0	0.066	6.4	52,115	1.00
2	BA	99.0	0.81	122.4	0.081	8.0	64,701	1.00
3	IA	97.0	0.81	148.4	0.098	9.5	77,338	1.01
4	VA	97.0	0.81	149.2	0.099	9.6	77,287	1.00
5	MIBK	99.5	0.80	169.8	0.113	11.2	89,873	1.00
6	IP	99.0	0.68	136.8	0.091	9.0	61,175	1.01
7	B	99.9	0.87	121.0	0.080	8.0	70,090	1.00
8	AN	99.0	0.81	89.6	0.059	5.9	47,658	1.01
9	T	99.8	0.87	144.4	0.096	9.6	82,677	1.00
10	X	99.0	0.86	168.8	0.112	11.1	95,326	1.01
11	S	99.0	0.91	157.2	0.104	10.3	93,524	1.01

Table S3. Estimation of degradation rate constants of 11 VOCs over TiO_2 and Cu@TiO_2 photocatalysts.

Order	**VOC**	**Degradation rate constant (k = min^{-1})**	
		TiO_2	Cu@TiO_2
Aliphatic VOCs			
1	PA	ND#	ND#
2	BA	ND#	6.30E-03
3	IA	3.53E-04	2.01E-02
4	VA	7.23E-04	2.08E-02
5	MIBK	3.53E-03	1.31E-02
6	AN	1.38E-04	1.70E-03
7	IP	2.23E-04	1.80E-03
Aromatic VOCs			
8	B	9.00E-05	6.00E-04
9	T	2.06E-04	1.60E-03
10	X	5.83E-04	4.10E-03
11	S	1.68E-03	8.90E-03

ND# = not determined

Table S4. Details on the by-products obtained and corresponding fragments identified during the photocatalytic VOC degradation reaction.

Order	By-product	Retention time (min)	Fragments m/z	Similarity index (%)
1.	Acetone	4.17	58, 43	98
2.	Acetic acid	23.62	60, 45, 43	97
3.	Hexanediol	24.04	82, 71, 67	96
4.	2-Ethylhexanol	24.79	83, 70, 57, 43	97
5.	Propionic acid	26.06	74, 57, 45	96
6.	Benzaldehyde	26.22	106, 77, 51	95
7.	Butanoic acid	28.02	87, 60, 43	97
8.	Pentanoic acid	30.28	73, 60, 55, 41	96
9.	Phenol	35.61	94, 66, 39	96

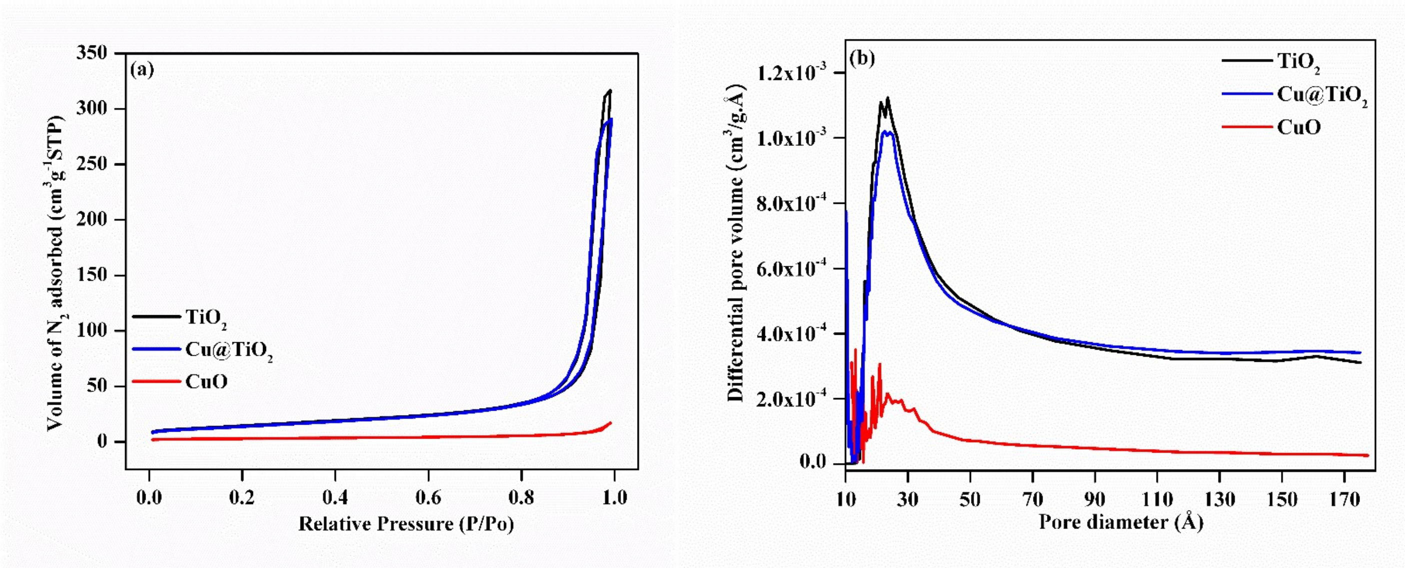


Fig. S1. Surface characterization of TiO_2, $Cu@TiO_2$, and CuO: (a) N_2 adsorption-desorption isotherms and (b) pore size distributions.

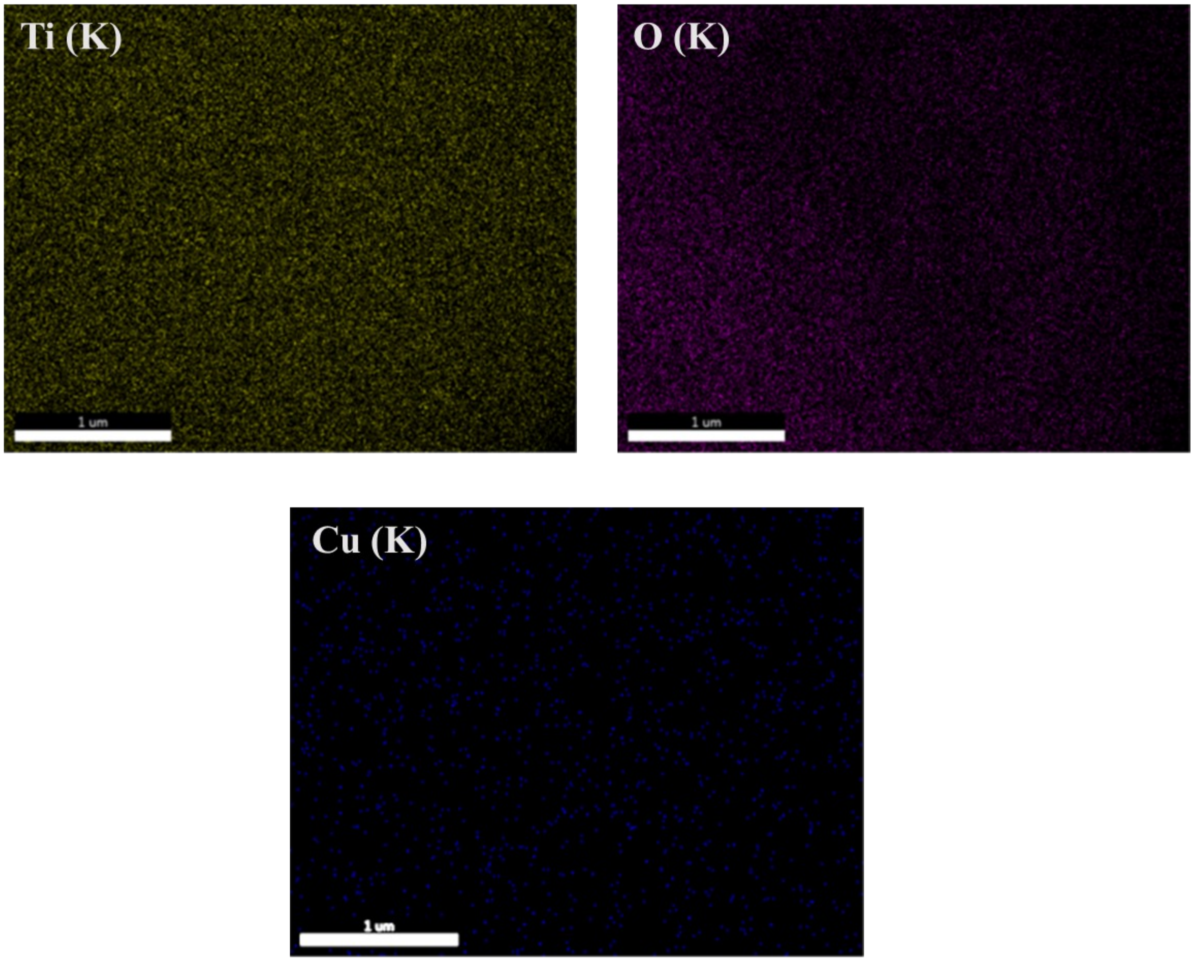


Fig. S2. Elemental maps showing distribution of Ti, O, and Cu elements in Cu@TiO_2.

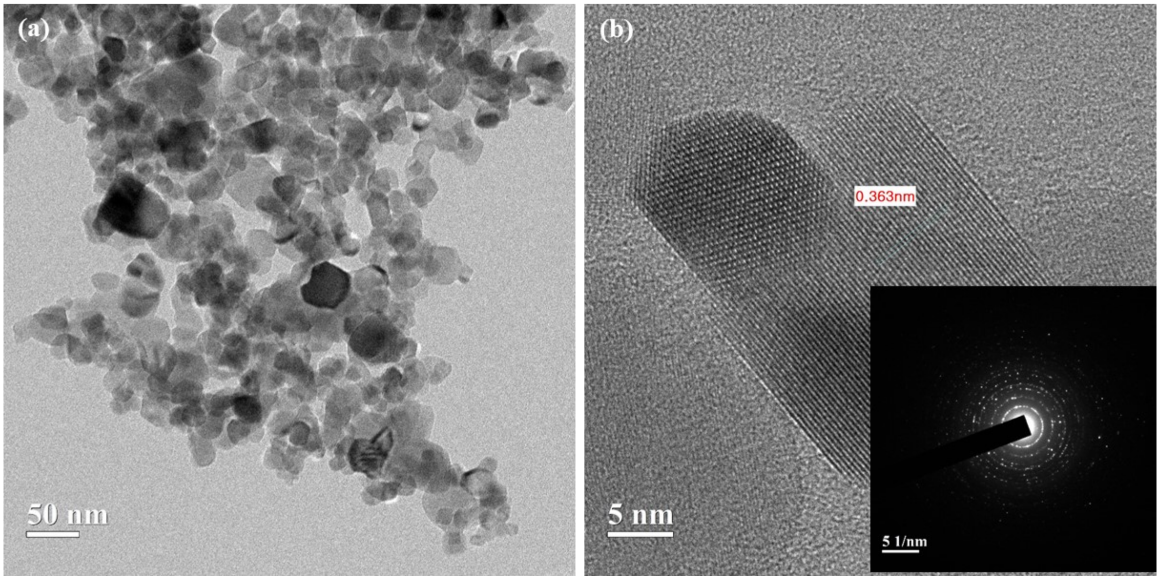


Fig. S3. Transmission electron microscope (TEM) image of titanium dioxide (TiO_2): (a) TEM image. (b) Magnified TEM image along with the corresponding selected area electron diffraction (SAED) pattern in the inset.

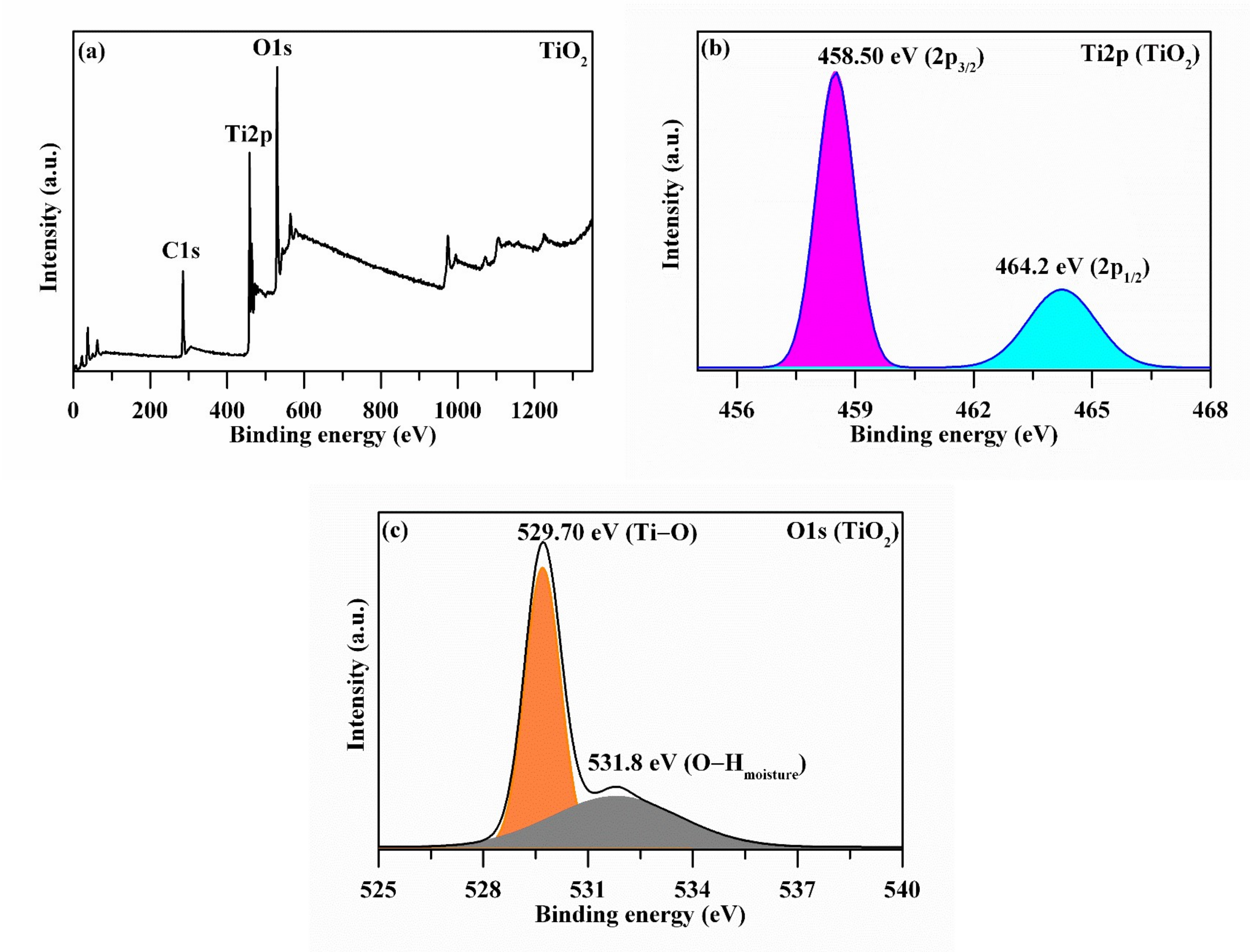


Fig. S4. XPS spectra of TiO_2: (a) full survey scan, (b) deconvoluted Ti 2p spectrum, and (c) deconvoluted O 1s spectrum.

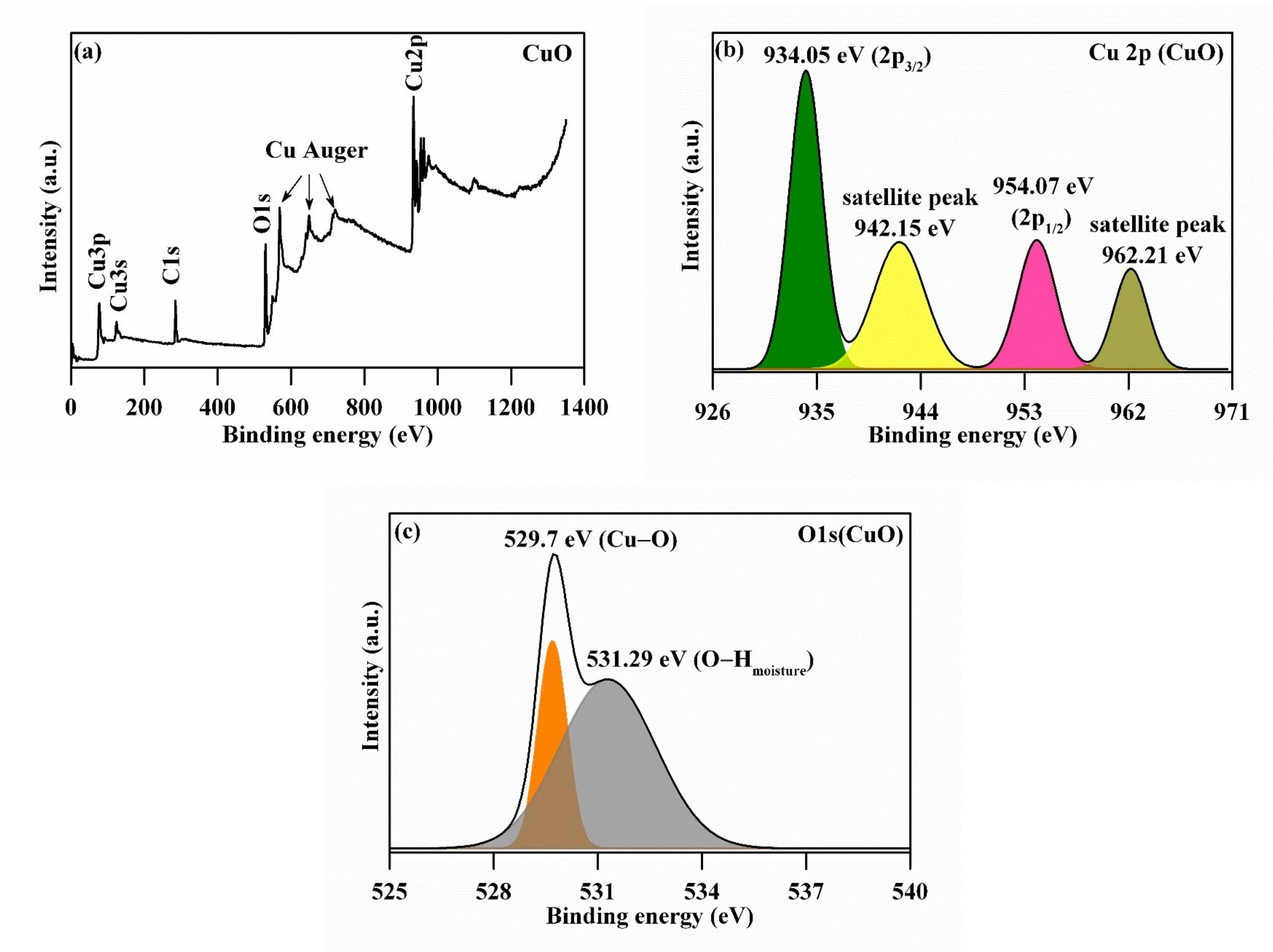


Fig. S5. XPS spectra of CuO: (a) full survey scan, (b) deconvoluted Cu 2p spectrum, and (c) deconvoluted O 1s spectrum.

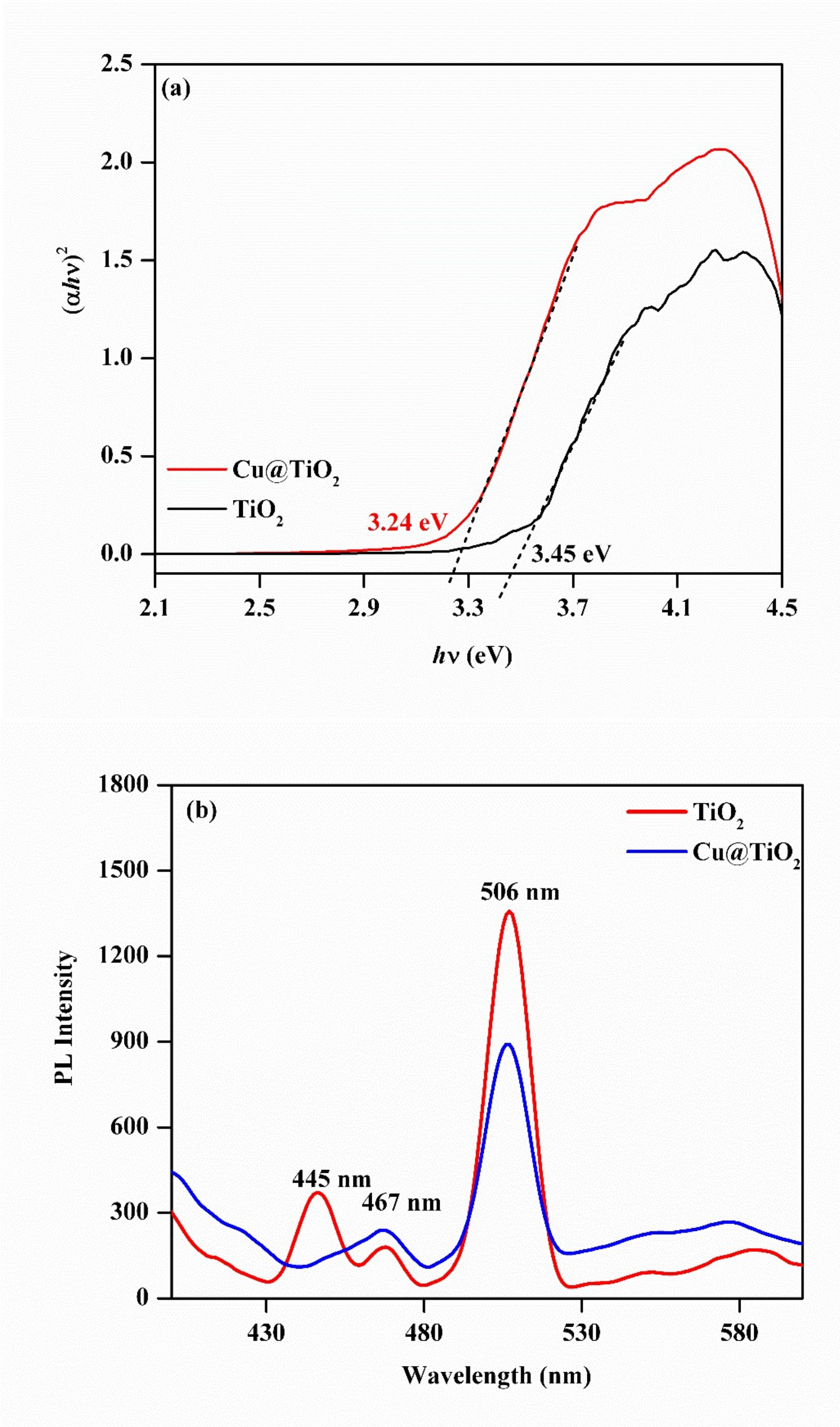


Fig. S6. Optical characterization of TiO_2 and Cu@TiO_2 by UV-Vis DRS and photoluminescence spectroscopy: (a) Tauc plot and (b) PL emission spectra.

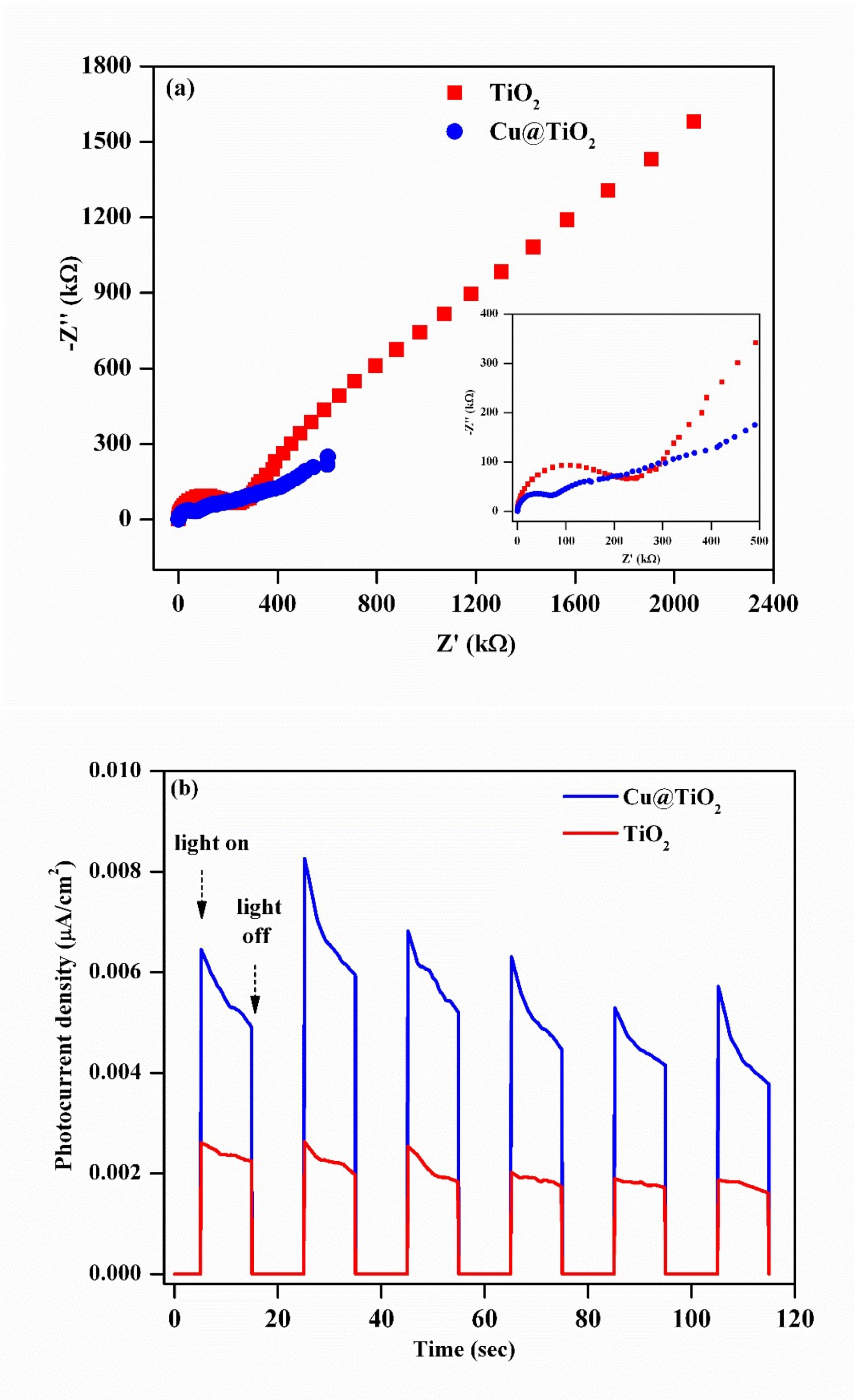


Fig. S7. Electrochemical characterization of TiO_2 and Cu@TiO_2: (a) electrochemical impedance and (b) photocurrent density measurements.

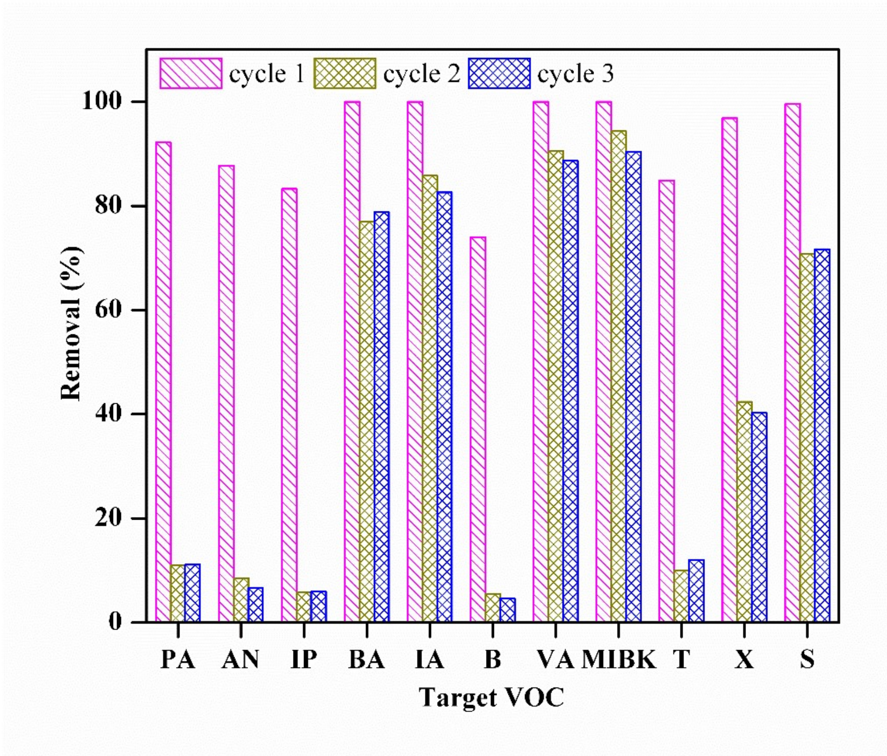


Fig S8. Reusability and recyclability of $Cu@TiO_2$ for photocatalytic VOCs removal.

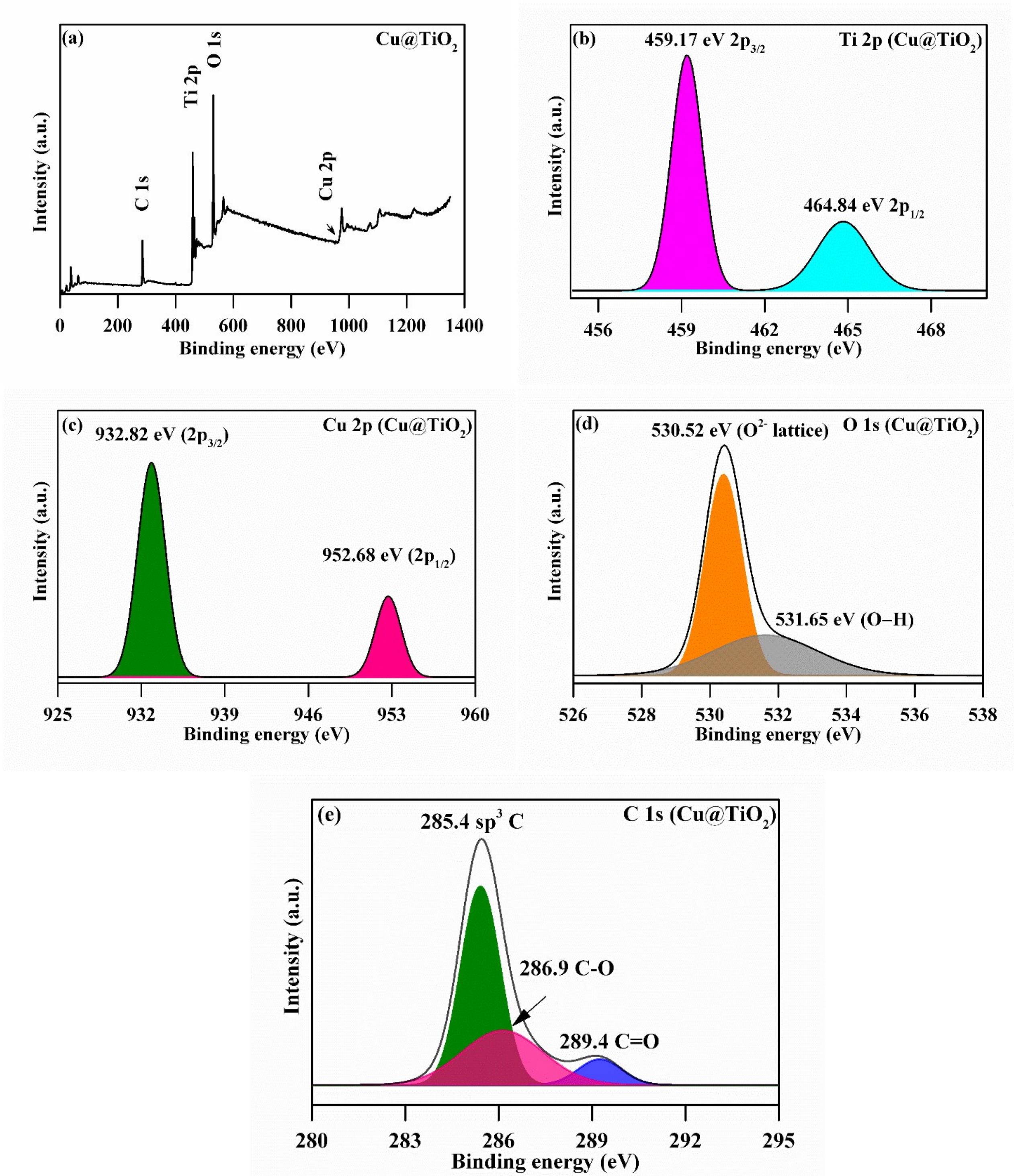


Fig. S9 XPS spectra of spent Cu@TiO_2 photocatalyst: (a) full survey scan, (b) deconvoluted Ti 2p spectrum, (c) deconvoluted Cu 2p spectrum, (d) deconvoluted O 1s spectrum, and (e) deconvoluted C1s spectrum.

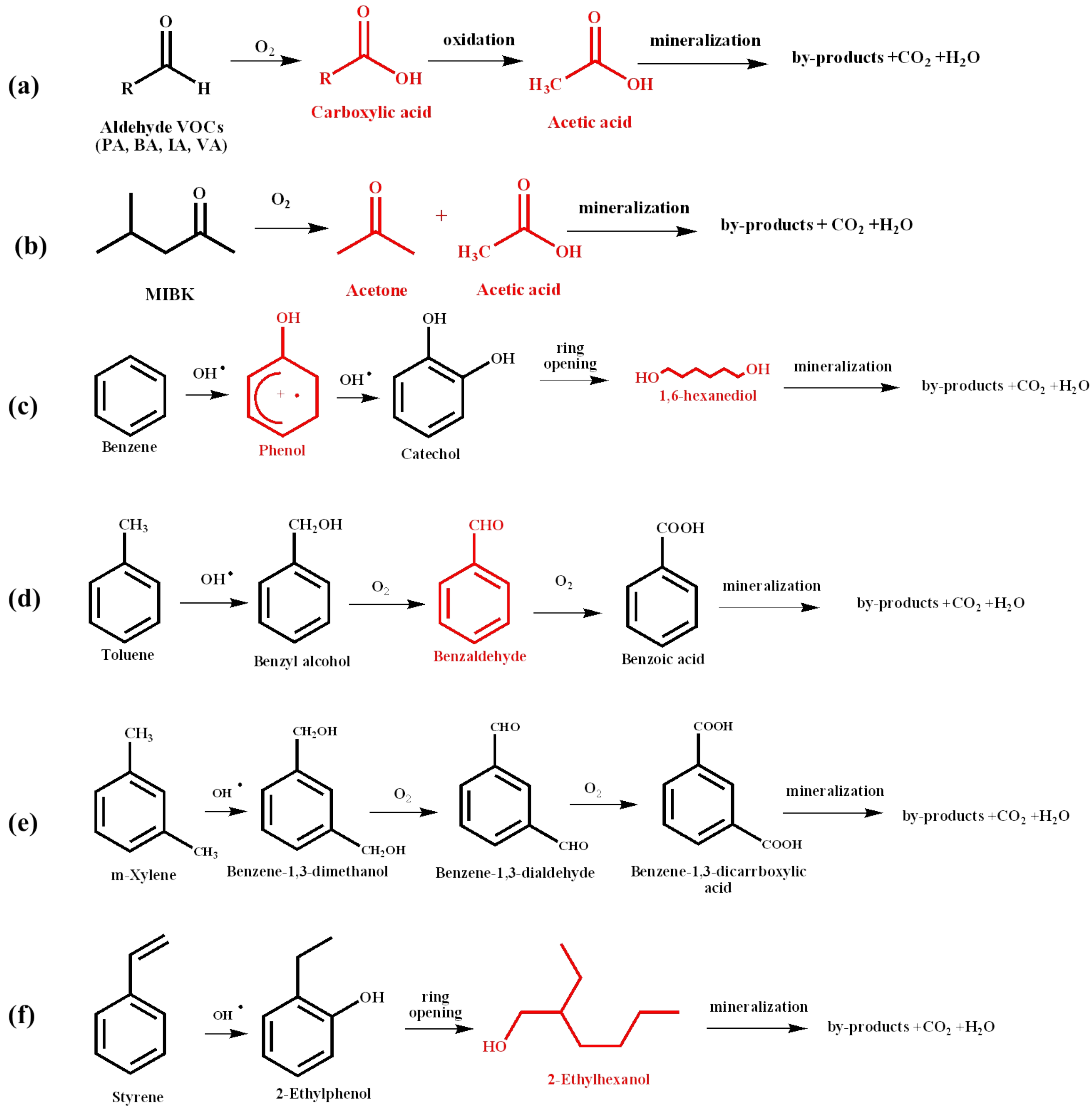


Fig. S10. Schematics for the photocatalytic degradation pathways proposed for diverse aliphatic and aromatic VOCs based on identified intermediates. The experimentally identified by-products are shown in red.