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Supplementary Materials

Novel photocatalytic NH_3 synthesis by NO_3^- reduction over $CuAg/TiO_2$

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Table S1. Summary of TiO_2 samples.

Entry	Catalyst	Loading (mg)	
		Cu	Ag
1	TiO_2	0	0
2	Cu/TiO_2	3	0
3	Ag/TiO_2	0	3
4	$Cu_{0.1}Ag/TiO_2$	0.167	2.833
5	$Cu_{0.3}Ag/TiO_2$	0.451	2.549
6	$Cu_{0.5}Ag/TiO_2$	0.683	2.317
7	$Cu_{0.7}Ag/TiO_2$	0.876	2.124
8	$Cu_{0.9}Ag/TiO_2$	1.039	1.961
9	$CuAg/TiO_2$	1.112	1.888
10	$Cu_{1.5}Ag/TiO_2$	1.407	1.593

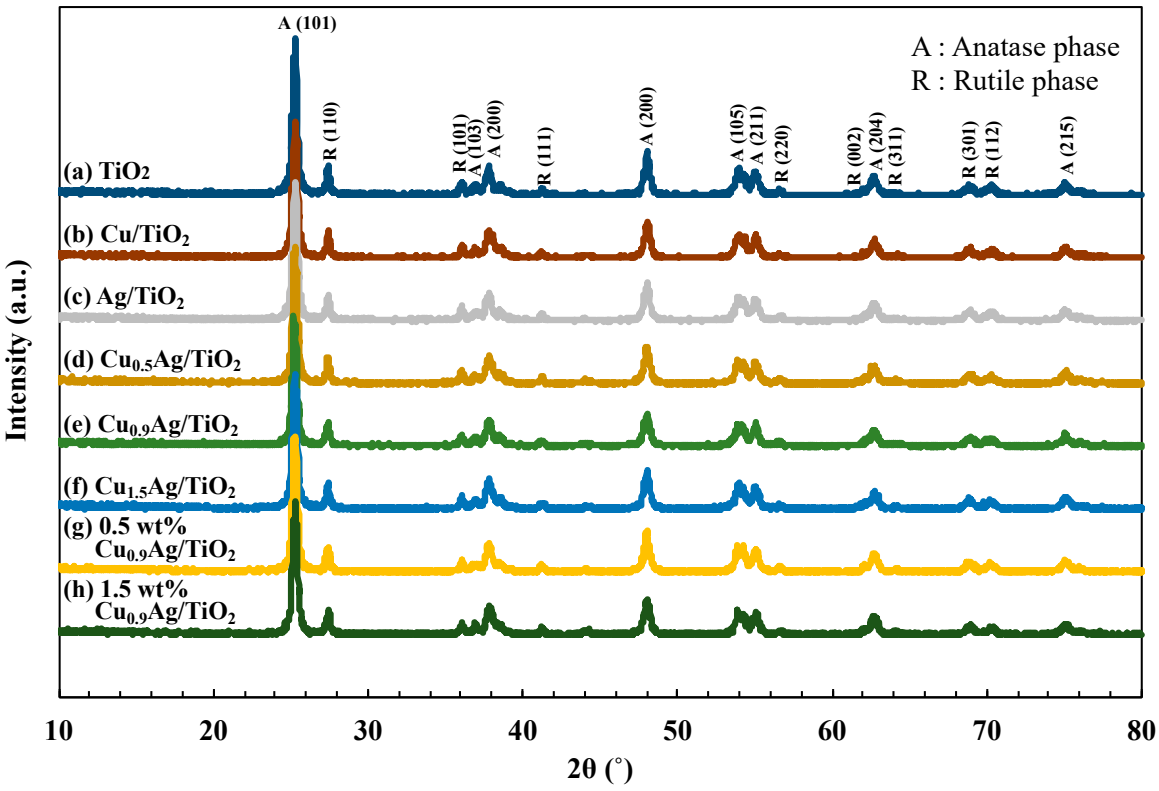

Figure S1. XRD spectra of (**a**) TiO_2, (**b**) Cu/TiO_2, (**c**) Ag/TiO_2, (**d**) $Cu_{0.5}Ag/TiO_2$, (**e**) $Cu_{0.9}Ag/TiO_2$, (**f**) $Cu_{1.5}Ag/TiO_2$, (**g**) 0.5 wt% $Cu_{0.9}Ag/TiO_2$, and (**h**) 1.5 wt% $Cu_{0.9}Ag/TiO_2$.

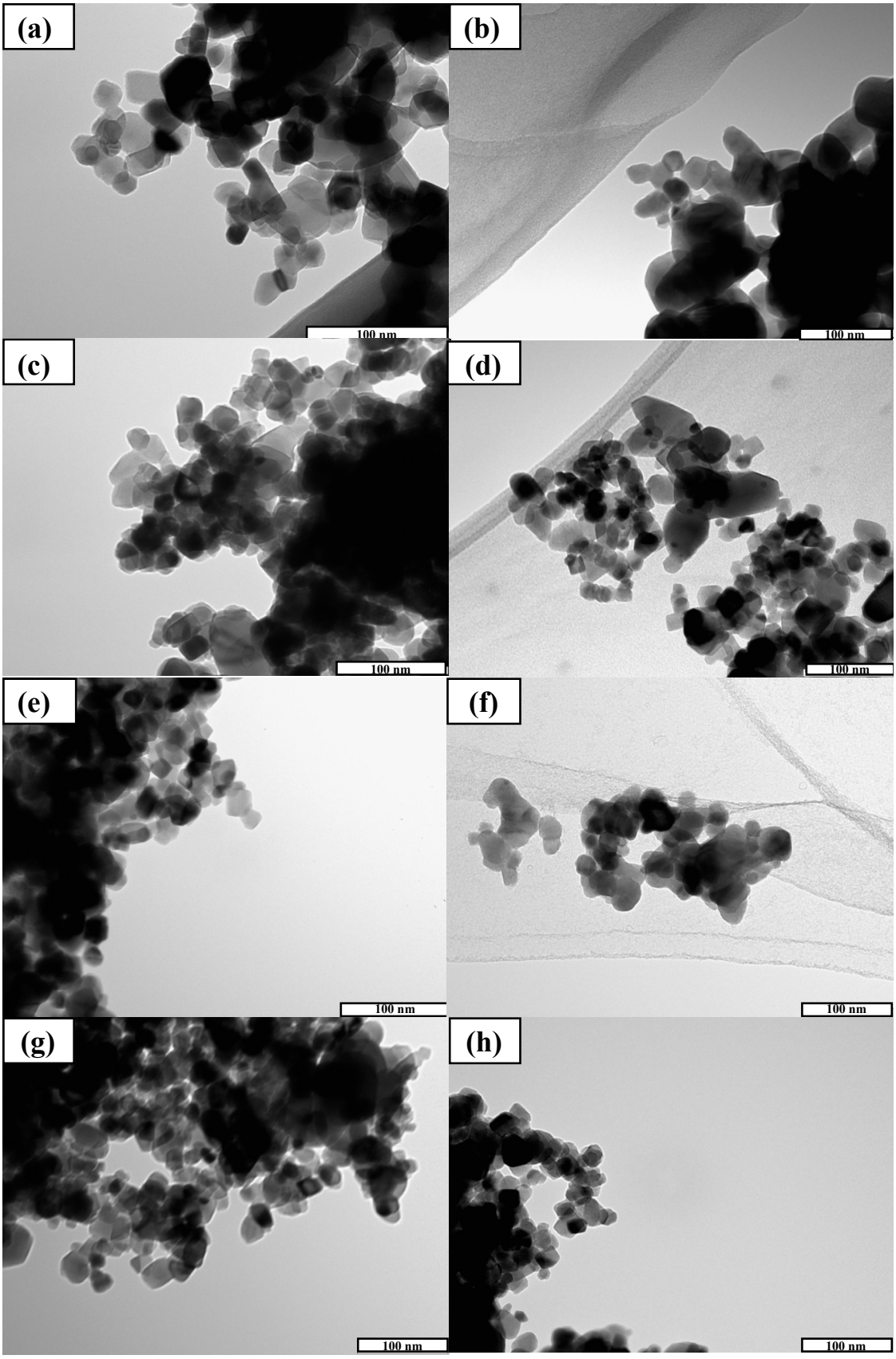

Figure S2. TEM images of (**a**) TiO_2, (**b**) Cu/TiO_2, (**c**) Ag/TiO_2, (**d**) $Cu_{0.5}Ag/TiO_2$, (**e**) $Cu_{0.9}Ag/TiO_2$, (**f**) $Cu_{1.5}Ag/TiO_2$, (**g**) 0.5 wt% $Cu_{0.9}Ag/TiO_2$, and (**h**) 1.5 wt% $Cu_{0.9}Ag/TiO_2$.

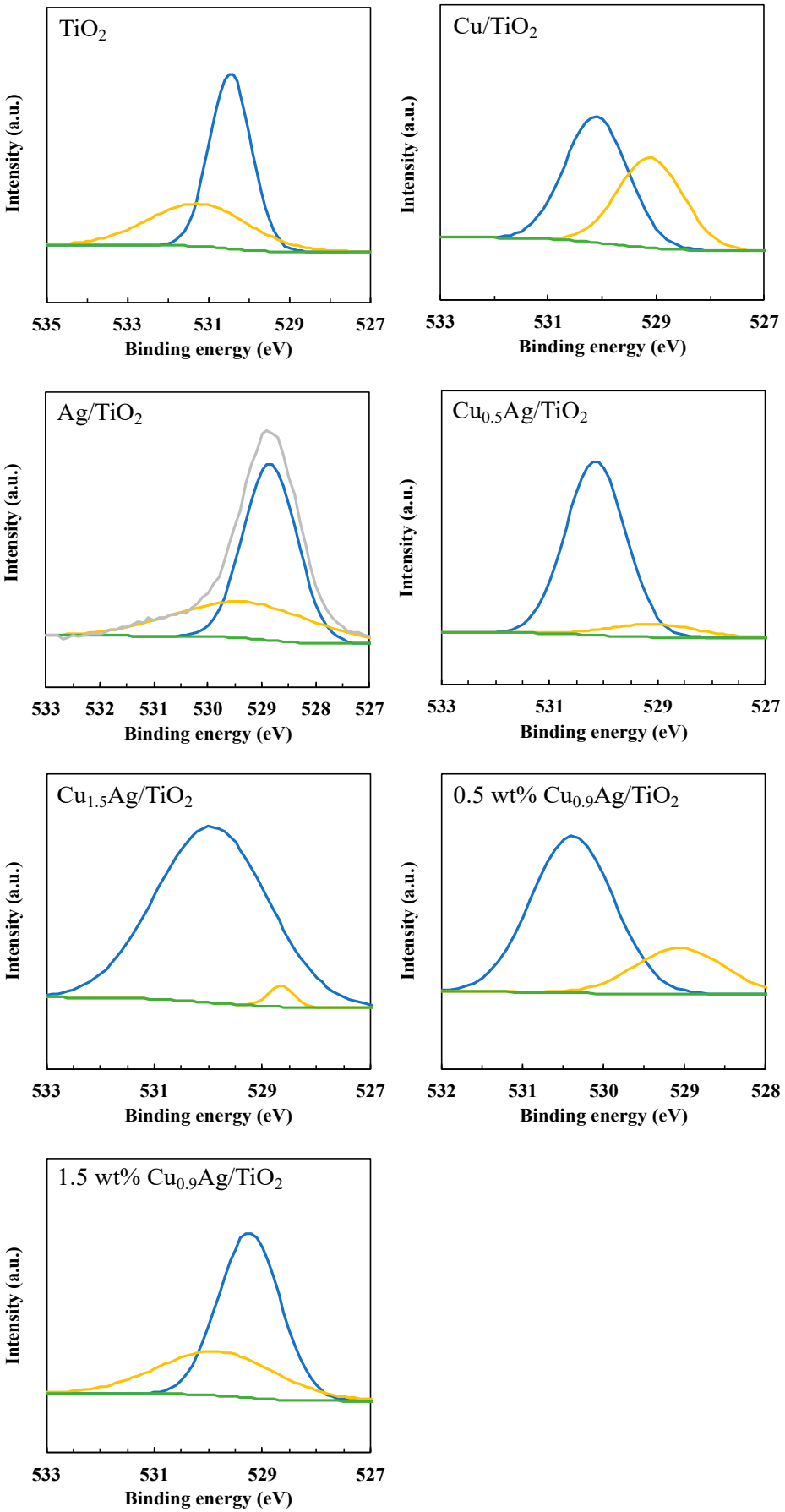

Figure S3. O 1s core level spectra in TiO_2 samples.

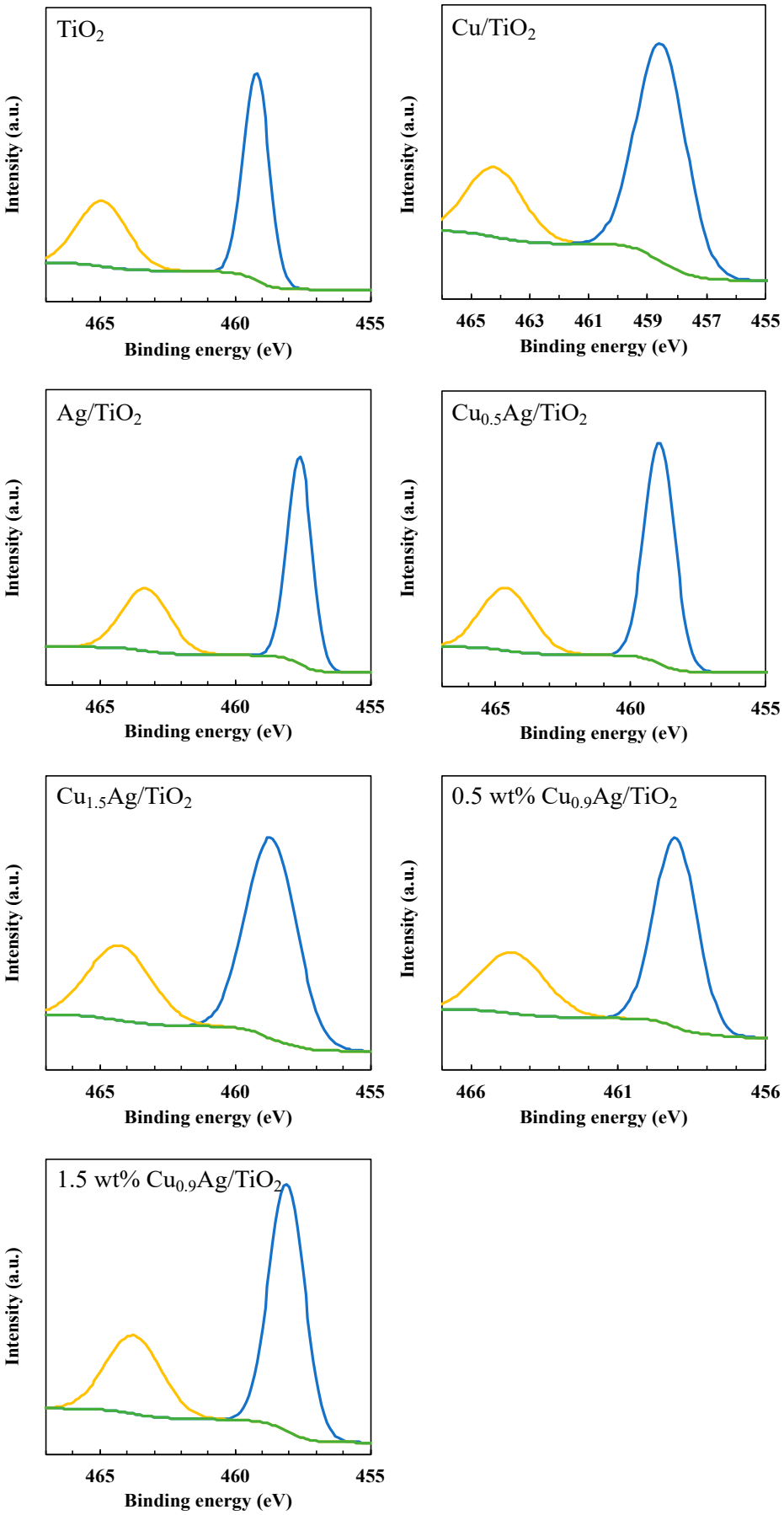

Figure S4. Ti 2p core level spectra in TiO_2 samples.

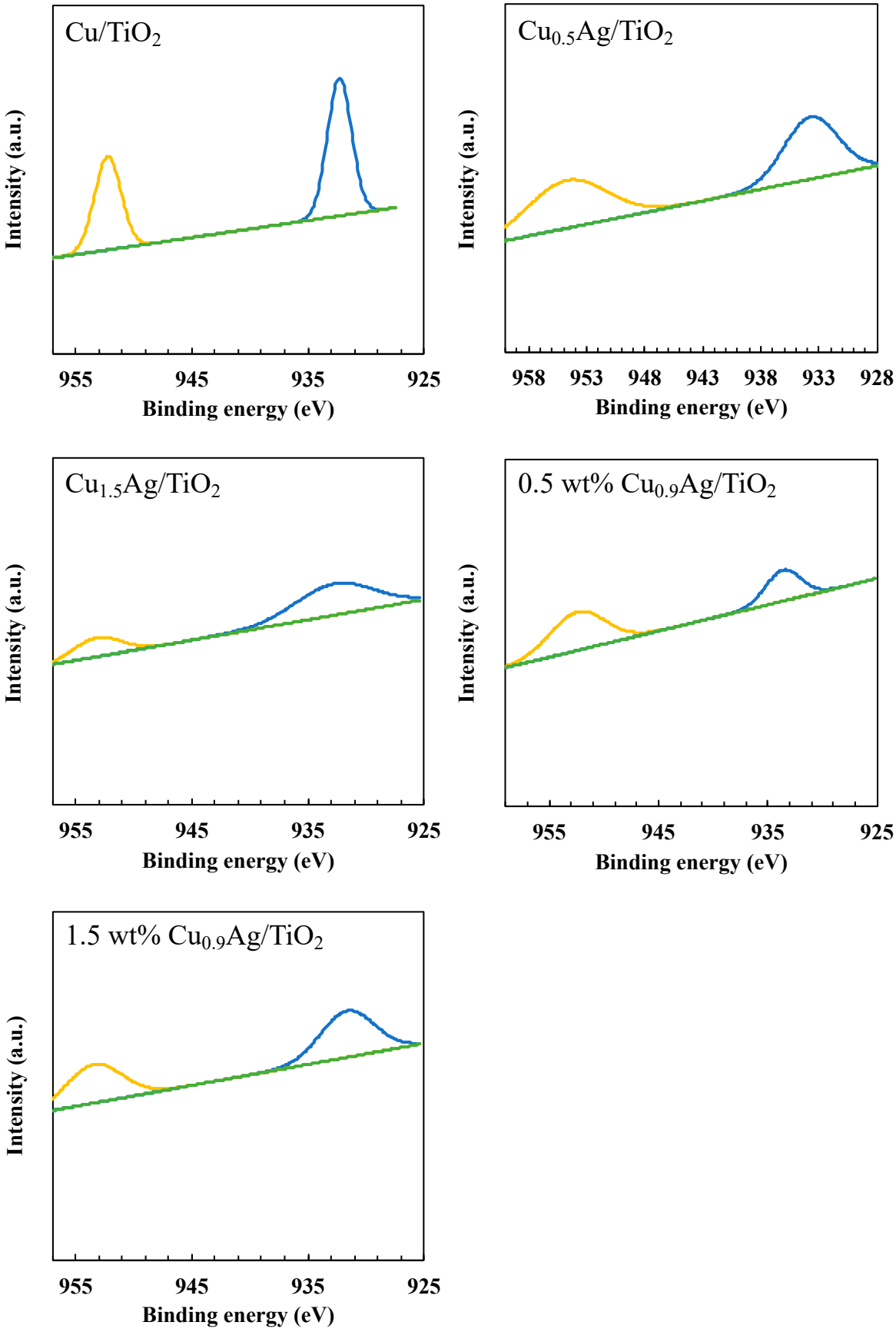

Figure S5. Cu 2p core level spectra in TiO_2 samples.

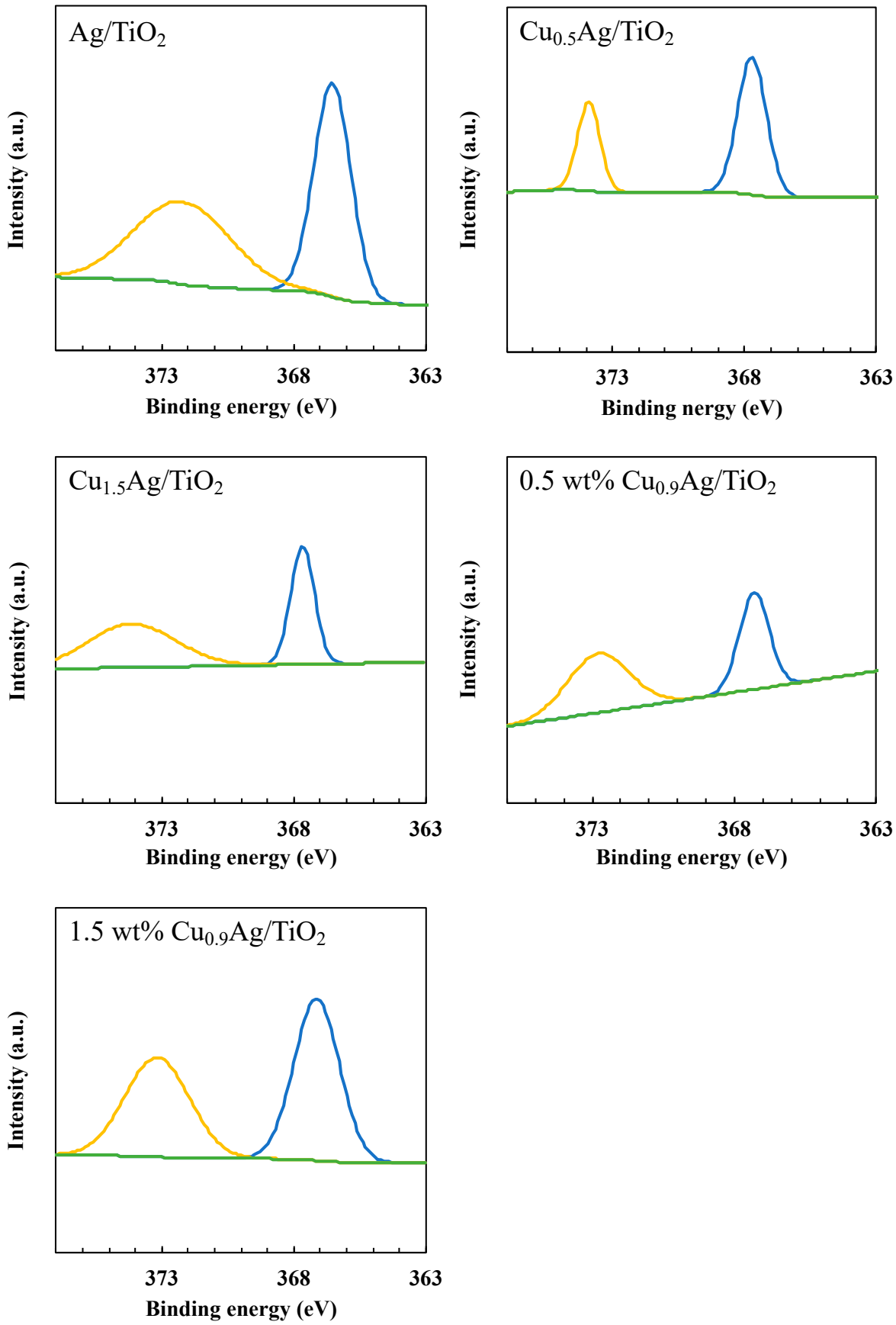

Figure S6. Ag 3d core level spectra in TiO_2 samples.

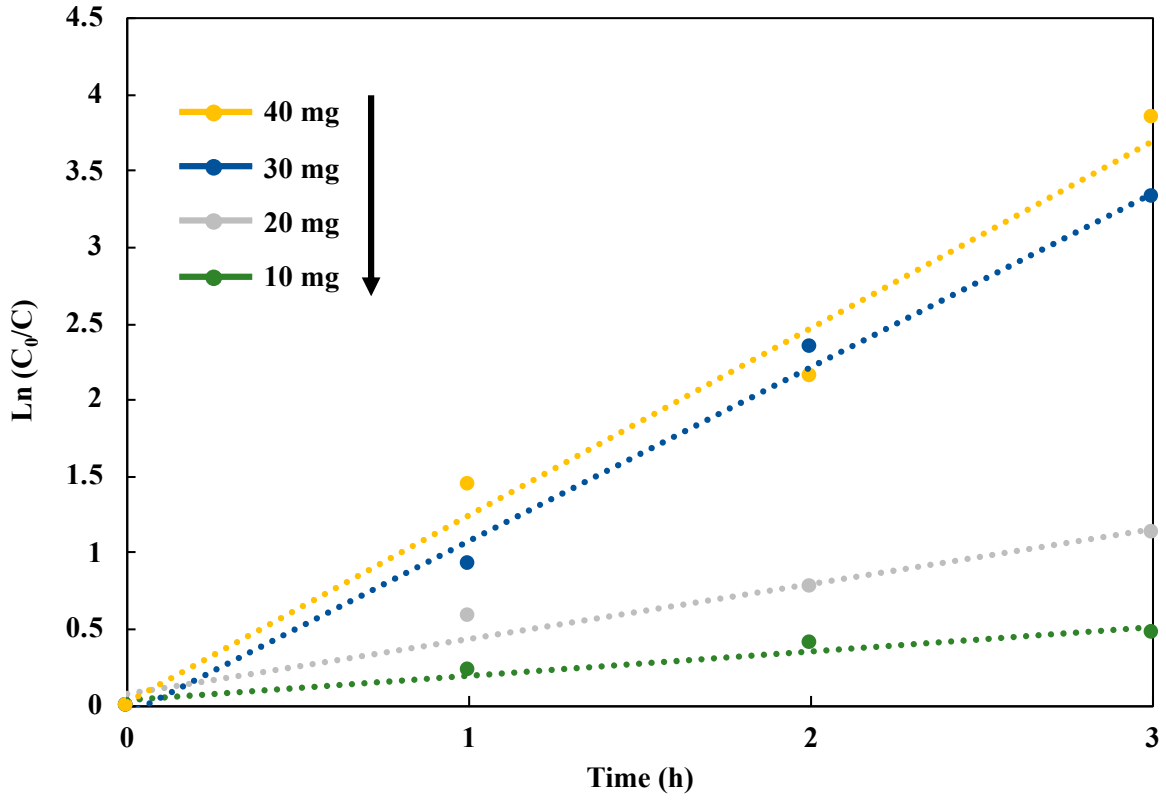

Figure S7. Reduction rate in NO_3^- reduction in 45 mL of 50 ppm NO_3^- aqueous solution including 10 vol% CH_3OH under UV irradiation.

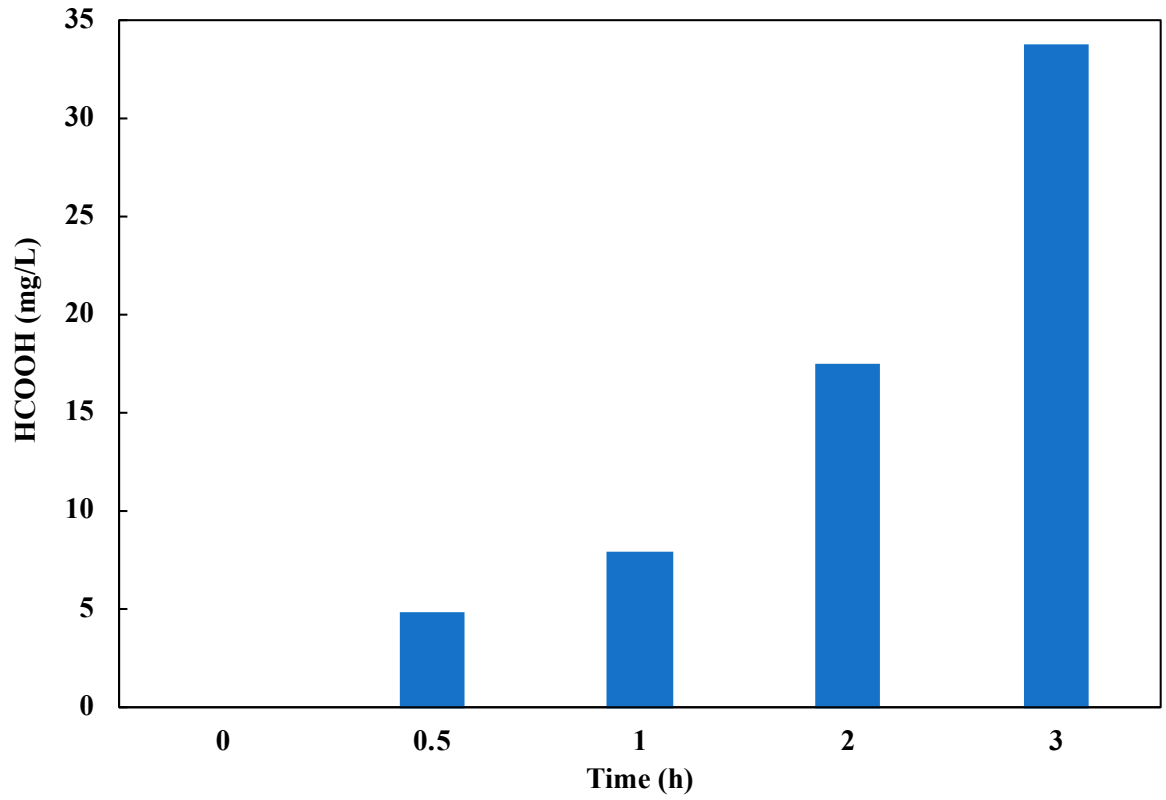

Figure S8. Oxidation of methanol to HCOOH during NO_3^- reduction under UV irradiation for 3 hours.

Table S2. Comparison of photocatalytic activity with other catalysts.

Catalyst	Amount (mg)	Concentration (ppm)	Time (h)	NO_3^- conversion (%)	NH_3 (NH_4^+) selectivity (%)	Reference
$CuPd/TiO_2$	100	145	3	99	78	[1]
Aldrich anatase	100	62	24	95	20	[2]
Aldrich rutile	100	62	24	99	37	[2]
TiO_2 P25	100	62	24	99	27	[2]
$Cu_{0.9}Ag/TiO_2$	30	50	3	96	85	This work

Reference

1. Yamaguchi, M.; Abe, R.; Tsukuda, T.; Kato, K.; Takata, M. Highly Selective Ammonia Synthesis from Nitrate with Photocatalytically Generated Hydrogen on CuPd/TiO_2, *J. Am. Chem. Soc.*, **2011**, *133*, 1150–1152.
2. Hirakawa, H.; Hashimoto, M.; Shiraishi, Y.; Hirai, T. Selective Nitrate-to-Ammonia Transformation on Surface Defects of Titanium Dioxide Photocatalysts, *ACS Catal.*, **2017**, *7*, 3713–3720.