

(Electronic Supplementary Information File)

Glycerol Valorization over ZrO₂-Supported Copper Nano-particles Catalysts

Prepared by Chemical Reduction Method

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Table S1. Compounds used in the synthesis of copper nanoparticles (Cu NPs)

Compound	Nomenclature	Supplier	Quantity
Copper nitrate trihydrate	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	99%, Sigma Aldrich	0.5 M
Glycerol	$\text{C}_3\text{H}_8\text{O}_3$	≥ 99.5 , Sigma Aldrich	5 mL
Buffer pH = 4	-	Merck	10 mL
Buffer pH = 7	-	Merck	10 mL
Buffer pH = 9	-	Merck	10 mL
Hydrazine monohydrate	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	98%, Merck	6 mL

Table S2. Compounds used in the synthesis of copper nanoparticles (Cu NPs) in the presence of ZrO_2 .

Compound	Nomenclature	Supplier	Quantity
Copper nitrate trihydrate	$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$	99%, Sigma Aldrich	285 mg
Zirconium Oxide	ZrO_2	Saint-Gobain	2 g
Glycerol	$\text{C}_3\text{H}_8\text{O}_3$	Sigma Aldrich	5 mL
Buffer pH 4	-	Merck	10 mL
Buffer pH 7	-	Merck	10 mL
Buffer pH 9	-	Merck	10 mL
Hydrazine monohydrate	$\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$	98%, Merck	6 mL

Table S3. Absorption maxima band of Cu NPs synthesized at pH = 4, 7 and 9

Cu NPs synthesized at:	Maxima band	Deconvoluted wavelength (nm)
pH = 4	(2) ^a	293
pH = 7	(3) ^a	280
pH = 9	(2) ^a	264

^a depicted in Fig. S1

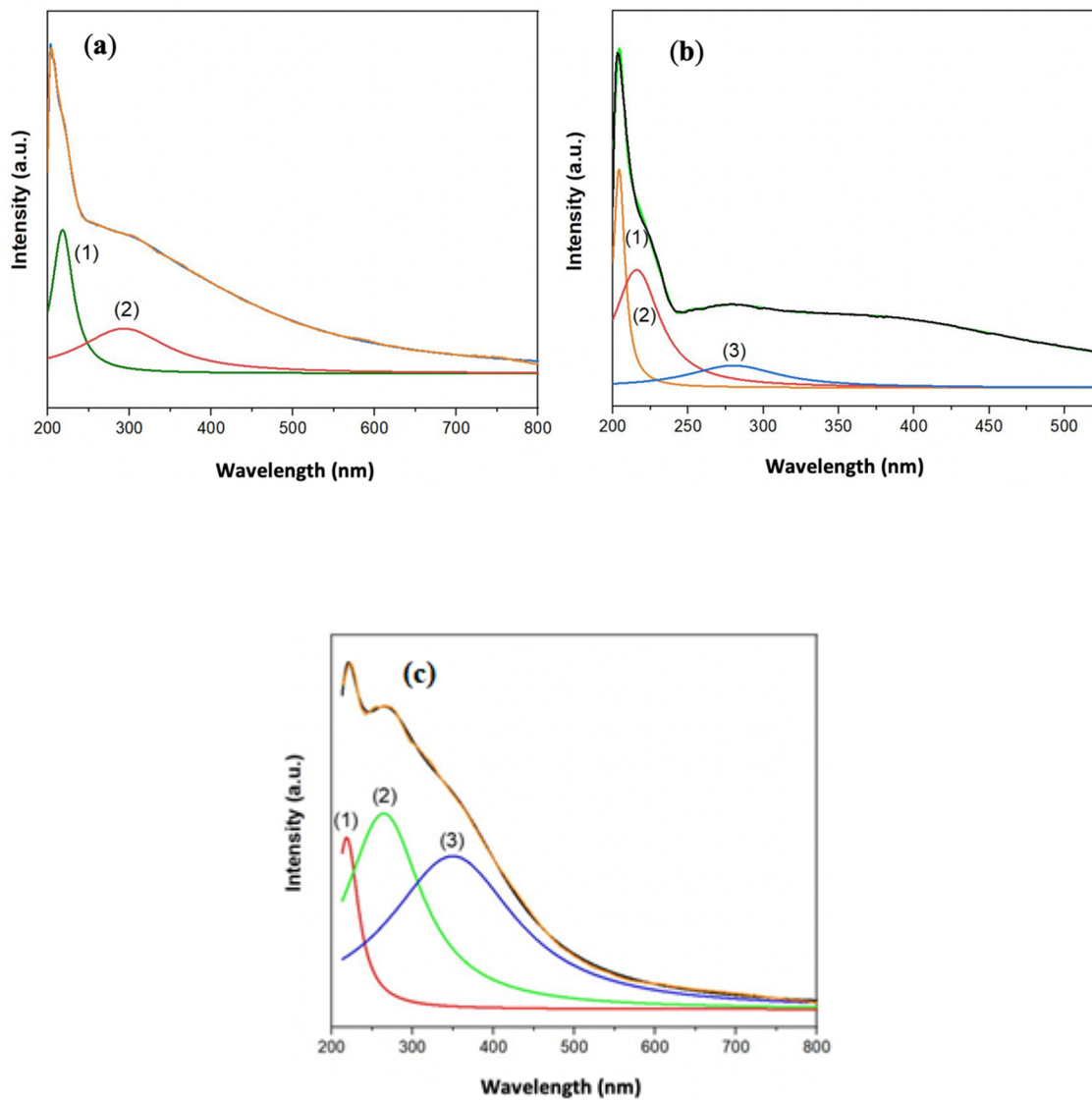


Figure S1. UV-vis spectra of (a) Cu NPs pH=4 and (b) Cu NPs pH=7 collected in ethanol at 22°C. (a) (1) 218 nm, (2) 293 nm; (b) (1) 204 nm, (2) 216 nm and (3) 280 nm. (c) (1) 218 nm, (2) 264 nm, and (3) 328 nm.

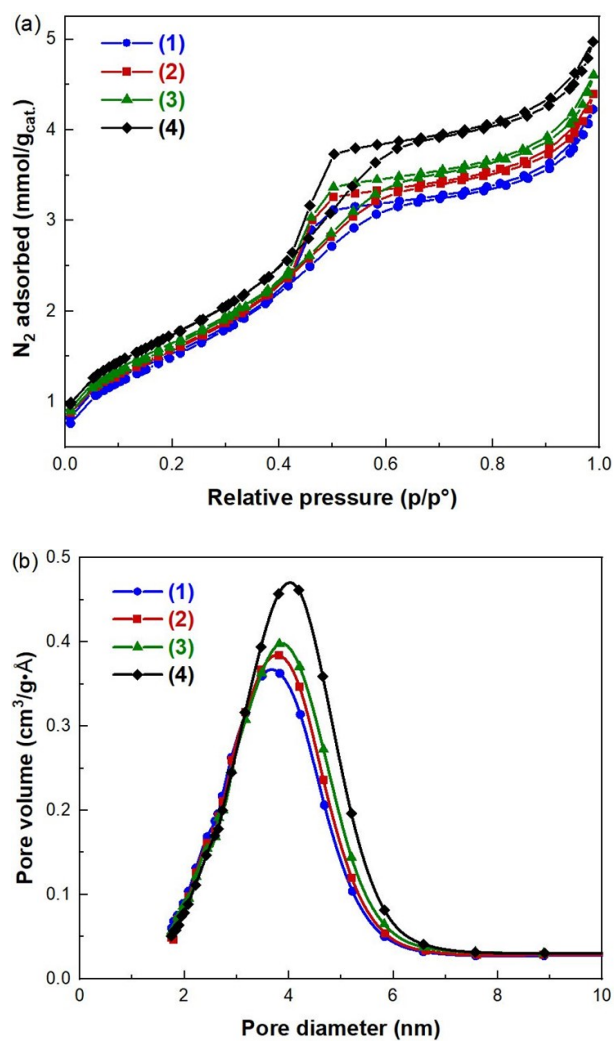


Figure S2. (a) N₂ adsorption desorption isotherms at 77 K. (b) Pore size distribution. (1) Cu NPs/ZrO₂ pH = 4, (2) Cu NPs/ZrO₂ pH = 7, (3) Cu NPs/ZrO₂ pH = 9, and (4) ZrO₂.

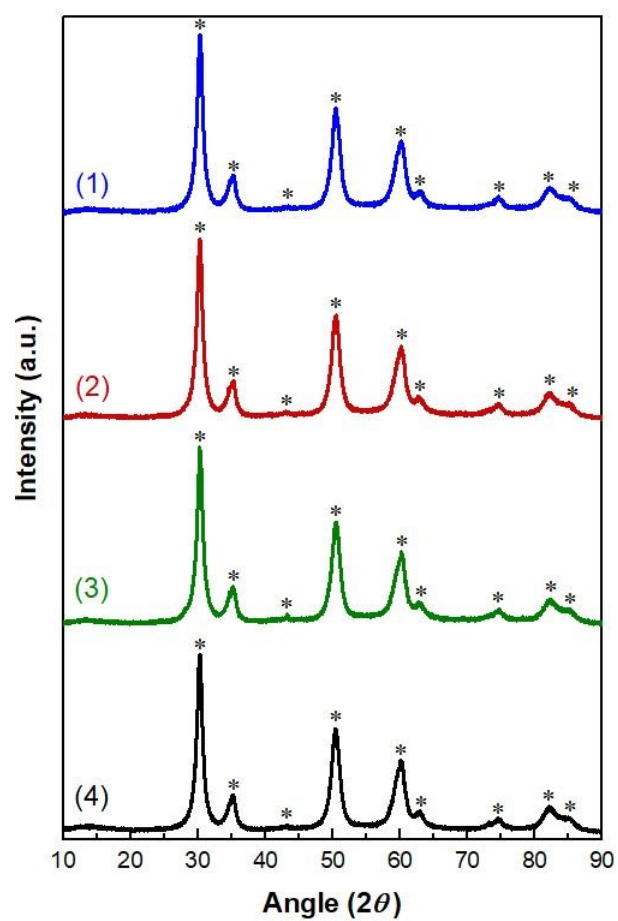


Figure S3. XRD pattern of ZrO_2 and copper NPs catalysts. (1) Cu NPs/ ZrO_2 pH = 4, (2) Cu NPs/ ZrO_2 pH = 7, (3) Cu NPs/ ZrO_2 pH = 9, and (4) ZrO_2 . * tetragonal phase of ZrO_2 .

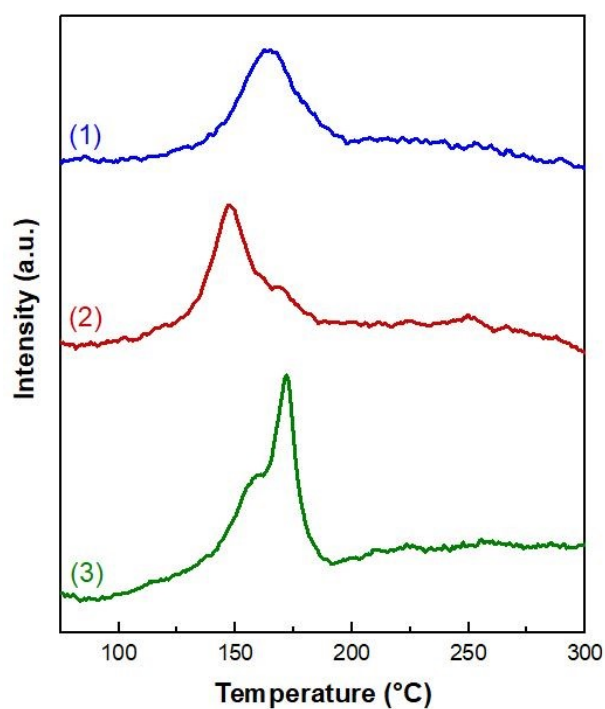


Figure S4. TPR profiles after the N_2O adsorptive decomposition on each catalyst. (1) Cu NPs/ ZrO_2 pH = 4, (2) Cu NPs/ ZrO_2 pH = 7, (3) Cu NPs/ ZrO_2 pH = 9.

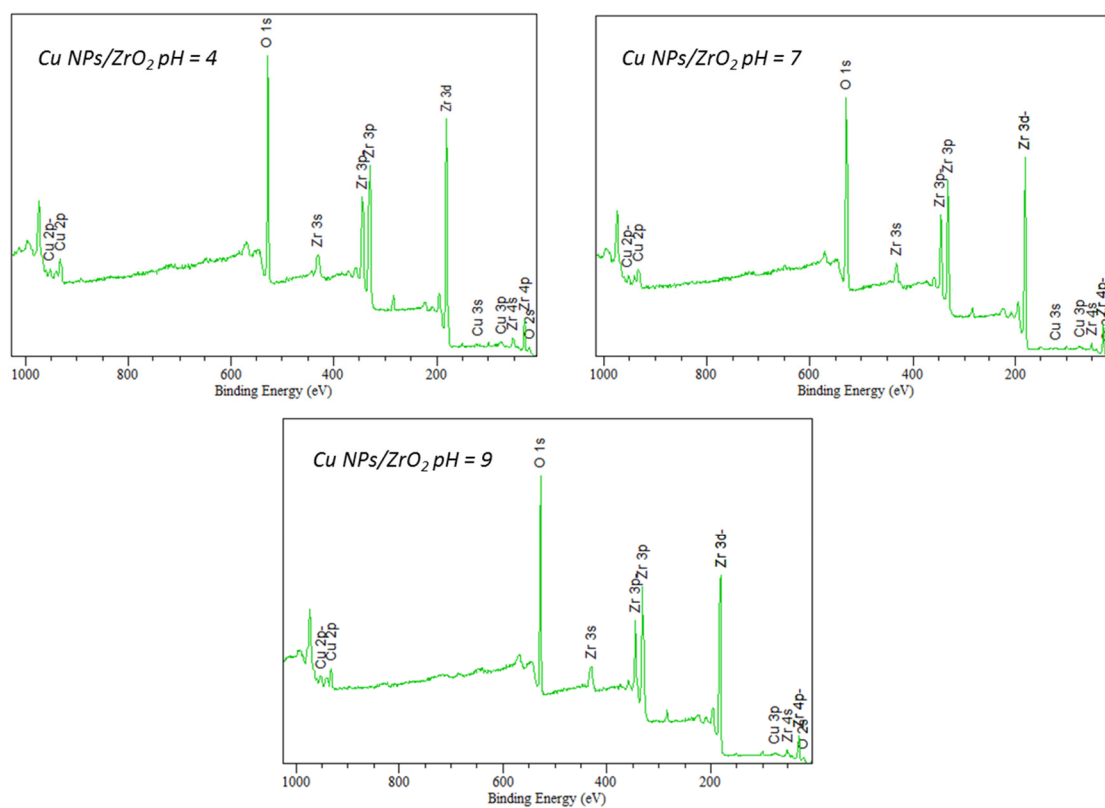


Figure S5. XPS survey spectra of Cu NPs/ ZrO_2 catalysts.

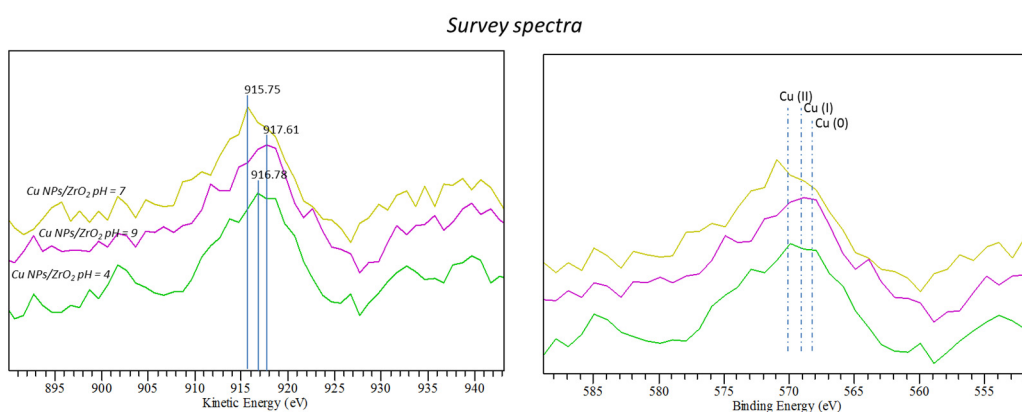


Figure S6. XPS survey spectra magnification of Cu NPs/ZrO₂ catalysts in the Cu LMM region.

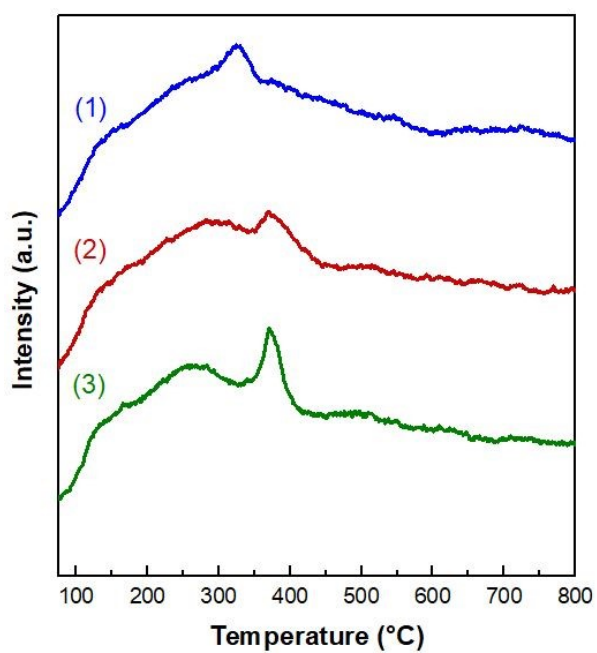


Figure S7. TPD profile of pre-adsorbed NH₃ on the Cu NPs/ZrO₂ catalysts. (1) Cu NPs/ZrO₂ pH = 4, (2) Cu NPs/ZrO₂ pH = 7, (3) Cu NPs/ZrO₂ pH = 9.

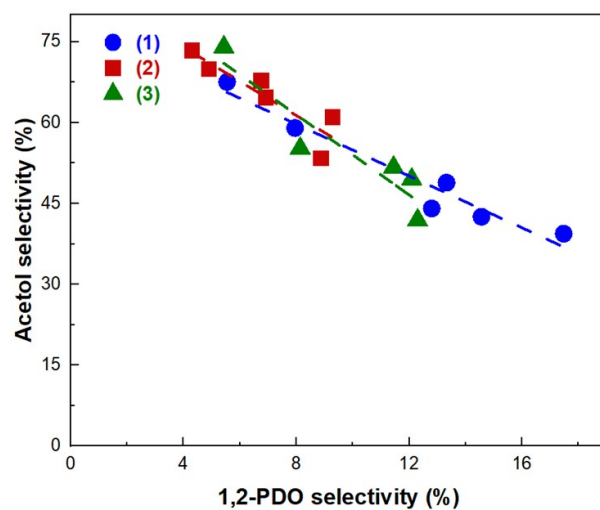


Figure S8. Selectivity to acetol versus selectivity to 1,2-PDO during the reaction. (1) Cu NPs/ZrO₂ pH = 4, (2) Cu NPs/ZrO₂ pH = 7, (3) Cu NPs/ZrO₂ pH = 9.

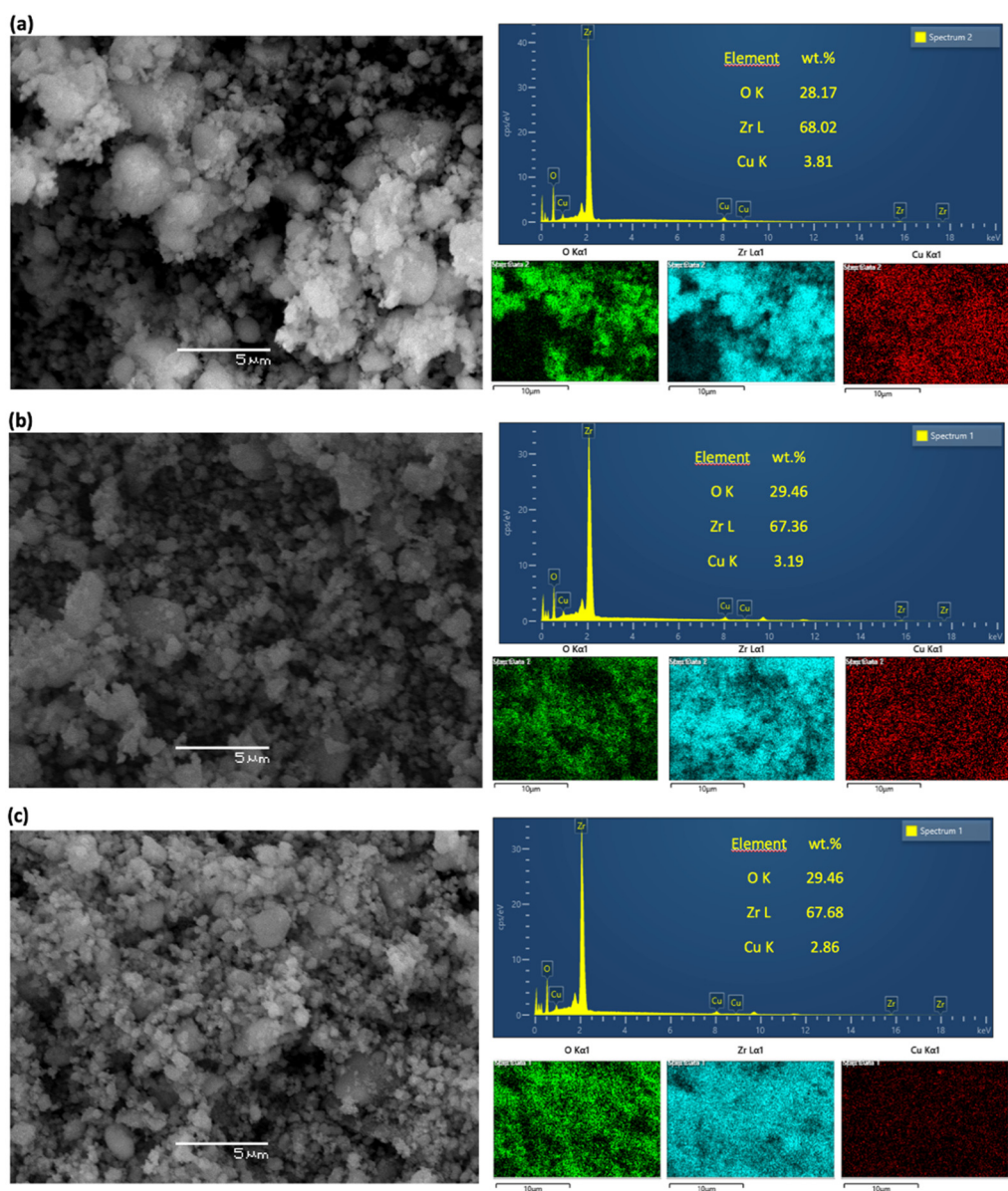


Figure S9. SEM-EDS image (left) and elemental mapping (right) of the copper nanoparticles catalysts. (a) Cu NPs/ZrO₂ pH = 4, (b) Cu NPs/ZrO₂ pH = 7, (c) Cu NPs/ZrO₂ pH = 9.

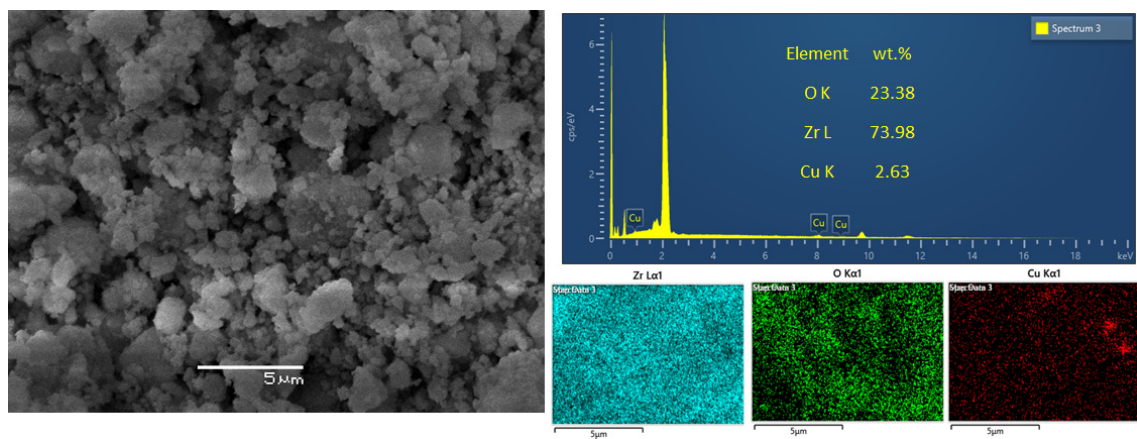


Figure S10 SEM-EDS image (left) and elemental mapping (right) of the copper nanoparticles/ZrO₂ catalyst: Cu NPs/ZrO₂ pH = 7 after glycerol conversion.