A Comparative Study of Medium-Entropy Oxide and Metal Oxide Nanoparticles on Graphene Oxide for Benzyl Alcohol Oxidation in Solvent-Free Conditions

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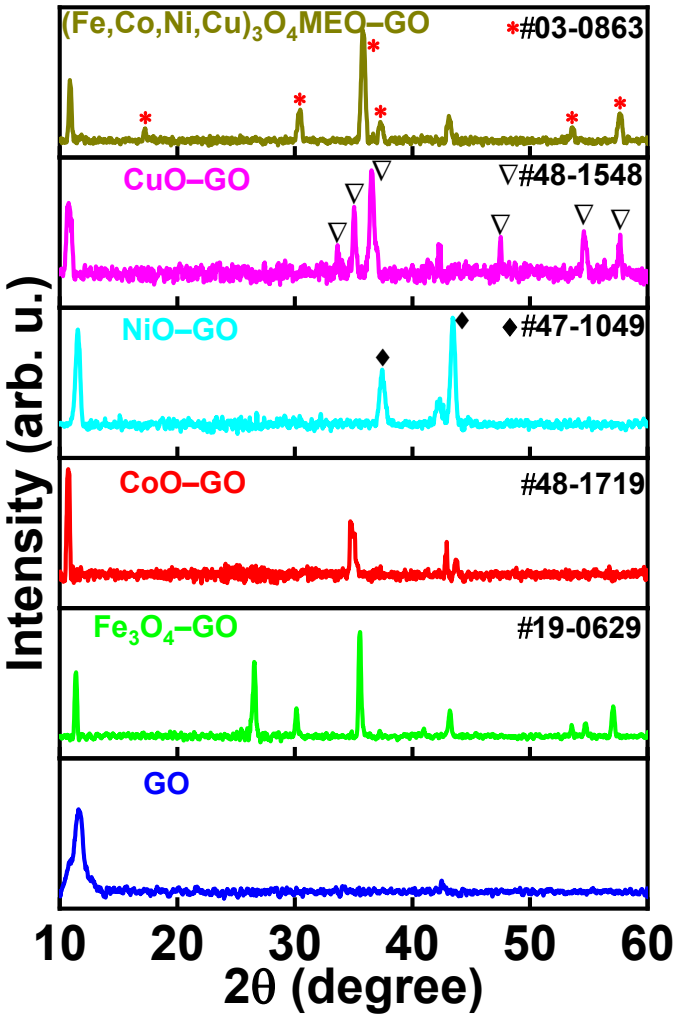

Figure S1. a) XRD patterns of GO, Fe_3O_4–GO, CoO–GO, NiO–GO, CuO–GO, and $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO with JCPDS No.

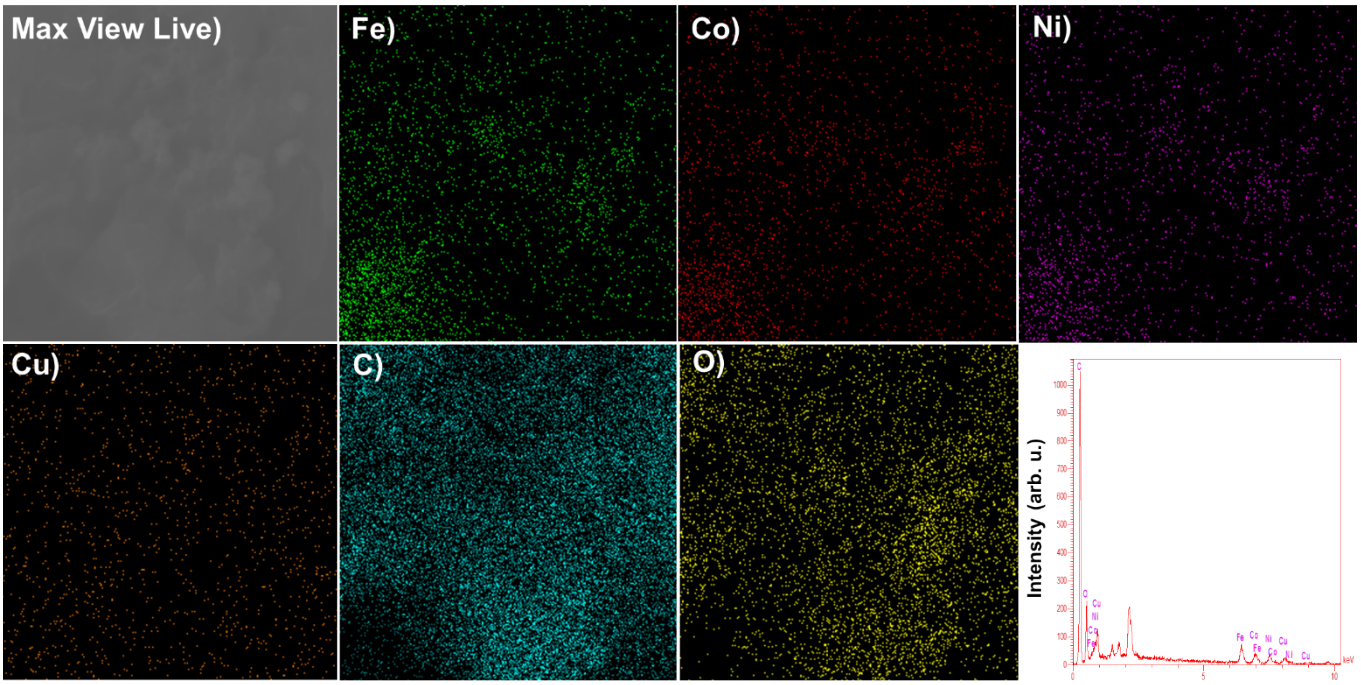

Figure S2. EDX mapping and corresponding elemental mapping of EDX patterns for the $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO nanocomposite.

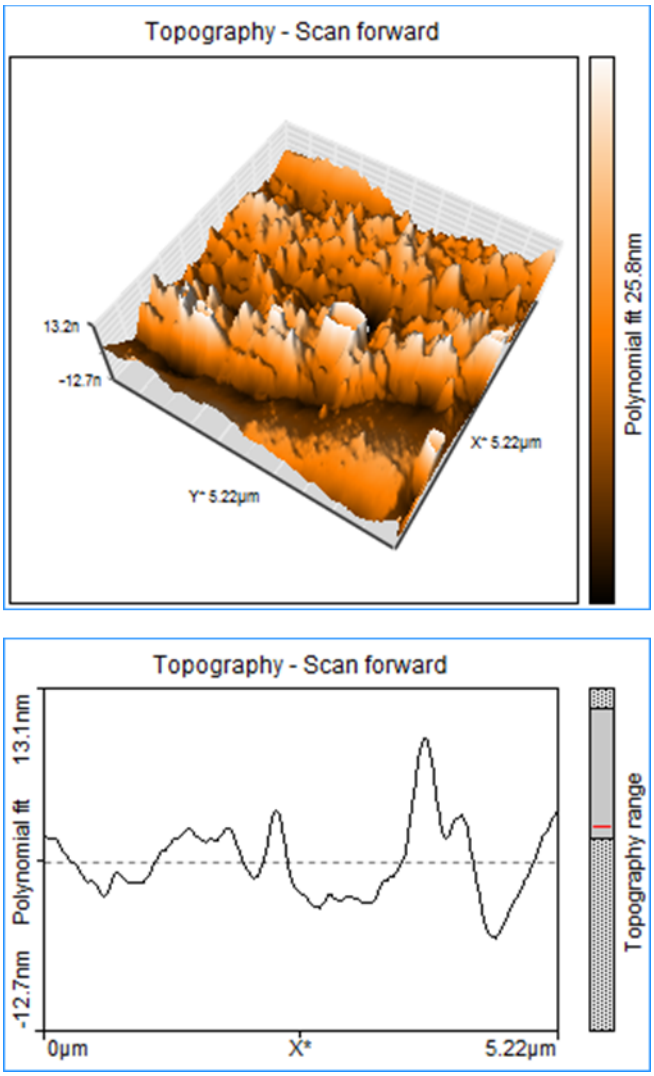

Figure S3. 3D surface topography by AFM, and AFM thickness profile of $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO nanocomposite.

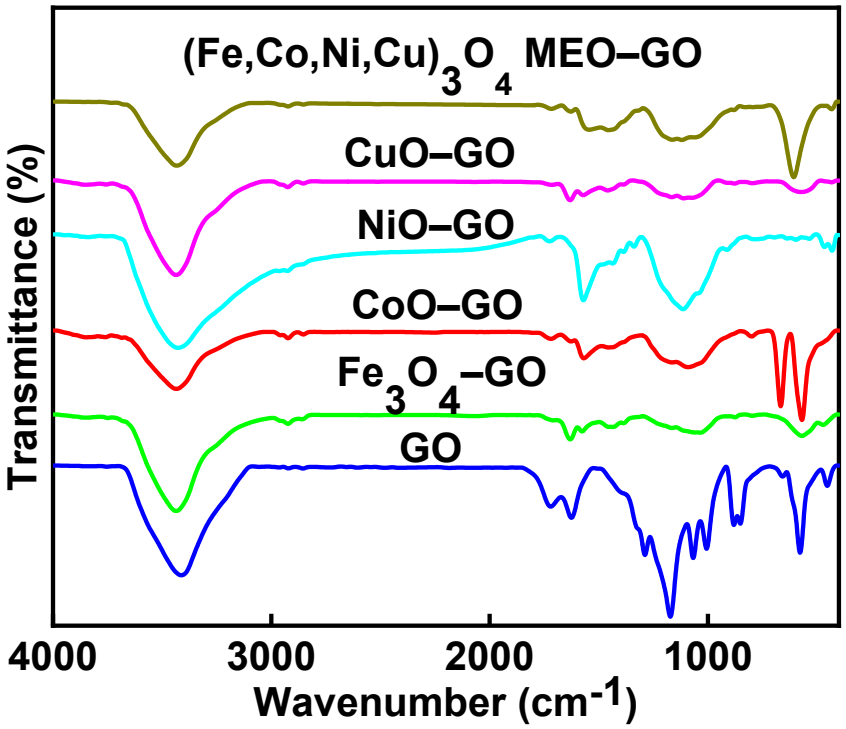

Figure S4. FTIR spectra of samples.

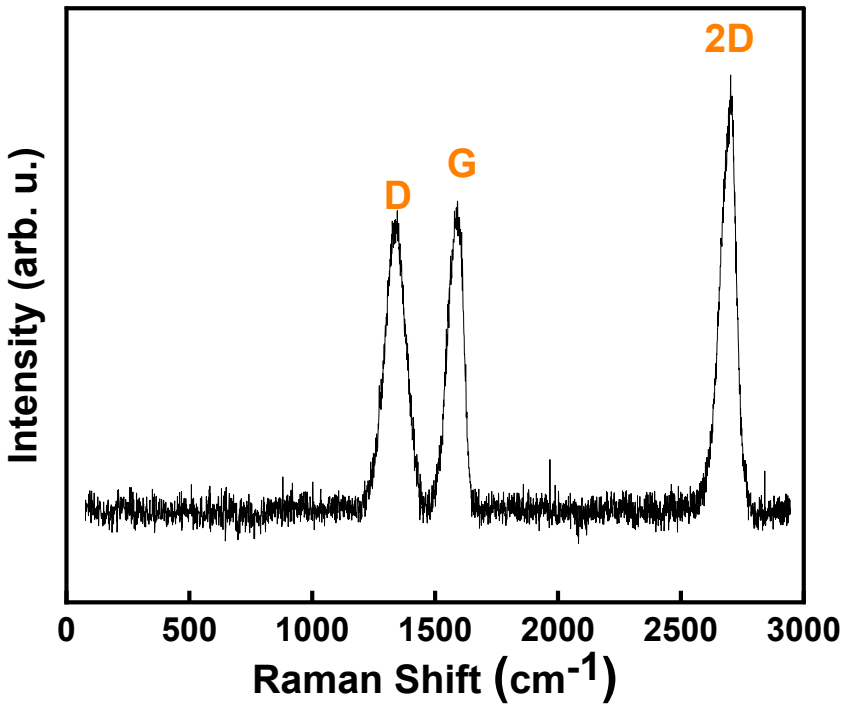

Figure S5. Raman spectrum of GO labeled (D, G, 2D).

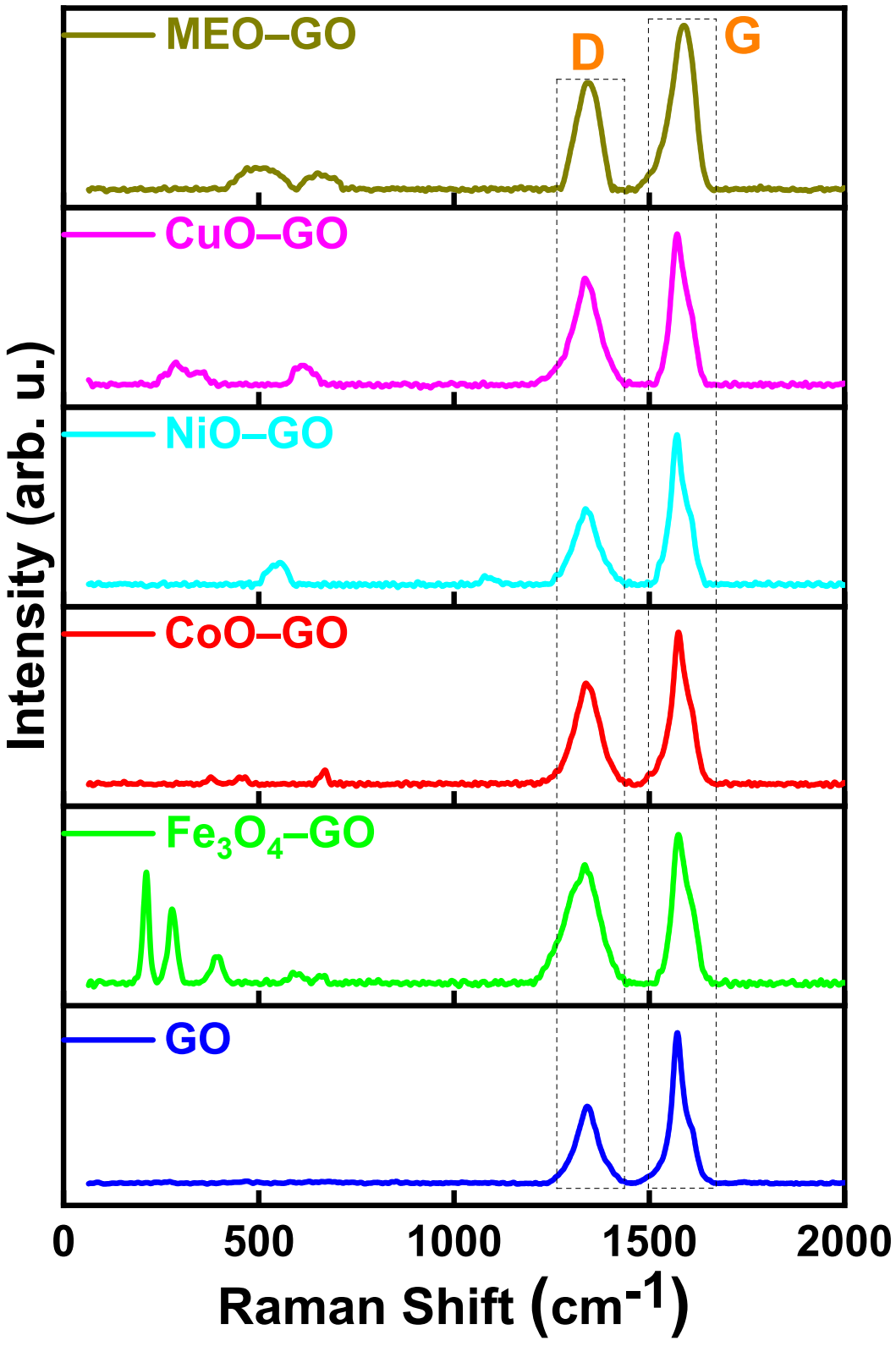

Figure S6. Raman spectra of samples with enhanced resolution.

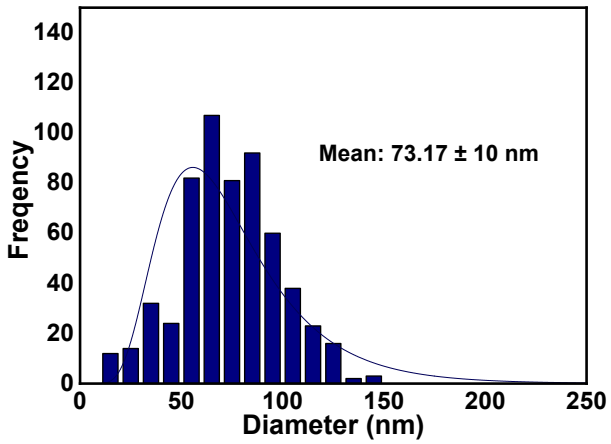

Figure S7. Particle size distribution of $(Fe,Co,Ni,Cu)_3O_4$ MEO on the surface of GO ($(Fe,Co,Ni,Cu)_3O_4$ MEO–GO).

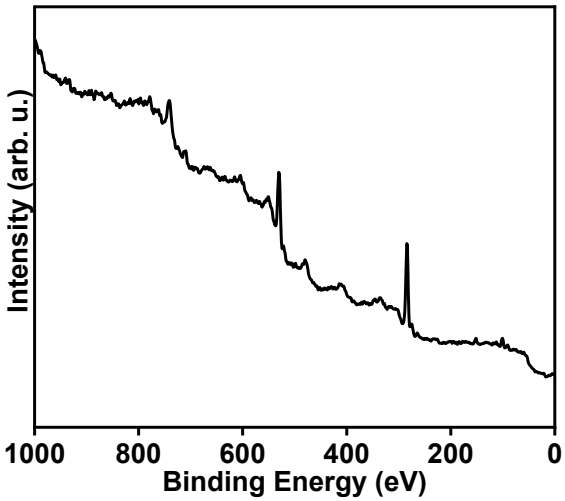

Figure S8. Survey XPS spectra of $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO.

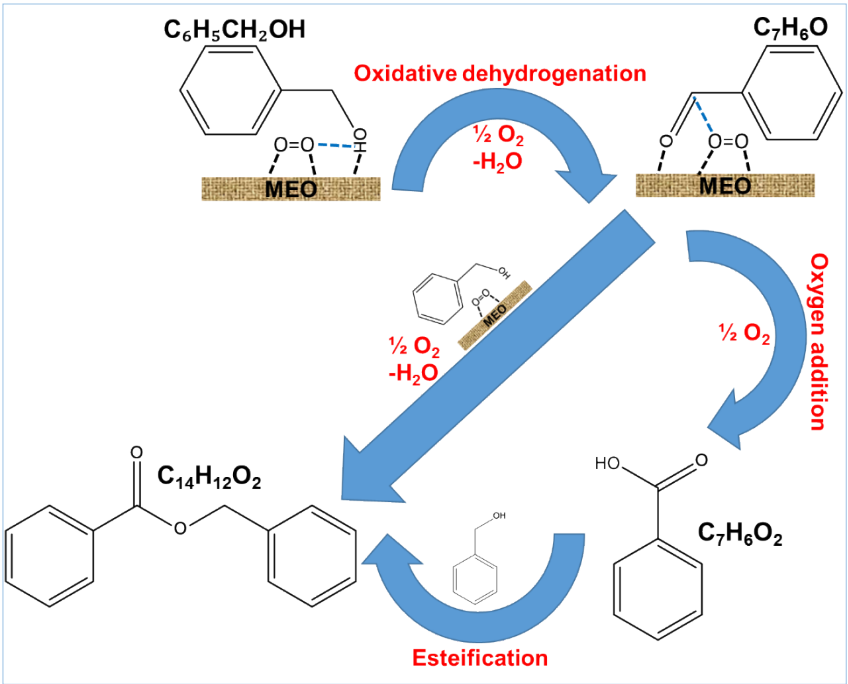

Figure S9. Possible reaction pathway of benzyl alcohol oxidation over $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO catalyst.

To confirm the product structure by NMR analysis, pure benzaldehyde was isolated from representative reaction mixtures. The clear supernatant was first diluted with dichloromethane (15 ml) and then washed with saturated aqueous $NaHCO_3$ (2×15 ml) to remove residual benzoic acid, followed by a brine wash (15 ml). The organic phase was dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure on a rotary evaporator (bath temperature 35–38 °C). The crude oil obtained was purified by flash column chromatography on silica gel (230–400 mesh) using n-hexane/ethyl acetate (95:5 → 90:10 v/v) as the eluent. Fractions containing pure benzaldehyde (identified by TLC, Rf = 0.54 in hexane/ethyl acetate 9:1) were combined and concentrated to afford benzaldehyde as a colorless oil.

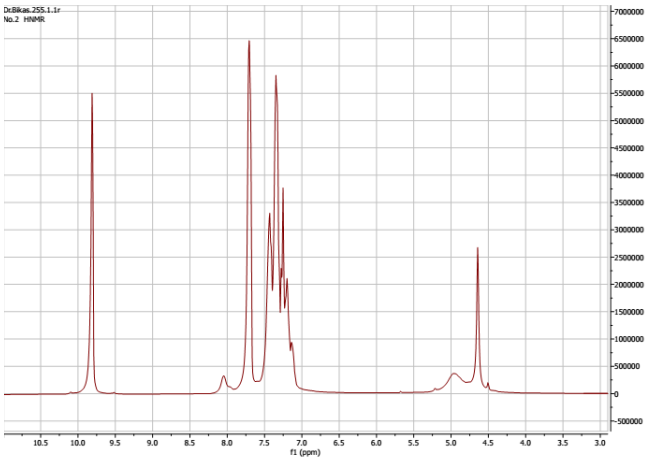

Figure S10. The ^{1}H NMR spectrum of isolated benzaldehyde from the oxidation reaction of benzyl alcohol.

Table S1. Aerobic and solvent-free oxidation of benzyl alcohol under different reaction conditions.

Entry†	Pressure (atm)	Catalyst	Cat. (g)	Temperature (°C)	Time (h)	Conversion (%)	Selectivity (%)		
							BAd	Bac	BBz
1	1	-	-	120	5	0.16	71.3	25.6	3.1
2	10	-	-	120	5	0.51	65.5	29.1	5.40
3	1	GO	0.2	120	5	5.31	53.4	31.1	15.5
4	10	GO	0.2	120	5	7.64	47.2	35.5	19.3
5	1	GO	0.2	120	10	11.31	43.8	38.3	17.9
6	10	GO	0.2	120	10	14.12	40.1	41.3	18.6
7	1	GO	0.2	120	24	15.53	41.8	40.1	18.1
8	10	GO	0.2	120	24	19.51	37.3	41.2	21.5
9	1	Fe_3O_4	0.2	120	5	11.61	50.8	29.3	19.9
10	10	Fe_3O_4	0.2	120	5	23.11	43.2	36.3	20.5
11	1	CoO	0.2	120	5	10.81	44.3	33.8	21.9
12	10	CoO	0.2	120	5	22.63	41.7	39.4	18.9
13	1	NiO	0.2	120	5	10.65	48.9	31.2	19.9
14	10	NiO	0.2	120	5	21.71	42.1	40.3	17.6
15	1	CuO	0.2	120	5	11.13	53.1	26.3	20.6
16	10	CuO	0.2	120	5	23.61	49.4	29.8	20.8
17	1	MEO	0.2	120	5	17.13	56.3	31.5	12.2
18	10	MEO	0.2	120	5	31.40	47.1	35.6	17.3
19	1	MEO	0.2	120	10	27.21	51.8	33.1	15.1
20	10	MEO	0.2	120	10	39.81	43.6	37.1	19.3
21	1	MEO	0.2	120	24	50.73	42.1	39.8	18.1
22	10	MEO	0.2	120	24	73.11	39.3	41.1	19.6
23	1	Fe_3O_4–GO	0.2	120	5	9.73	56.7	25.3	18.0
24	10	Fe_3O_4–GO	0.2	120	5	16.53	54.5	23.7	21.8
25	1	CoO–GO	0.2	120	5	9.62	55.1	27.8	17.1
26	10	CoO–GO	0.2	120	5	17.13	53.6	29.1	17.3
27	1	NiO–GO	0.2	120	5	9.35	56.3	24.3	19.4
28	10	NiO–GO	0.2	120	5	17.81	55.4	26.7	17.9
29	1	CuO–GO	0.2	120	5	10.13	58.1	23.4	18.5
30	10	CuO–GO	0.2	120	5	18.11	59.6	21.7	18.7
31	1	MEO–GO	0.2	120	5	17.19	71.4	15.1	13.5

32	10	MEO–GO	0.2	120	5	28.78	65.7	22.1	12.2
33	1	MEO–GO	0.2	120	10	24.17	58.5	26.4	15.1
34	10	MEO–GO	0.2	120	10	35.44	55.7	27.1	17.2
35	1	MEO–GO	0.2	120	24	43.71	52.1	29.6	18.3
36	10	MEO–GO	0.2	120	24	69.87	50.7	31.8	17.5
37	1	MEO–GO	0.2	140	5	23.72	70.1	18.2	11.7
38	10	MEO–GO	0.2	140	5	33.63	63.8	23.1	13.1
39	1	MEO–GO	0.4	120	5	32.15	65.3	19.5	15.2
40	10	MEO–GO	0.4	120	5	52.23	61.5	25.7	12.8
41	1	MEO–GO	0.6	120	5	41.16	59.4	24.6	16.0
42	10	MEO–GO	0.6	120	5	63.33	56.2	28.7	15.1

†Typical aerobic oxidation conditions of benzyl alcohol: 5 mL of benzyl alcohol, catalyst amount (actual weight ratio of $(Fe,Co,Ni,Cu)_3O_4$ MEO to GO in the synthesized nanocomposite is 1 to 3), rotation speed 500 rpm, under optimal pressure (air) of 1 and 10 atm and specific temperature for a certain period of time. BAd: benzaldehyde, BAc: benzoic acid, and BBz: benzyl benzoate.

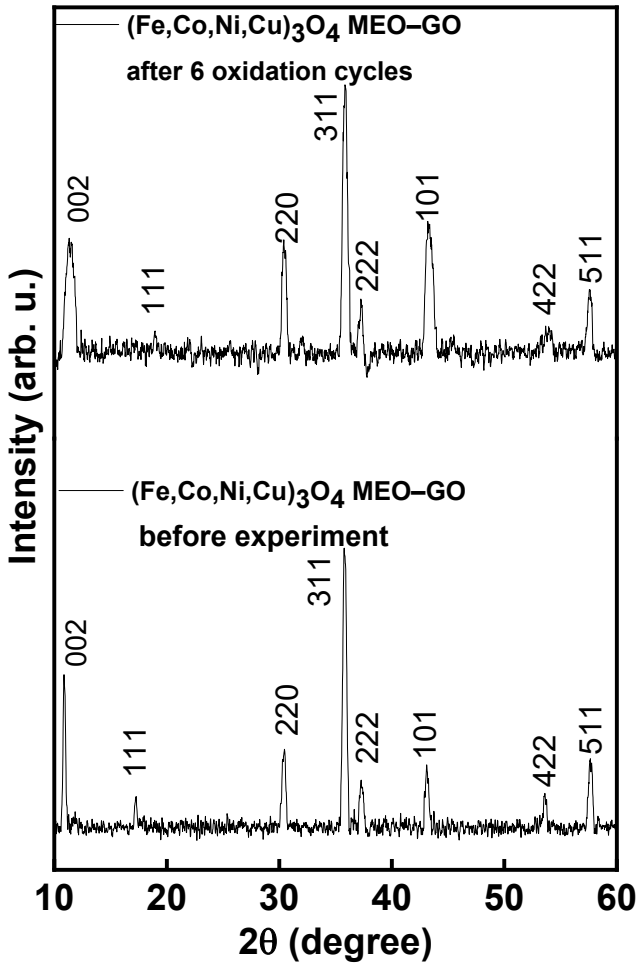

Figure S11. XRD patterns of $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO before and after 6 oxidation cycles.

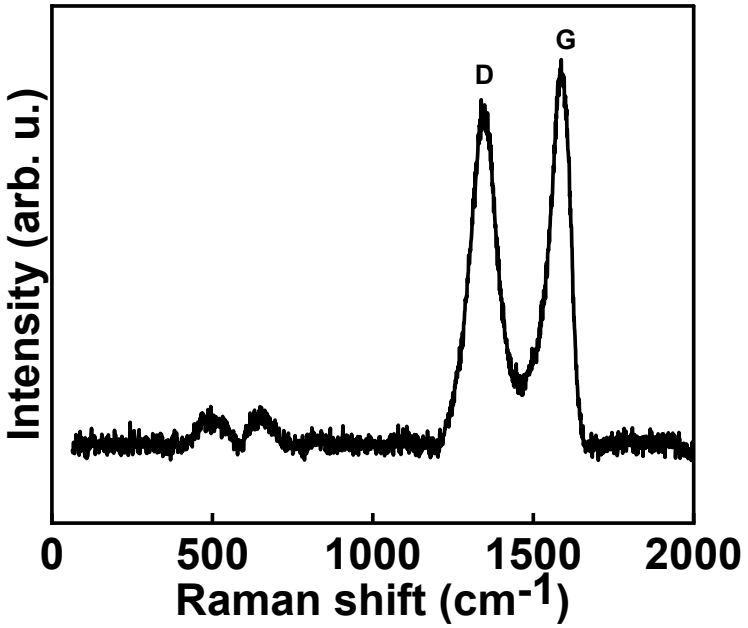

Figure S12. Raman spectra of $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO after 6 oxidation cycles.

Table S2. Fe, Co, Ni, and Cu ratios in $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO as obtained by ICP-MS before and after.

Sample(s)	Percentage (Atom, %)			
	Fe	Co	Ni	Cu
$(Fe,Co,Ni,Cu)_3O_4$ MEO–GO	25.56	24.45	23.86	26.13
$(Fe,Co,Ni,Cu)_3O_4$ MEO–GO	25.64	24.94	23.81	25.61

Table S3. Catalytic performance of $(Fe,Co,Ni,Cu)_3O_4$ MEO–GO in aerobic solvent-free benzyl alcohol oxidation: conversion and selectivity at 1 and 10 atm air pressure (n=3, Mean ± SD)

Entry†	Pressure (atm)	Conversion (%)	Selectivity (%)
			BAd
1	1	17.2±0.2	71.4±0.4
2	10	28.8±0.1	65.7±0.2
3	1	17.1±0.1	71.1±0.3
4	10	28.6±0.2	65.3±0.1
5	1	17.0±0.1	70.1±0.5
6	10	28.3±0.1	64.9±0.4
7	1	17.0±0.3	70.1±0.2
8	10	28.4±0.3	64.7±0.2
9	1	16.9±0.1	69.7±0.1
10	10	27.9±0.2	65.0±0.3

11	1	16.8±0.2	69.3±0.3
12	10	27.7±0.3	64.1±0.1

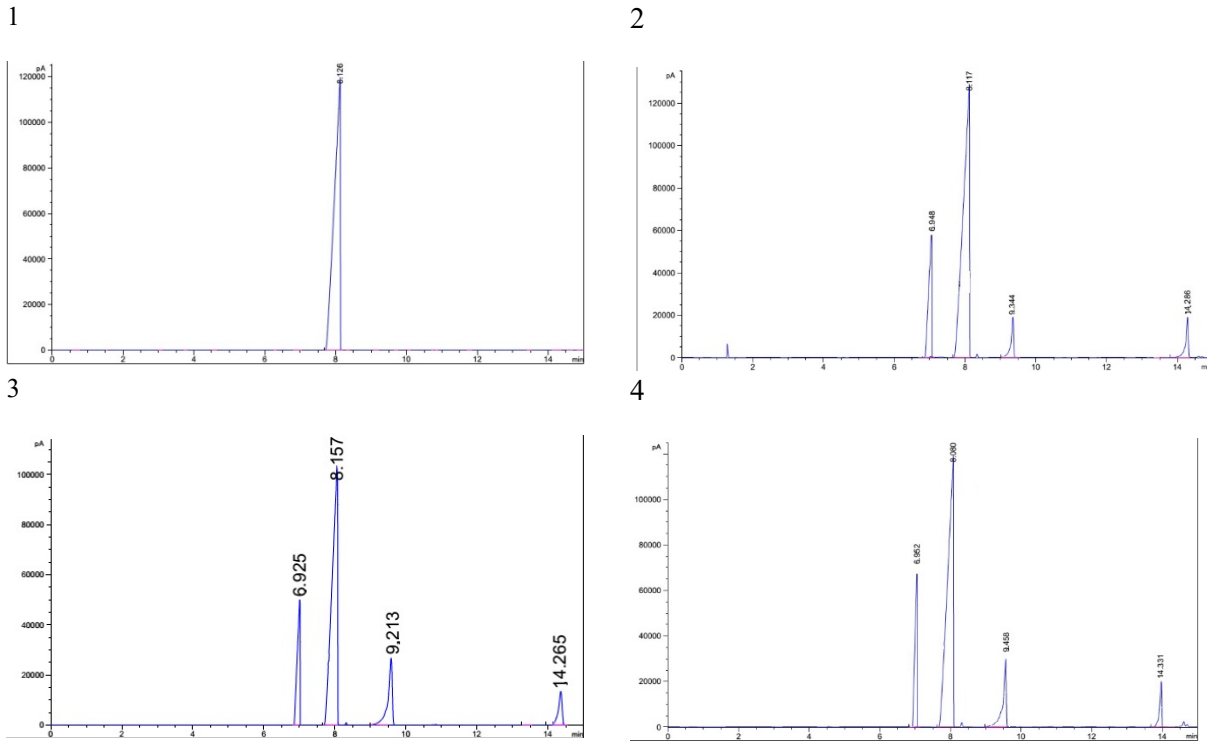

Figure 13. Gas chromatography (GC) spectra of the (1) initial benzyl alcohol and some selected spectra related to Table 1: (2) MEO–GO (5h), (3) MEO–GO (10h), and (4) MEO–GO (20h).