Electronic Supplementary Information for

Metal Nanoparticle-Decorated Germanane for Selective Photocatalytic Aerobic Oxidation of Benzyl Alcohol

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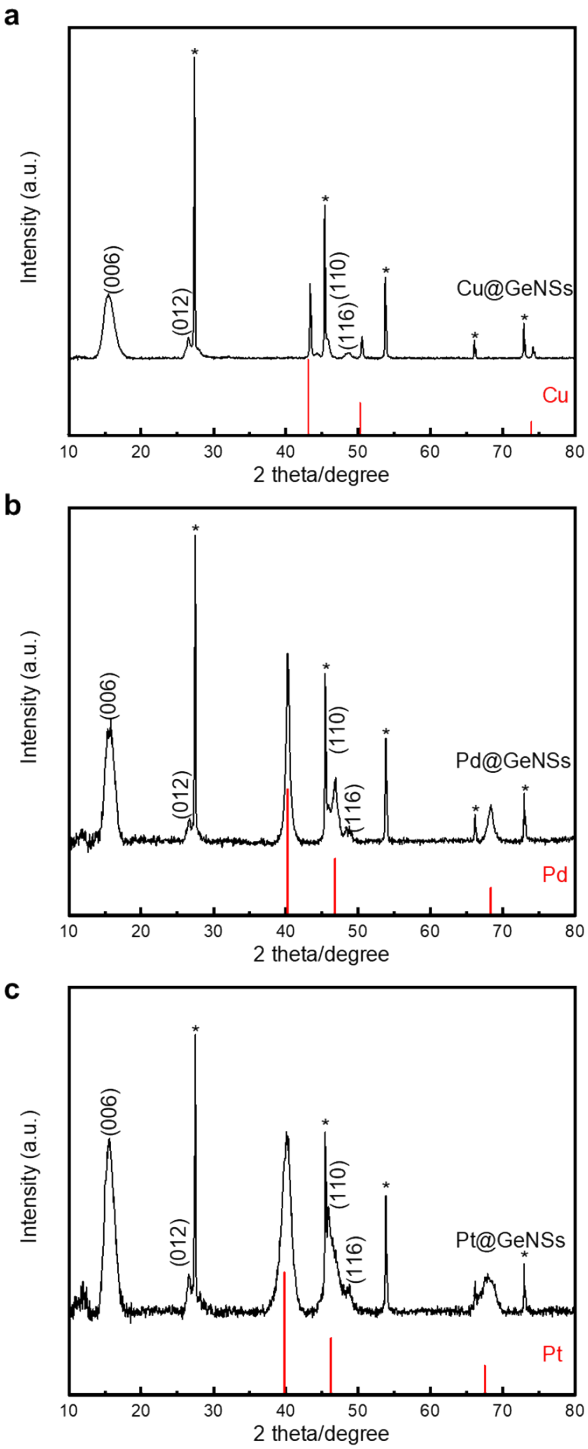

Figure S1. XRD patterns of (a) Cu@GeNSs, (b) Pd@GeNSs, and (c) Pt@GeNSs. Asterisks correspond to the Ge reflection; Cu, Pd and Pt reflections are from PDF#89-2838,88-2335 and 88-2343.

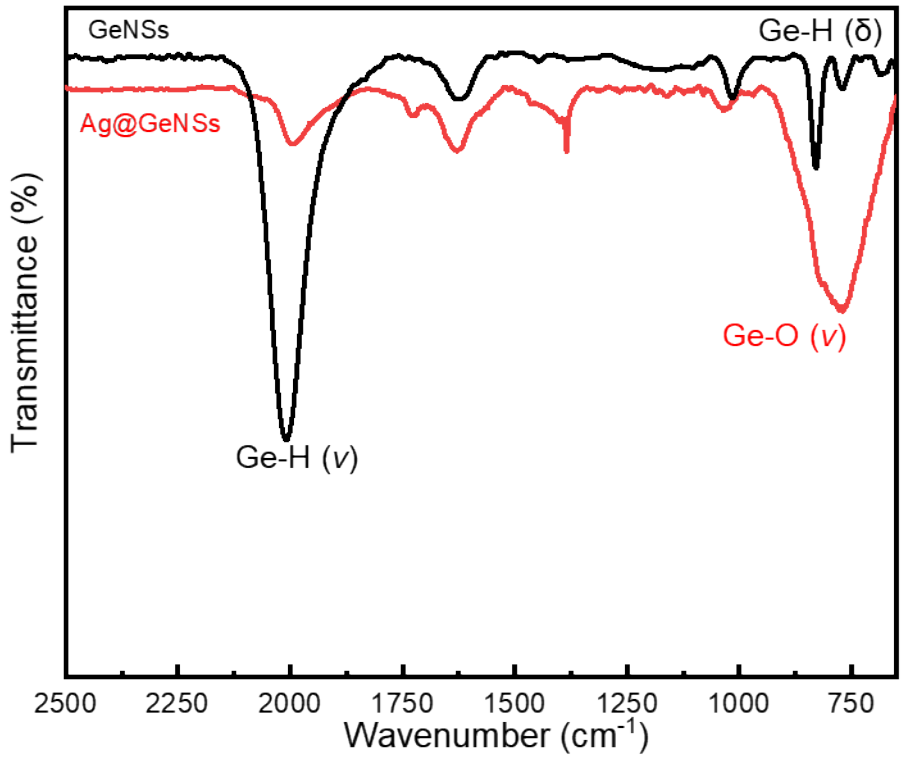

Figure S2. Representative FTIR spectra of Ge nanosheets before (black) and after (red) Ag deposition.

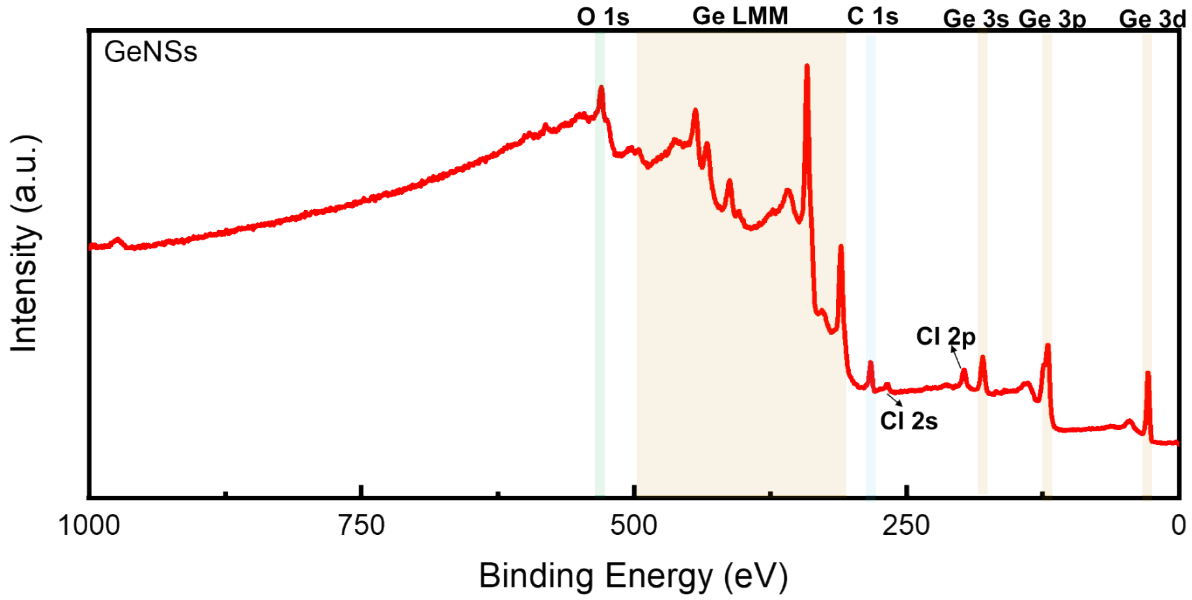

Figure S3. A representative survey XP spectrum of GeNSs.

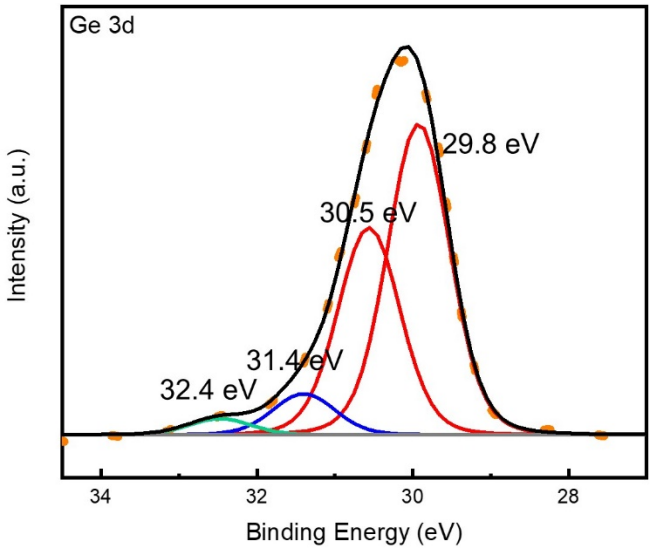

Figure S4. A representative high-resolution XP spectrum of Ge 3d region of GeNSs.

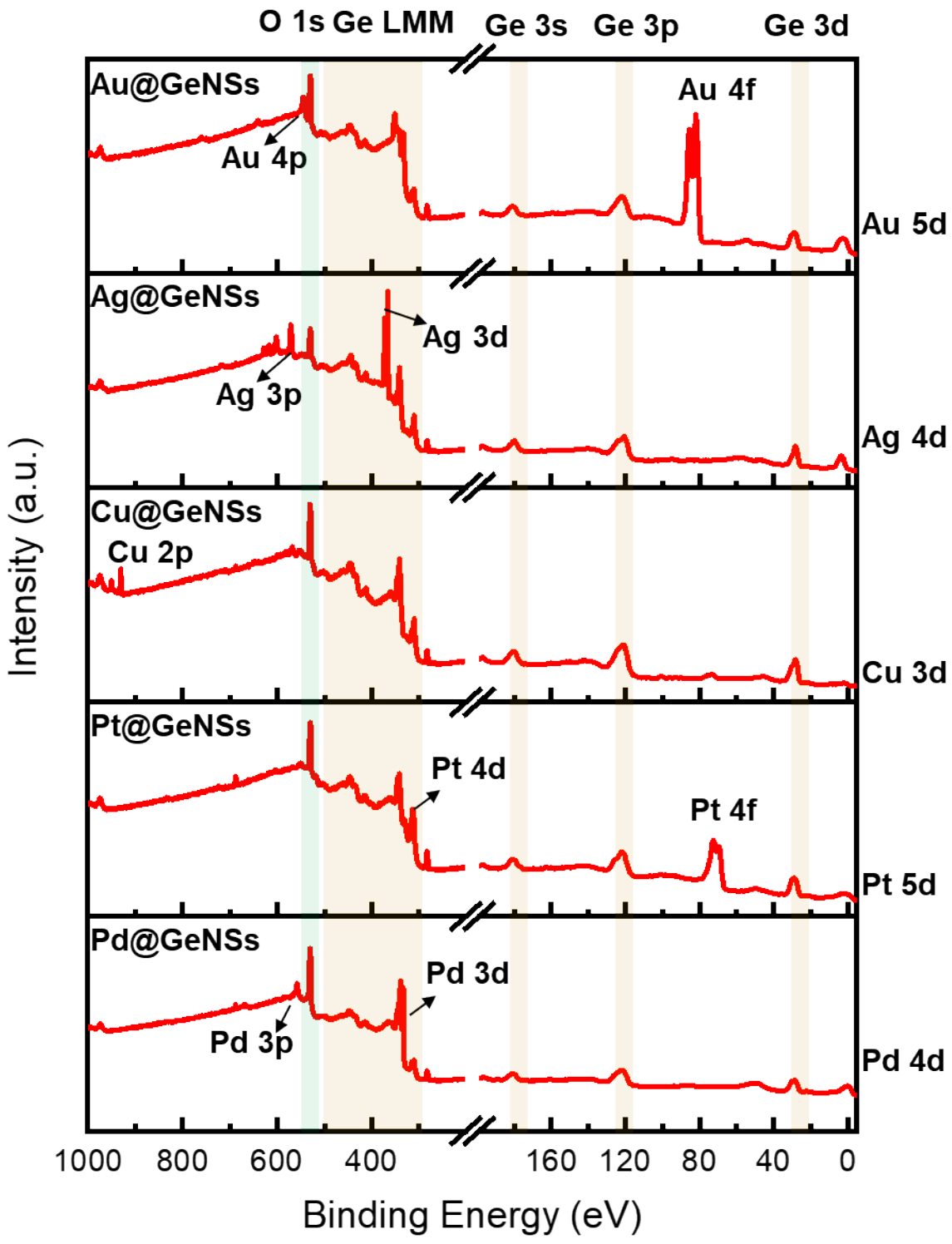

Figure S5. Representative survey XP spectra of (a) Au@GeNSs (b) Ag@GeNSs, (c) Cu@GeNSs, (d) Pt@GeNSs and (e) Pd@GeNSs

Table S1. Summary of XPS data.

	Au@GeNSs	Ag@GeNSs	Cu@GeNSs	Pd@GeNSs	Pt@GeNSs
Ge 3d emission (eV)	29.8	29.7	29.7	29.8	29.7
Metal emission (eV)[a]	83.8 (84.0)	368.2 (368.2)	932.8 (933.0)	335.2 (335.0)	70.7 (71.0)
M/Ge ratio[b]	0.063	0.081	0.072	0.075	0.058

[a] Values in parentheses represent the standard metallic binding energies; [b] The ratios were calculated from the atomic percentage of metal and Ge obtained from the survey spectra in question.

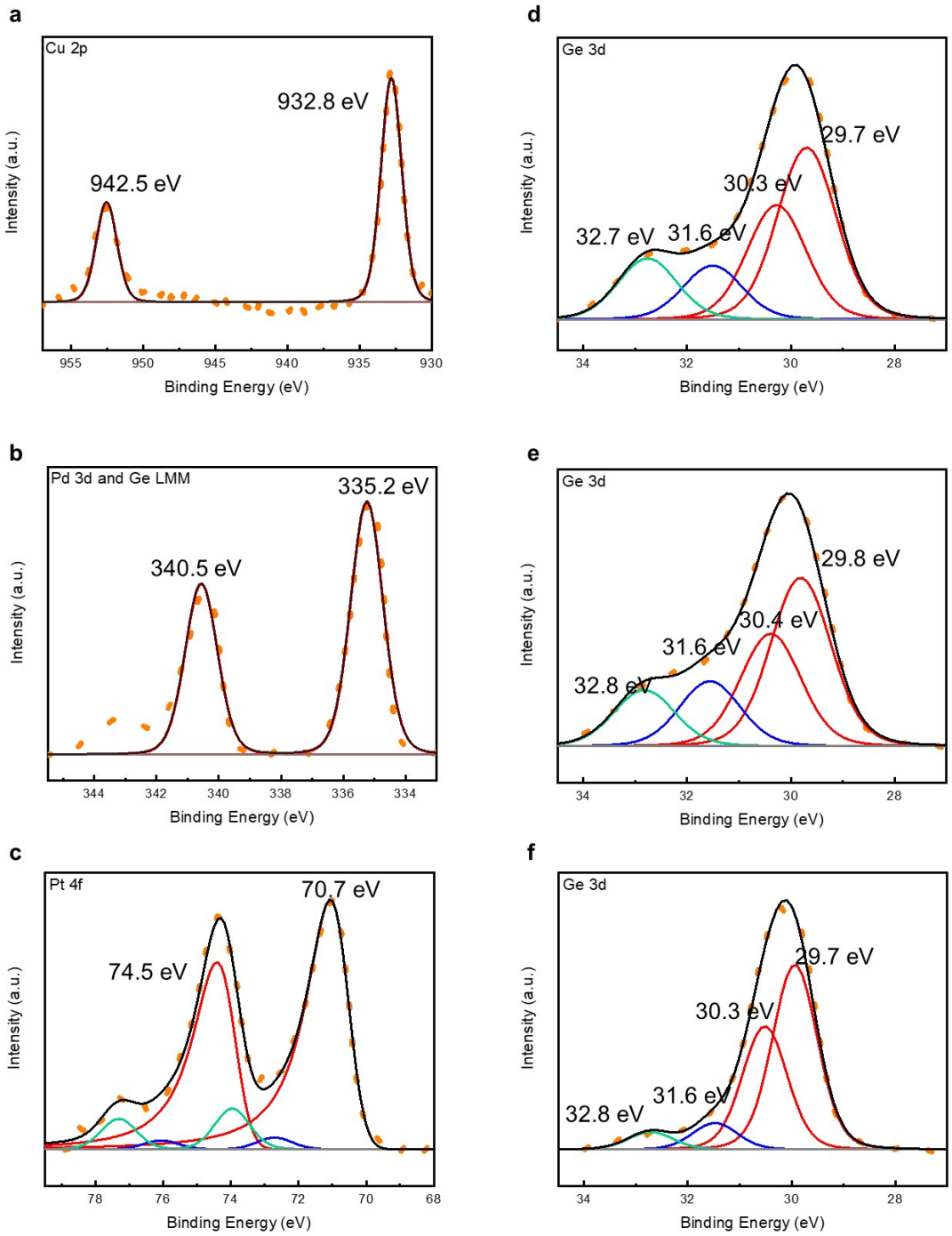

Figure S6. Representative high-resolution XP spectra of (a, d) Cu@GeNSs, (b, e) Pd@GeNSs and (c, f) Pt@GeNSs. Corresponding metal (left) and Ge 3d (right) regions are presented in rows.

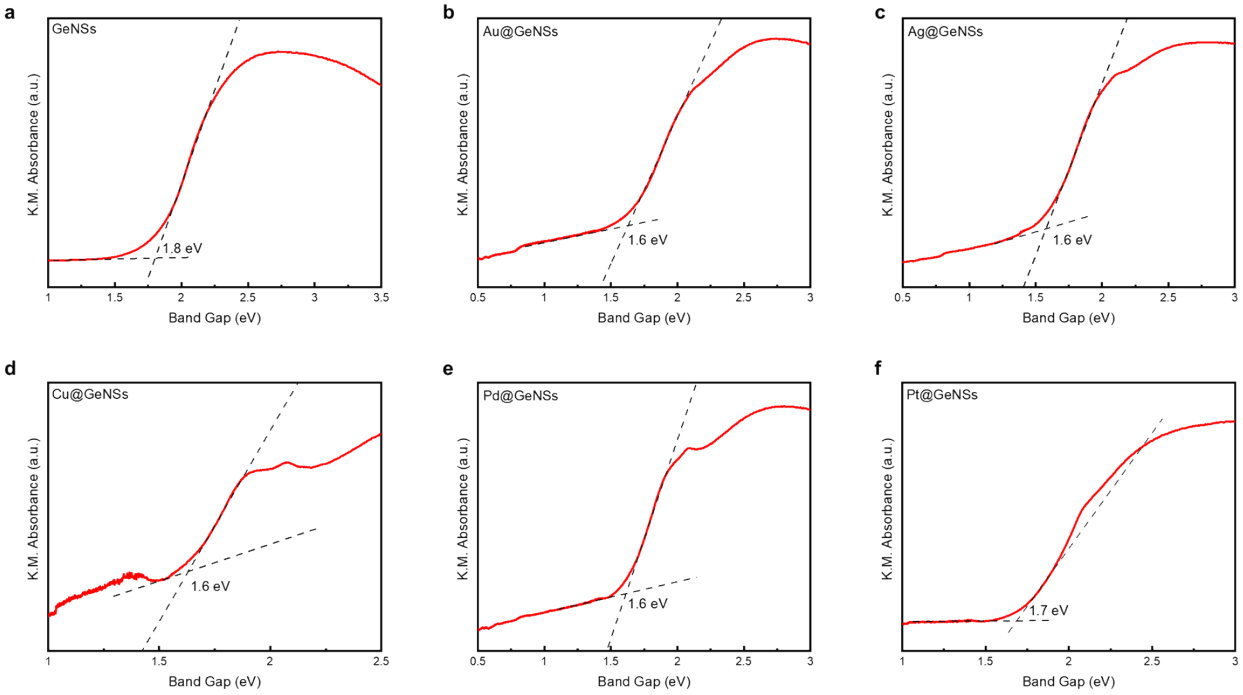

Figure S7. Representative DRA (Diffuse reflective absorption) spectra of Ge nanosheets and M@GeNSs.

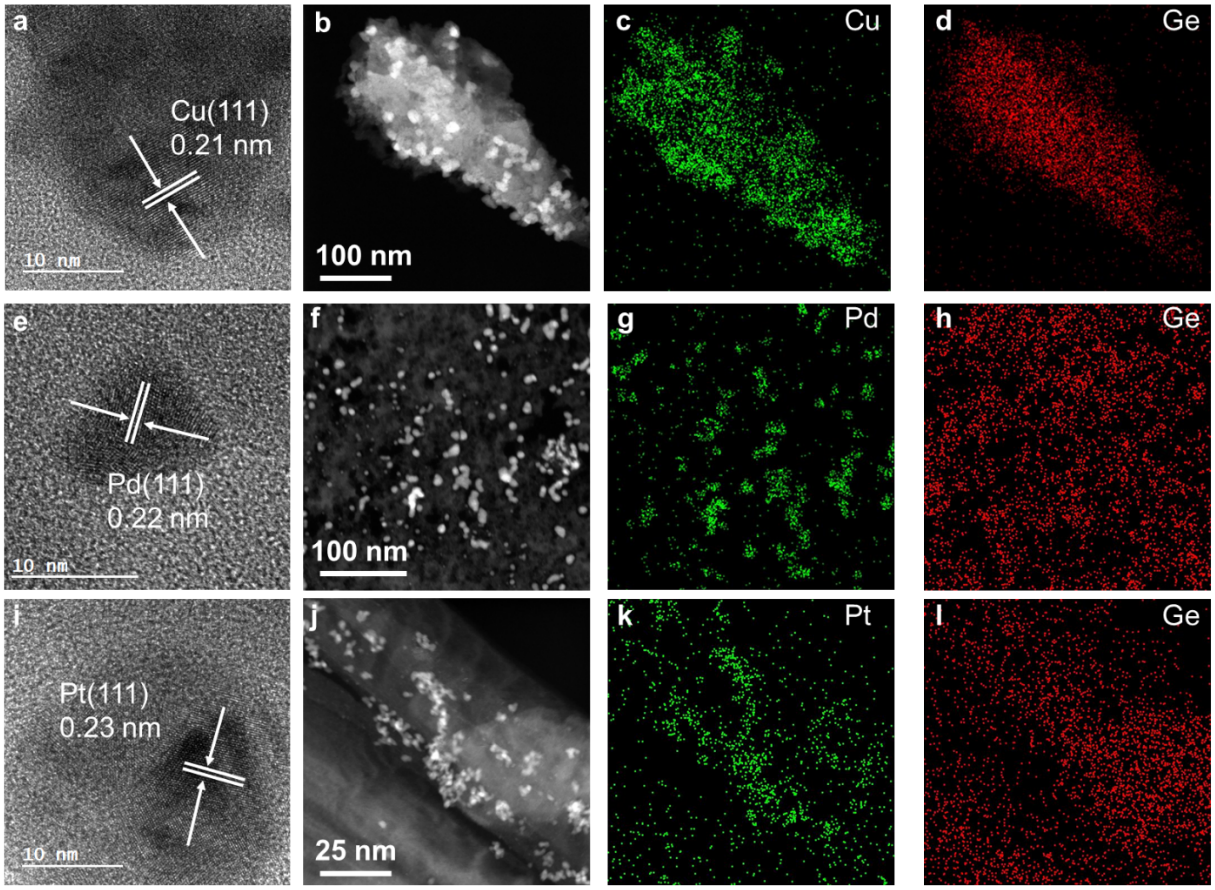

Figure S8. Representative HRTEM, HAADF-STEM images and EDX mapping of (a-d) Cu@GeNSs, (e-h) Pd@GeNSs, and (i-l) Pt@GeNSs.

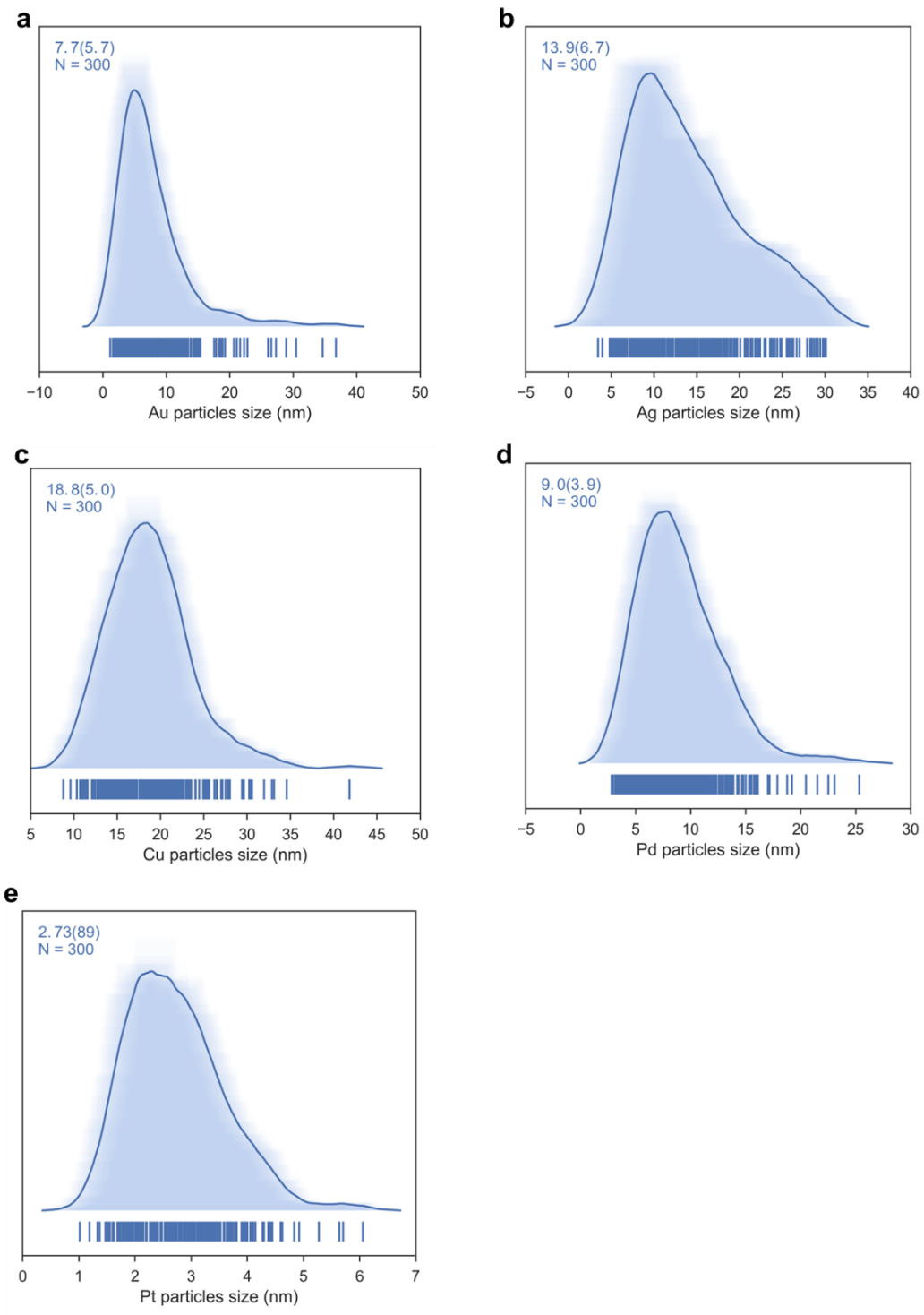

Figure S9. Representative average shift histograms for metal nanoparticles on (a) Au@GeNSs (b) Ag@GeNSs, (c) Cu@GeNSs, (d) Pd@GeNSs and (e) Pt@GeNSs.

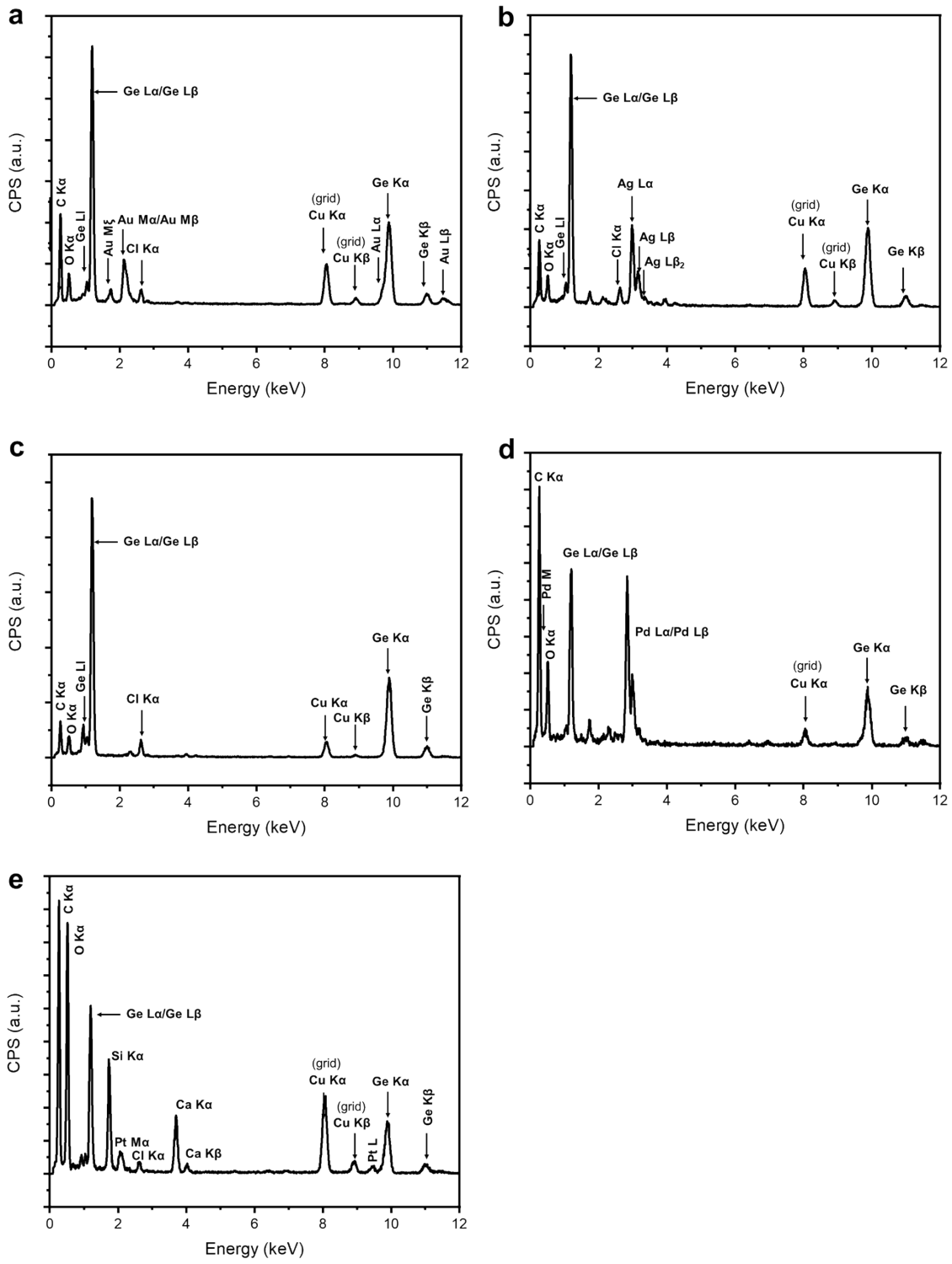

Figure S10. Representative EDX spectra for (a) Au@GeNSs (b) Ag@GeNSs, (c) Cu@GeNSs, (d) Pd@GeNSs, and (e) Pt@GeNSs

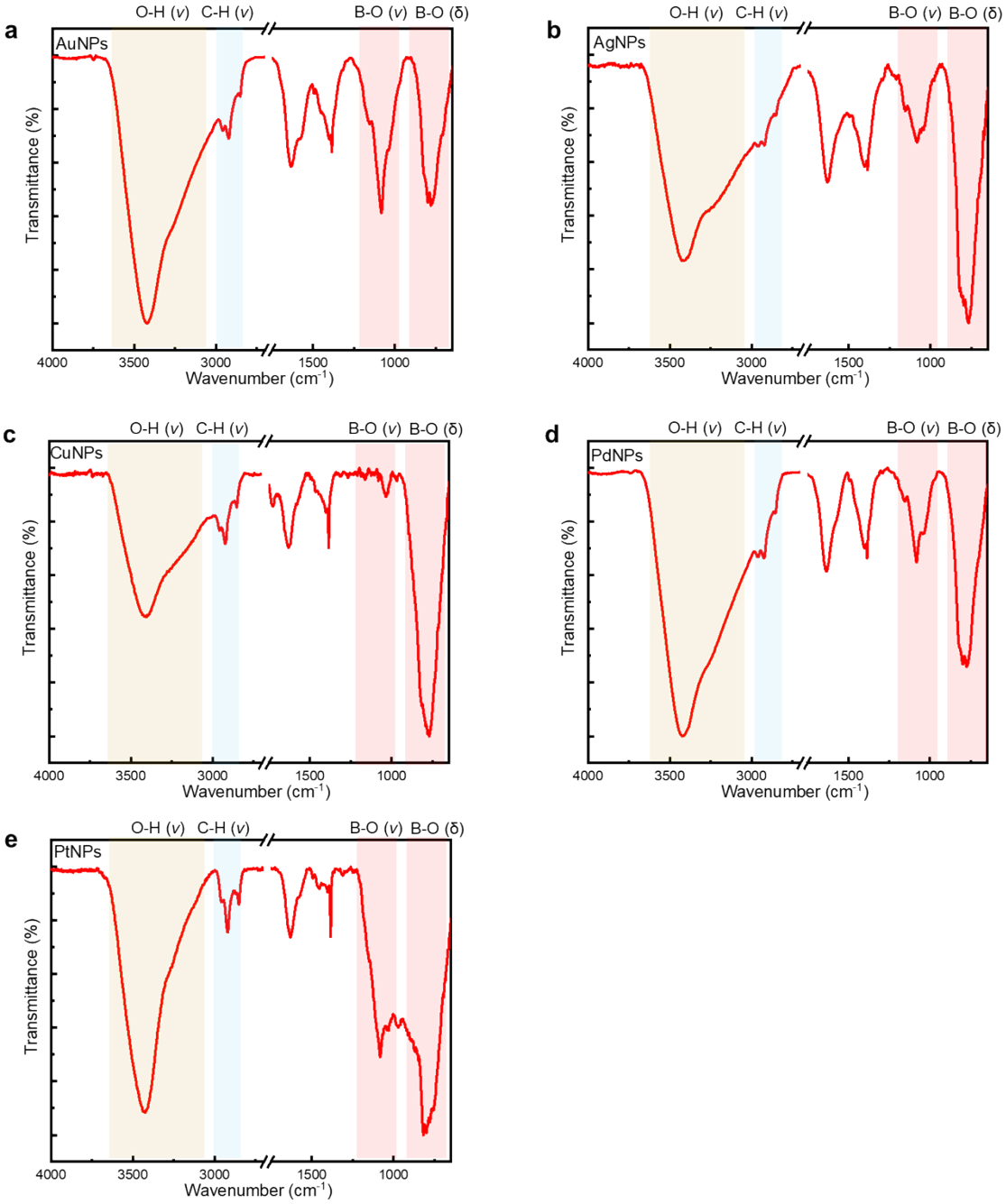

Figure S11. Representative FTIR spectra of the indicated metal nanoparticles.

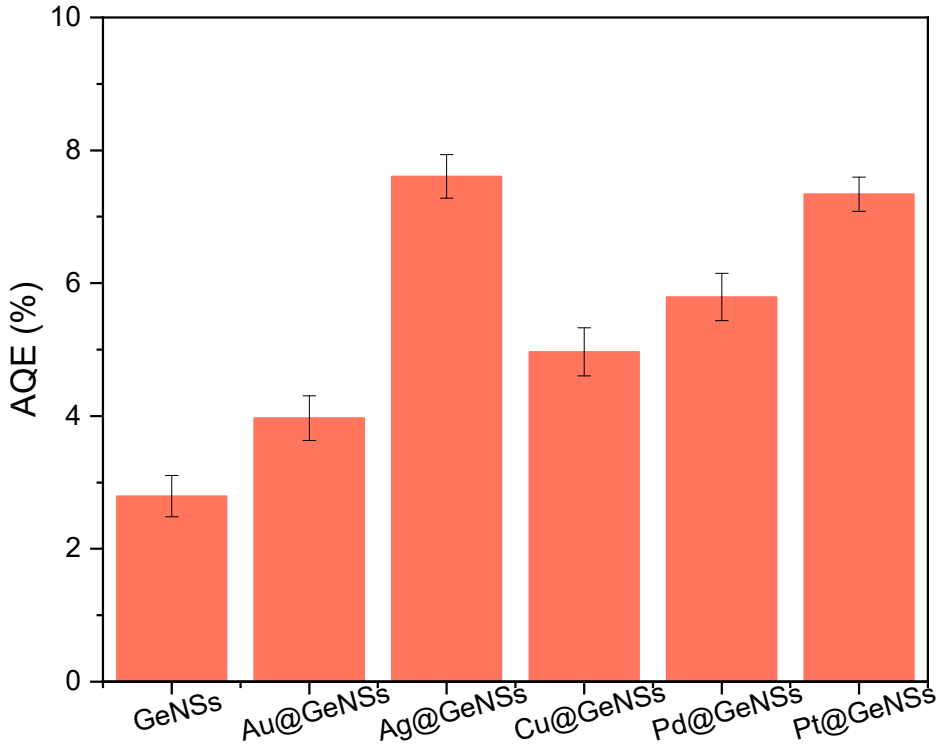

Figure S12. AQE (apparent quantum efficiency) of the photooxidation of benzyl alcohol to produce benzaldehyde of indicated catalysts after 1 h of reaction.

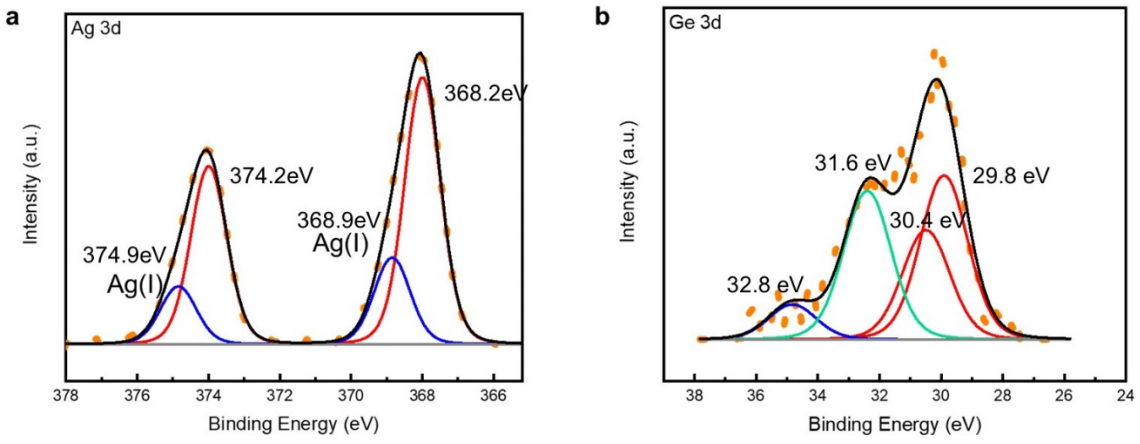

Figure S13. Representative high-resolution XP spectra of a) Ag 3d regions of Ag@GeNSs after the photooxidation of benzyl alcohol to produce benzaldehyde showing Ag(I) species, (b) Ge 3d regions after photooxidation of benzyl alcohol to produce benzaldehyde.

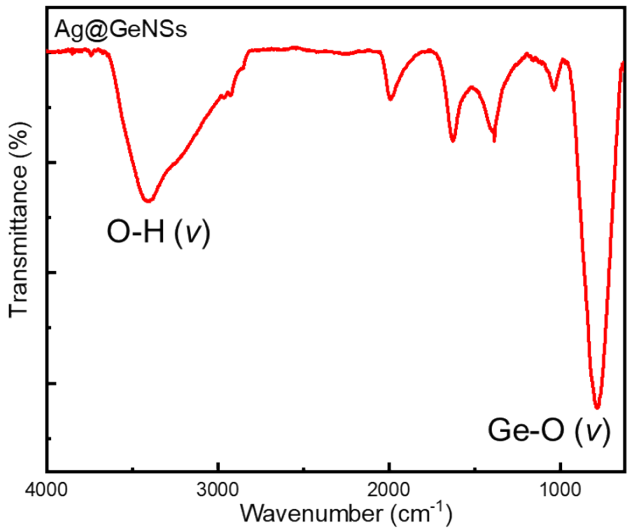

Figure S14. Representative FTIR spectrum of Ag@GeNSs after the photooxidation of benzyl alcohol to produce benzaldehyde.

Table S2. Summary of photocatalytic oxidation performance of benzyl alcohol to produce benzaldehyde.

	GeNSs	Au@GeNSs	Ag@GeNSs	Cu@GeNSs	Pd@GeNSs	Pt@GeNSs
Conversion (%)	30.7	43.6	83.7	54.6	63.7	80.7
Selectivity (%)	82.4	65.4	73.7	70.4	75.3	79.4
Yield (%)	25.3	28.6	61.6	38.5	48.1	64.1
AQE (%)	2.79	3.97	7.61	4.97	5.79	7.34

Table S3. Comparison of the photocatalytic oxidation of benzyl alcohol to produce benzaldehyde using free metal particles, M@GeNSs, as well as physical mixtures of free metal nanoparticles and GeNSs (MNPs+GeNSs).

Conversion (%)	Au	Ag	Cu	Pd	Pt
M@GeNSs	43.6	83.7	54.6	63.7	80.7
MNPs+GeNSs	35.7	45.6	32.5	50.2	60.3
MNPs	4.85	8.66	3.15	5.22	7.36

Table S4. Representative nanoparticle size distributions for metal nanoparticles and M@GeNSs obtaining from measuring 300 nanoparticles under TEM.

Sizes (nm)	Au	Ag	Cu	Pd	Pt
M@GeNSs	7.7 ± 5.7	13.9 ± 6.7	18.8 ± 7.0	9.0 ± 3.9	2.7 ± 0.8
MNPs	8.3 ± 5.3	14.3 ± 6.1	20.1 ± 6.5	9.2 ± 3.3	3.2 ± 0.6

Table S5. Effect of Ag loading on catalytic performance of Ag@GeNSs in selective oxidation of benzyl alcohol to benzaldehyde.

	1%Ag@GeNSs	2.5%Ag@GeNSs	5%Ag@GeNSs	10%Ag@GeNSs
Conversion (%)	64.6	70.2	83.7	85.4
Selectivity (%)	76.2	74.6	73.7	71.2
Yield (%)	49.2	52.4	61.6	60.8

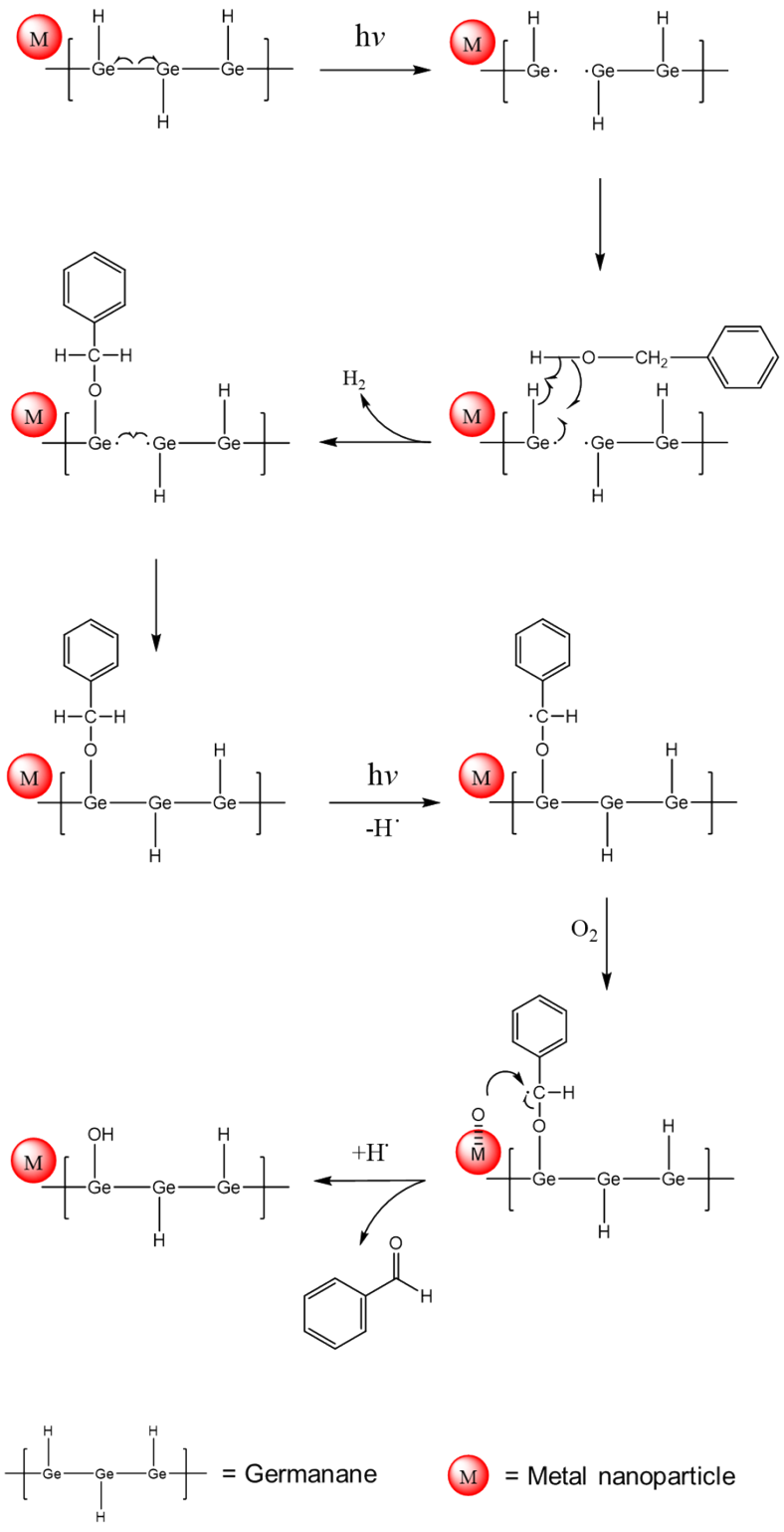

Figure S14. Proposed mechanism for the presented catalytic activity of M@GeNSs in the photooxidation of benzyl alcohol to produce benzaldehyde.

Table S6. Reported studies on the selective oxidation of benzyl alcohol.

Catalyst	Irradiation source	T (K)	t(h)	Solvent	Conversion (%)	Selectivity (%)
Ag@GeNSs	**Hg lamp (140 W, >366 nm)**	**RT**	**4**	N/A	**83.7**	**73.7**
Ru/g-C_3N_4[1]	UV LED (220 W, 390 nm)	RT	4	H_2O	73	72
Ir/TiO_2[2]	Hg lamp (250 W, >315 nm)	333	6	N/A	8.9	92
Pt/TiO_2[3]	Xe lamp (250 W, >420 nm)	727	2	H_2O	87	68
Au/CeO_2[4]	Vis LED (220 W, 530 nm)	RT	10	H_2O	52	99
Ag/SBA[5]	N/A	595	1	N/A	74.8	85.2
Au-Pd/TiO_2[6]	N/A	393	10	N/A	51.7	76.7
Pd/TiO_2[7]	N/A	363	6	N/A	4.5	85.9
Cu/TiO_2[8]	N/A	393	6	N/A	1.1	99.9
Cu-Pd/TiO_2[8]	N/A	393	6	N/A	35.9	98.7

Table S7. Photocatalytic oxidation activity of benzyl alcohol to benzaldehyde and recovery comparison of Ag@GeNS thin films and powders.

	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Ag@GeNS thin films					
Conversion (%)	80.2	79.9	80.2	79.4	79.2
Recovery (%)	98.0	97.3	97.1	98.4	98.1
Ag@GeNS powders					
Conversion (%)	83.7	75.5	61.6	55.2	46.7
Recovery (%)	87.6	80.7	88.8	83.6	88.3

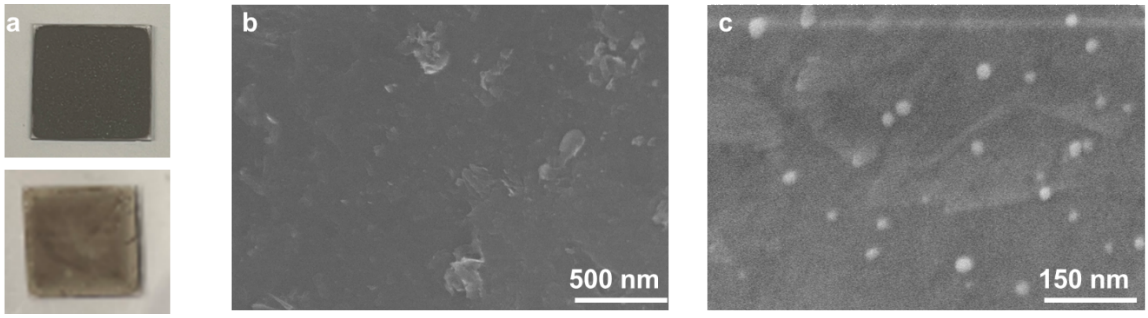

Figure S15. (a)Photos of Ge nanosheet thin film before (top) and after (bottom) Ag deposition. High-resolution SEM images of (b) GeNS and (c) Ag@GeNS thin films

Reference

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