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Interfacial synergism of Pd-decorated BiOCl ultrathin nanosheets for selective oxidation of aromatic alcohols

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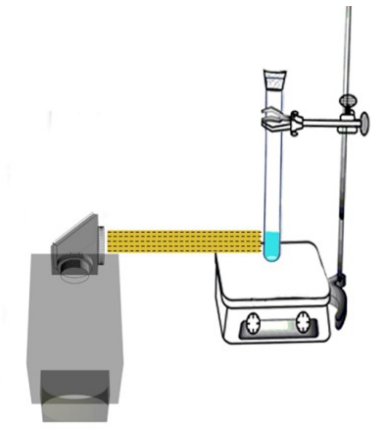

Figure S1. Schematic diagram of the experiment set-up for photocatalytic reactions.

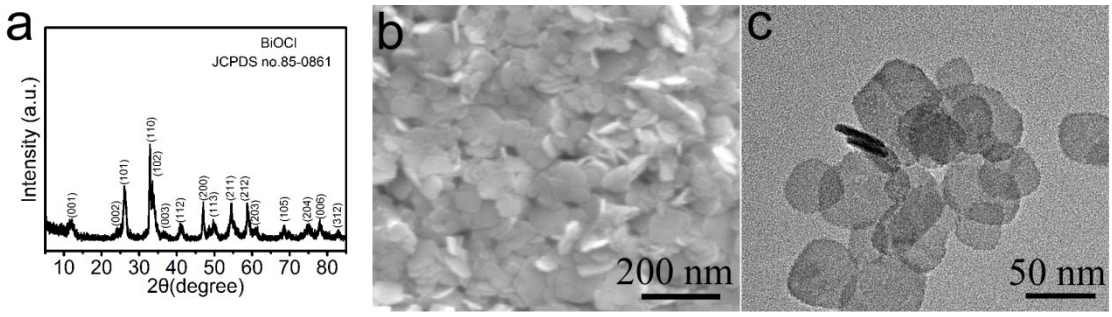

Figure S2. (a) XRD pattern, (b) SEM image, and (c) TEM image of BiOCl ultrathin nanosheets.

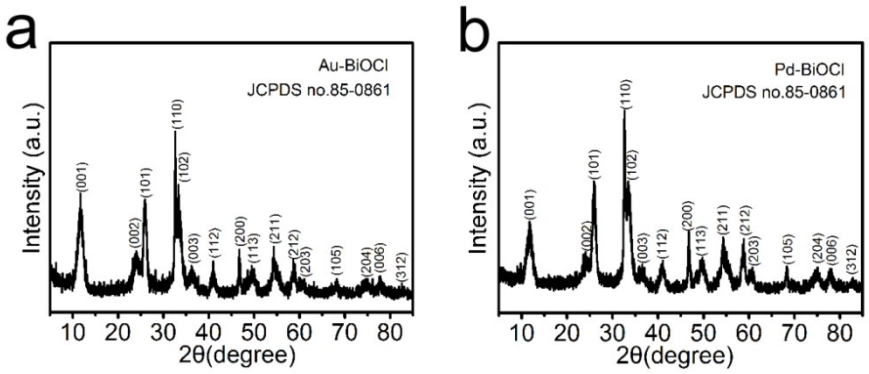

Figure S3. XRD patterns of (a) Au-BiOCl and (b) Pd-BiOCl samples.

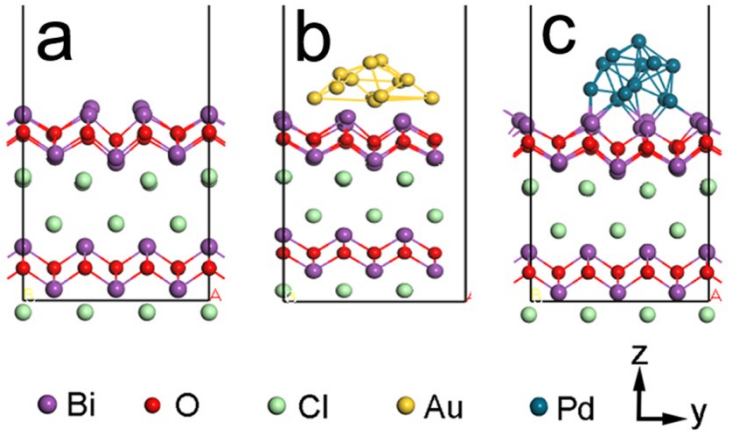

Figure S4. Optimized structures of (a) BiOCl(001), (b) Au-BiOCl(001), and (c) Pd-BiOCl (001) surface models with a V_O site.

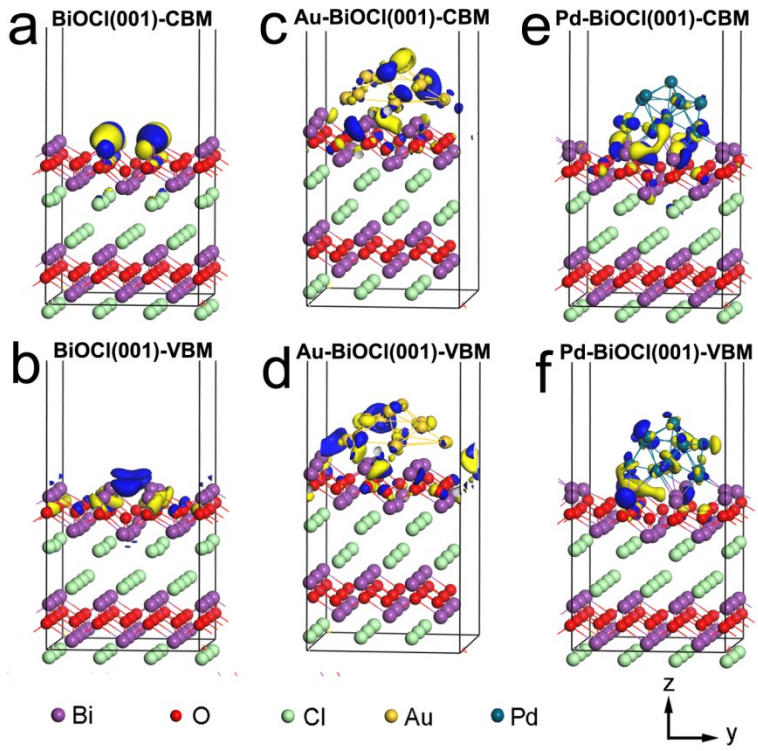

Figure S5. CBM and VBM of (a-b) BiOCl(001), (c-d) Au-BiOCl(001), and (e-f) Pd-BiOCl (001).

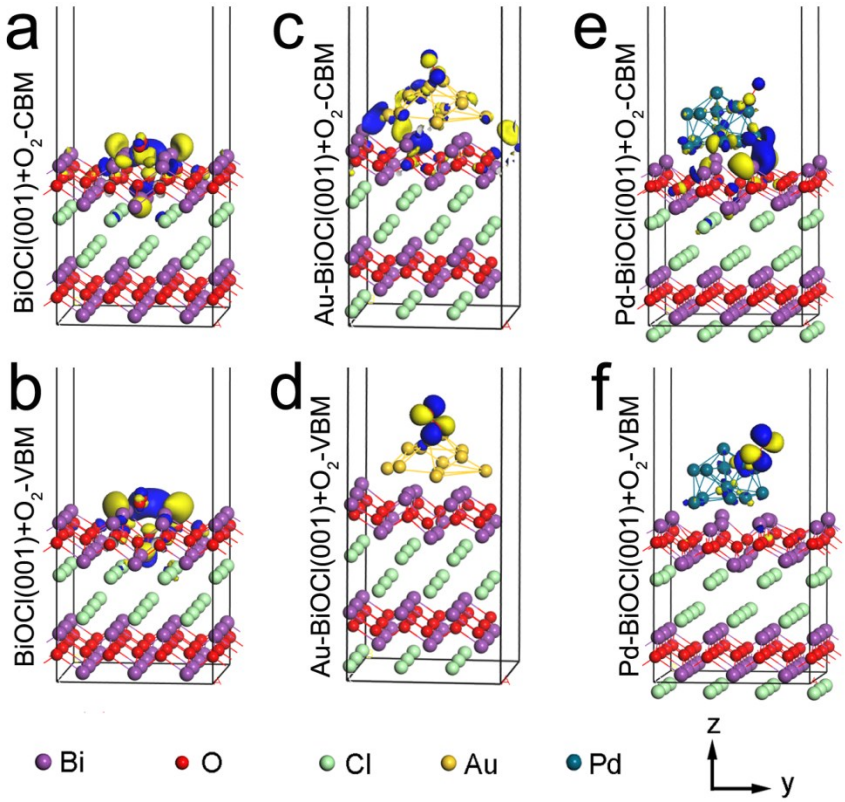

Figure S6. CBM and VBM of the different material systems with the adsorbed O_2. (a-b) bare, (c-d) Au decorated, (e-f) Pd decorated BiOCl (001) with a V_O site, respectively.

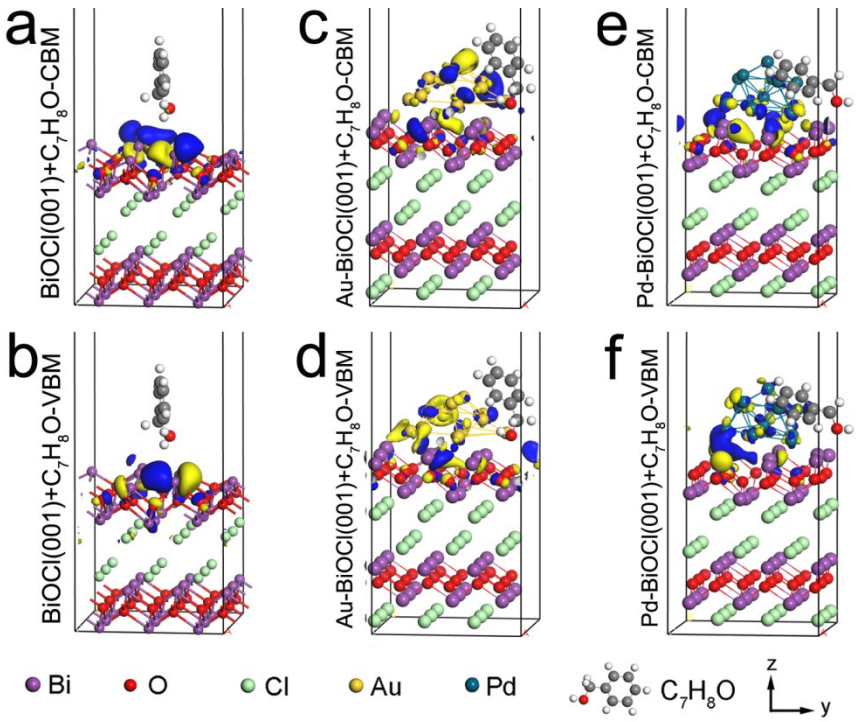

Figure S7. CBM and VBM of the different material systems with the adsorbed benzyl alcohol. (a-b) bare, (c-d) Au decorated, (e-f) Pd decorated BiOCl (001) with a V_O site, respectively.

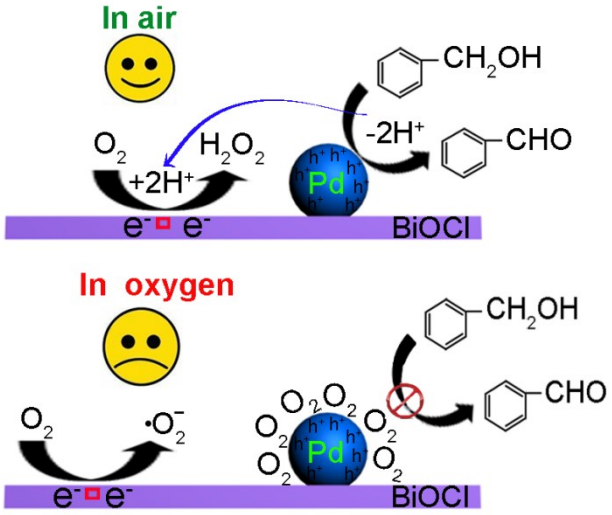

Figure S8. Schematic illustrations for photocatalytic reactions carried out in air and pure O_2 atmosphere, respectively.

Table S1. Theoretical and ICP-OES measured metal loading amounts of the photocatalysts.

Sample	Theoretical Au(or Pd) contents (wt.%)[a]	Actual Au (or Pd) contents (wt.%)[b]
Au-BiOCl	1.5	1.24
Pd-BiOCl	1.5	1.31

[a] The theoretical metal loading mass percent calculated from the experimental dosage of $HAuCl_4$ or $(NH_4)_2PdCl_4$ for photo-deposition.

[b] The actual mass percent of metal in each photocatalyst from the ICP-OES measured results.

Table S2. The Hirshfeld charge of each atom in the different material systems and the adsorption energies for O_2 (E_{ads+O2}) and C_7H_8O ($E_{ads+C7H8O}$) on different surfaces, respectively.

System	$\mathbf{e_{Bi}}$	$\mathbf{e_{Cl}}$	$\mathbf{e_O}$	$\mathbf{e_M}$	$\mathbf{E_{ads+O2}}$ **(eV)**	$\mathbf{E_{ads+C7H8O}}$ **(eV)**
BiOCl	0.09*2 0.35*2 0.48*4 0.56*18	-0.22*27	-0.34*17 -0.36*18	--	-2.442	-0.554
Au-BiOCl	0.30*4 0.42*4 0.56*18	-0.20*3 -0.22*10 -0.24*14	-0.33*4 -0.35*27 -0.37*4	0.05*1 -0.01*3 -0.03*4 -0.04*4	-1.213	-0.827
Pd-BiOCl	0.27*4 0.35*2 0.48*2 0.57*28	-0.21*6 -0.22*10 -0.24*11	-0.34*10 -0.35*11 -0.37*14	-0.02*2 -0.04*4 -0.07*3 -0.09*3	-1.611	-1.094

Table S3. Lifetimes (τ_1, τ_2 and τ_m[a]) and relative intensities (A_i) obtained by fitting the time-resolved PL decay spectra of BiOCl, Au-BiOCl and Pd-BiOCl to a bi-exponential decay function.

Sample	τ_1/ns(int$_1$)	τ_2/ns(int$_2$)	τ_m/ns
BiOCl	0.295(0.868)	2.320(0.132)	0.560
Au-BiOCl	0.298(0.878)	3.200(0.122)	0.645
Pd-BiOCl	0.800(0.828)	3.597(0.172)	1.283

[a] average lifetime, $\tau_m = \frac{A_1 \cdot \tau_1 + A_2 \cdot \tau_2}{A_1 + A_2}$

Table S4. Photocatalytic oxidation of benzyl alcohol to benzaldehyde over the different photocatalysts under UV-vis irradiation for 8 h [a].

Photocatalyst	Atmosphere	Conversion (%)	Yield(%)	selectivity (%)
BiOCl	Air	46	46	>99
L-BiOCl	Air	58	58	>99
Au-BiOCl	Air	71	71	>99
Pd-BiOCl	Air	99	99	>99
	O_2	62	62	>99
	N_2	37	37	>99
Pd/BiOCl*	Air	76	76	>99

[a] In a typical reaction, 1 mg of catalyst was added to 2 mL of acetonitrile in a quartz tube, 50 μmol of benzyl alcohol were injected into the quartz tube. Keep the quartz tube sealed and start illuminating.

*The Pd/BiOCl sample was prepared by simply soaking BiOCl nanosheets into a Pd nanoparticles solution which was obtained by the reduction of $(NH_4)_2PdCl_4$ using $NaBH_4$.

Table S5. Photocatalytic selective oxidation of various aromatic alcohols to corresponding aldehydes over Pd-BiOCl under UV-vis irradiation for 8 h[a]

Aromatic alcohol	Conversion (%)	Yield (%)	Selectivity (%)
Benzyl alcohol	99	92.07	＞99
4-Methylbenzyl alcohol	81	80.19	＞99
4-Methoxybenzyl alcohol	47	47	＞99
Cinnamyl alcohol	47	47	＞99
2-Phenylethanol	40	40	＞99

[a] In a typical reaction, 1mg of catalyst was added to 2 mL of acetonitrile in a quartz tube, 50 μmol of aromatic alcohol were injected into the quartz tube. Keep the quartz tube sealed and start illuminating.

Table S6. Photocatalytic oxidation of benzyl alcohol to benzaldehyde over Pd-BiOCl by adding different scavengers under UV-Vis irradiation for 8 h [a].

Scavenger	Conversion (%)	Yield (%)	Selectivity (%)
No scavenger	99	92.07	＞99
IPA	89	84.55	＞99
BQ	52	52	＞99
EDTA-2Na	36	36	＞99

[a] In a typical reaction, 1mg of catalyst was added to 2 mL of acetonitrile in a quartz tube, 50 μmol of benzyl alcohol and 0.05mol/L scavengers were injected into the quartz tube. Keep the quartz tube sealed and start illuminating.