Supporting Information

Investigating Catechol adsorption to the ZnO ($10\bar{1}0$) surface with and without an oxygen vacancy using the DFT-D2 method

By

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S1. Characterization and Instrumentation

The prepared sample was characterized using several advanced techniques. X-ray diffraction (XRD) analysis was performed using a Rigaku Miniflex 600 desktop instrument (Rigaku Corporation) with a Cu Kα radiation source (λ = 1.54056 Å), scanning at a rate of 5° per minute and a step size of 0.01°. The presence of functional groups and the stretching frequency of the metal oxide were detected using Fourier-transform infrared spectroscopy (FTIR) analysis conducted with a Nicolet iS5 instrument (Thermo Electron Scientific Instruments LLC). X-ray photoelectron spectroscopy (XPS) was performed using a K-alpha instrument (Physical Electronics) to identify the elemental composition and oxidation states. The surface morphology and element composition were obtained from Field Emission Scanning Electron Microscopy (FE-SEM) with Zeiss GeminiSEM 560. The images of the nanostructure were obtained using transmission electron microscopy (TEM) with a Tecnai G2 20 TWIN instrument. The UV–visible spectrophotometer (Agilent Cary 60) was used to monitor the adsorption spectra of the supernatants. All adsorption experiments were performed in a thermostatic agitator or shaker (Narang Scientific Works PVT. LTD.) maintained at 150 rpm.

S2. Materials

Analytical reagent (AR) grade materials used for the synthesis of ZnO were $Zn(NO_3)_2.6H_2O$ (SRL ~99%), NaOH (Merck, ≥ 97%), and catechol (SRL, 99%) used without further purification. For the synthesis of ZnO and the adsorption of catechol on ZnO, double-distilled water was used.

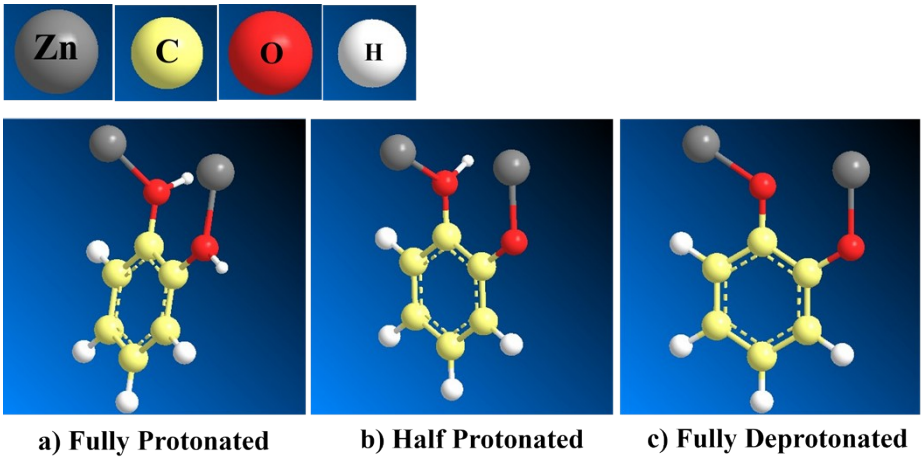


Figure. S1 Structure of catechol in **(a)** fully protonated, **(b)** half protonated, and **(c)** fully deprotonated form.

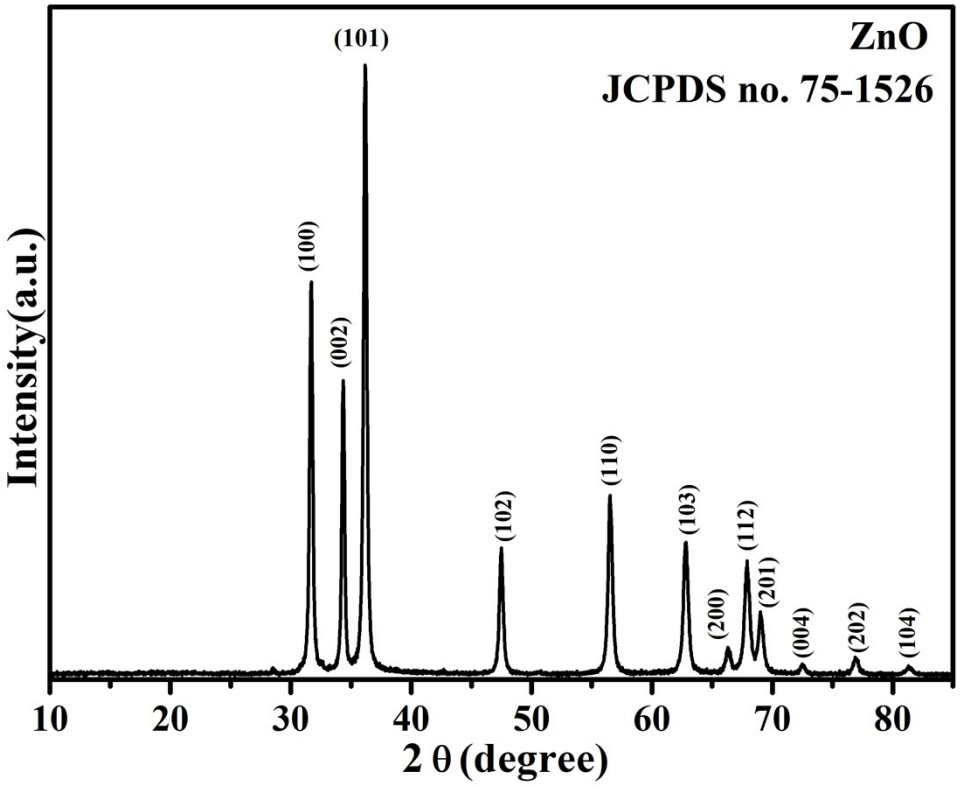


Figure. S2 XRD pattern of the synthesized ZnO particles.

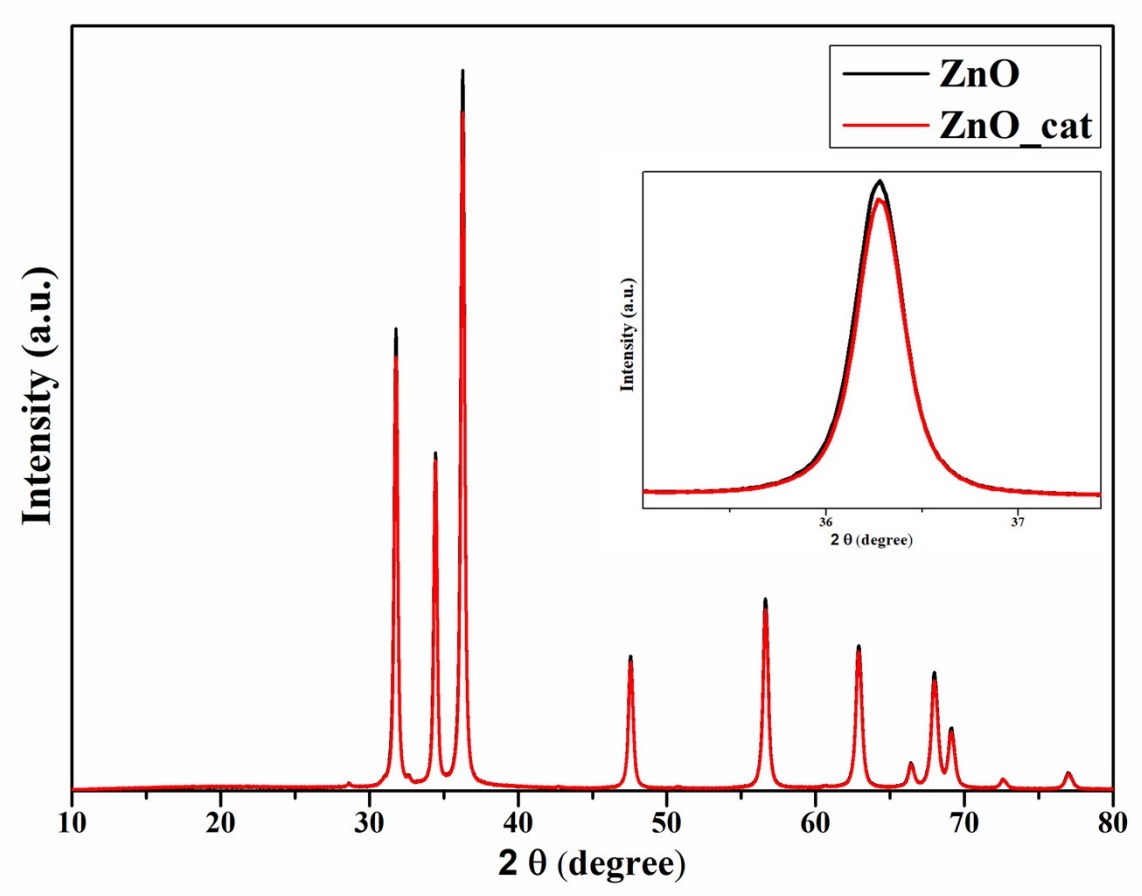


Figure. S3 XRD pattern of the synthesized ZnO particles before and after adsorption.

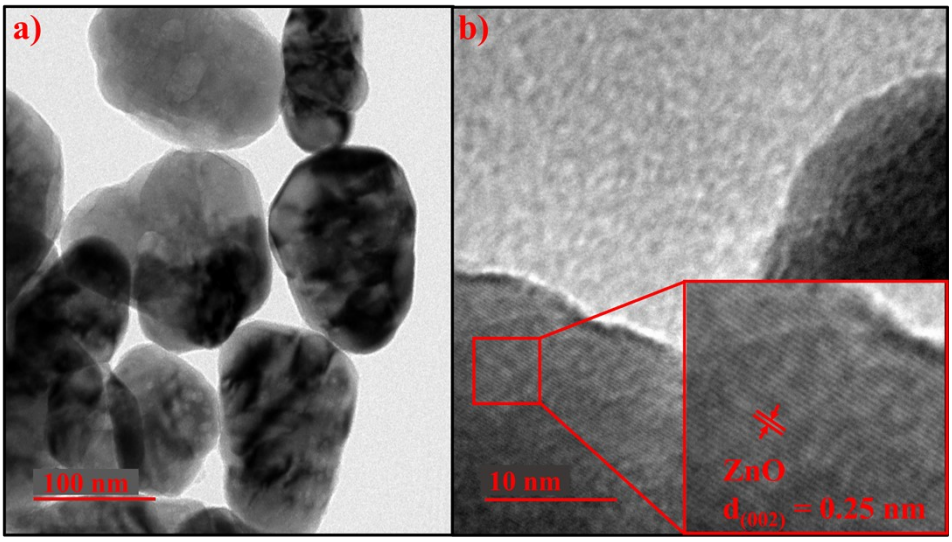
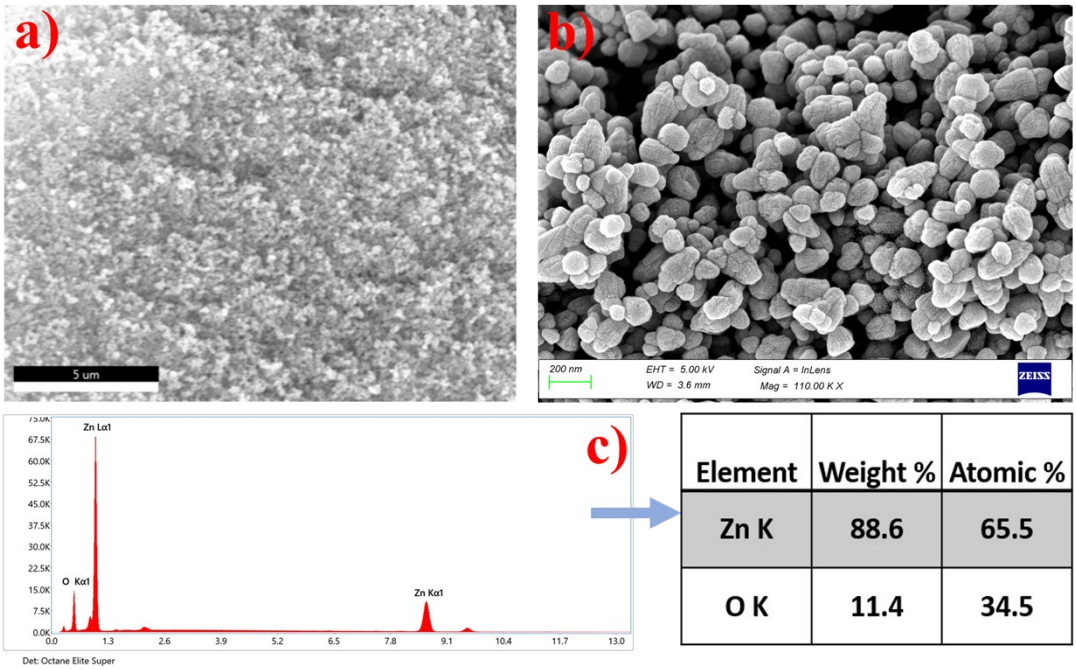


Figure. S4 a) TEM and **b)** HR-TEM image of ZnO.



Element	Weight %	Atomic %
Zn K	88.6	65.5
O K	11.4	34.5

Figure. S5 a) SEM image, **b)** HR-SEM image, **(c)** Atomic percentage distribution of elements in the ZnO determined by EDX analysis.

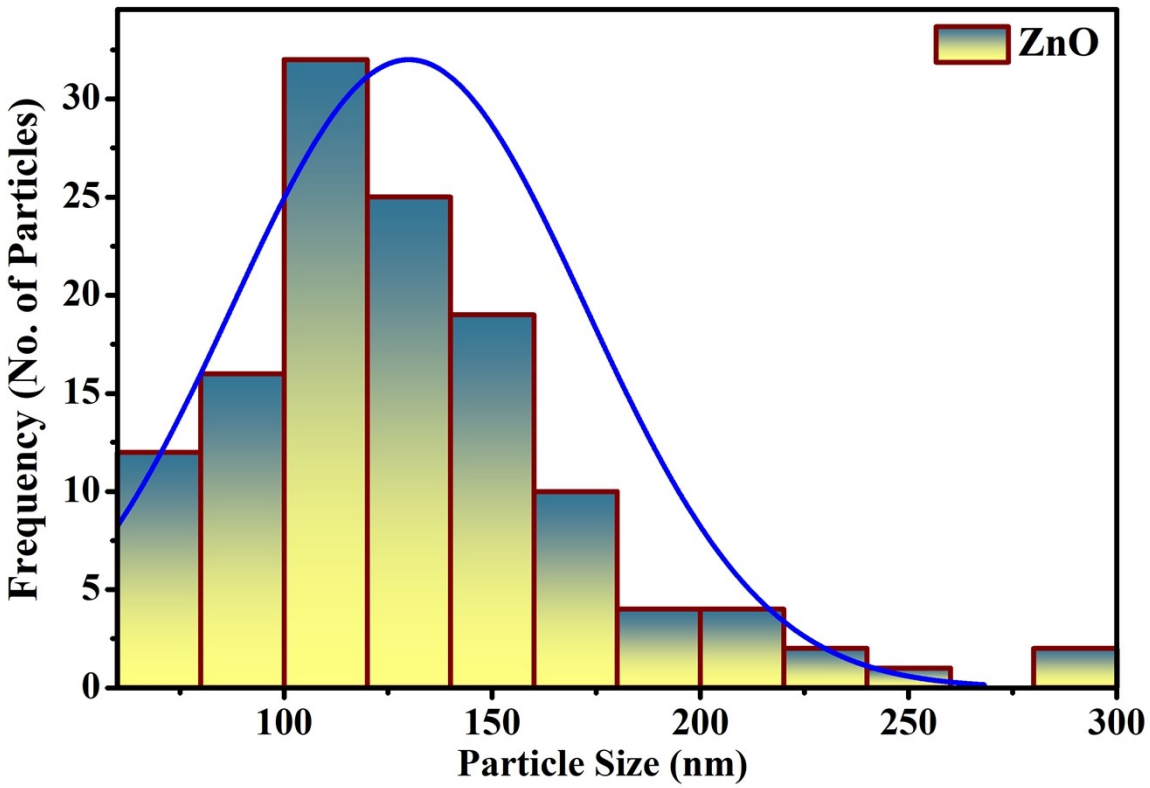


Figure. S6 Particle size distribution of ZnO found from FE-SEM images of the samples.

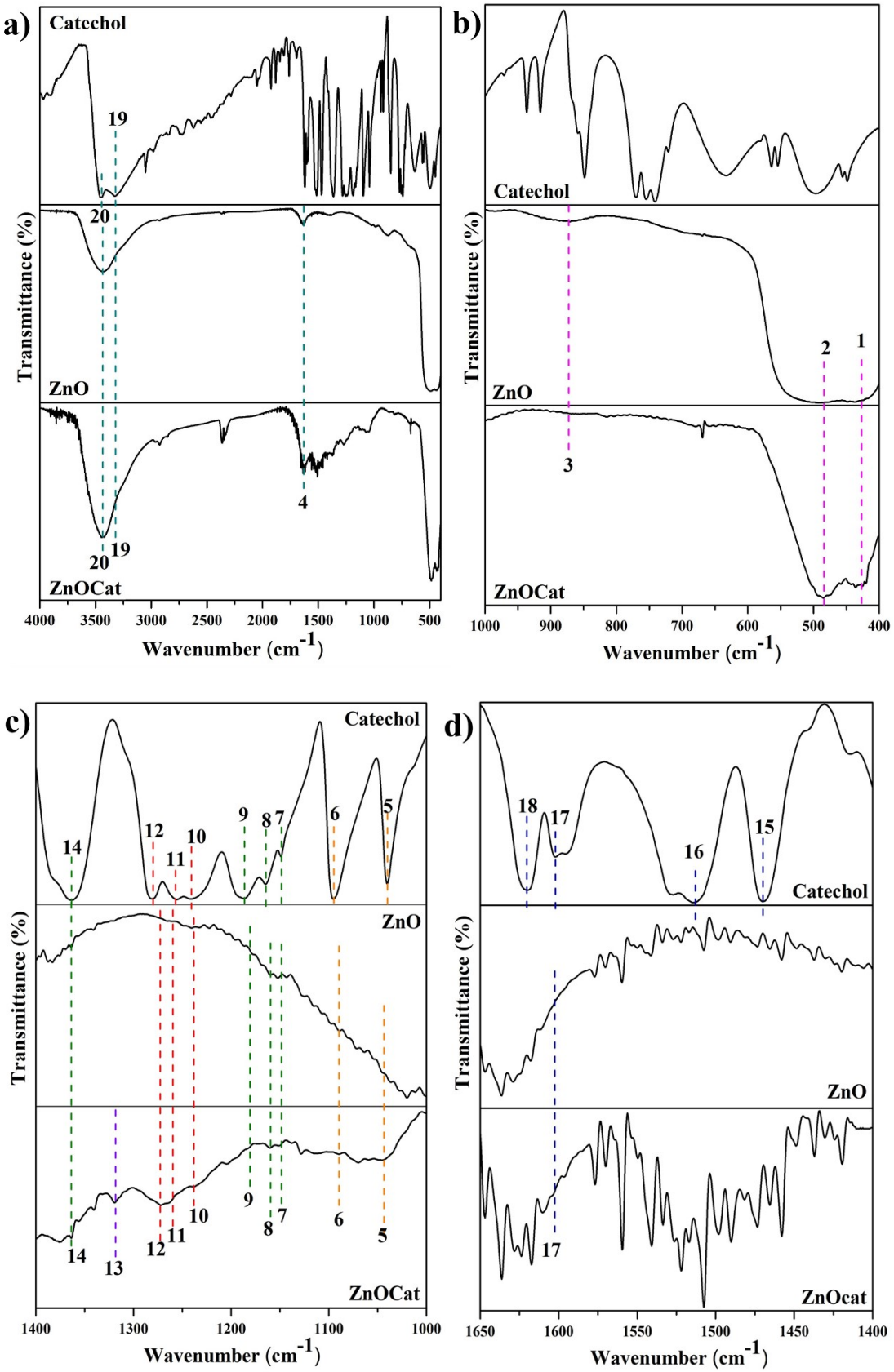


Figure. S7 A comparison of FTIR of catechol, ZnO, and ZnOcat. **a)** FTIR of catechol, ZnO and Znocat from 400 to 4000 cm^{-1} and vibrations of the O-H bond of water in ZnO and Znocat. Magnified graph of **b)** stretching vibrations of ZnO, **c)** assignment of vibrations of C-H and C-OH bonds of catechol **d)** vibrations of the C-C and C=C bonds of the phenyl ring.

Table S1. FTIR peaks of ZnO, Catechol and ZnOcat

Peak Number	Vibrations	ZnO* Wavenumber (cm^{-1})	Catechol** Wavenumber (cm^{-1})	ZnOcat*** Wavenumber (cm^{-1})
1	ν (Zn-O)	439	-	439
2	ν (Zn-O)	490	-	490
3	ν (Zn-O)	870	-	-
4	δ (O-H)	1636	-	1636
5	δ (C-H)	-	1040	1045
6	δ (C-H)	-	1093	1089
7	δ (C-OH)	-	1149	150
8	δ (C-OH)	-	1164	1160
9	δ (C-OH)	-	1187	1190
10	ν (C-OH)	-	1241	1239 (broad)
11	ν (C-OH)	-	1255	1260 (broad)
12	ν (C-OH)	-	1278	1271 (broad)
13	ν (C-O)	-	-	1319
14	δ (C-OH)	-	1363	1363
15	ν (C-C)/ ν (C=C)	-	1468	-
16	ν (C-C)/ ν (C=C)	-	1513	-
17	ν (C-C)/ ν (C=C)	-	1598	1596
18	ν (C-C)/ ν (C=C)	-	1619	-
19	ν (O-H) (bond involved in Hydrogen bonding)	-	3327	-
20	ν (O-H) (not involved in hydrogen bonding)	3443	3447	3443 (broad)

* FTIR peaks of ZnO before adsorption

**FTIR peaks of catechol before adsorption

*** FTIR peaks after adsorption of catechol on ZnO

Note: ν and δ represent stretching and bending vibrations, respectively

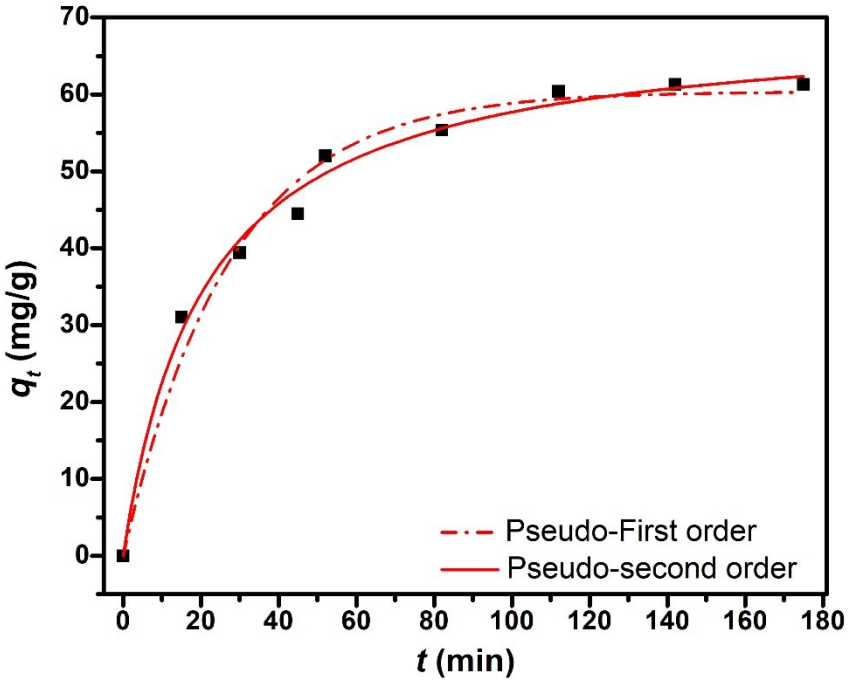


Figure. S8 Non-linear kinetics models fitting for the adsorption of catechol over the ZnO surface. (Reaction condition- 10mg ZnO adsorbent was added into the 20 ml solution of 100 ppm catechol, pH=neutral)

Table S2. Nonlinear kinetics data for the PFO and PSO kinetics model for the adsorption of catechol on ZnO

Kinetics model	k**(min^{-1})**	q_e **(mg.g^{-1})**	**R^2**
Pseudo-first order	0.037	60.36	0.979
Pseudo-second order	6.82	69.81	0.992

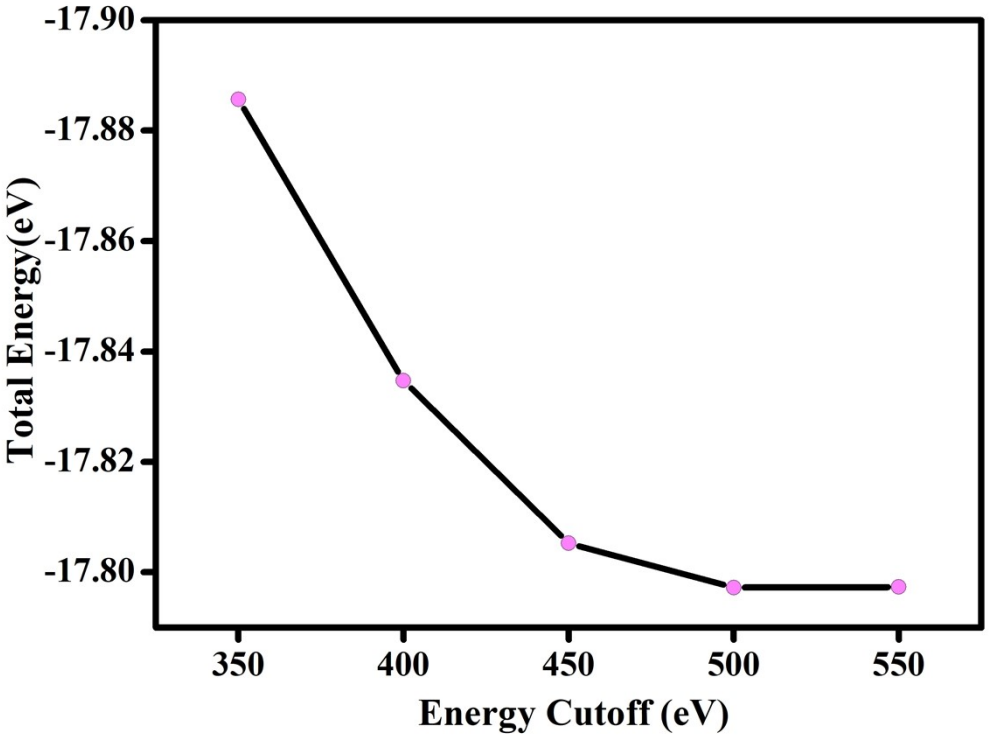


Figure. S9 Energy cut off optimization of unit cell of (ZnO)2

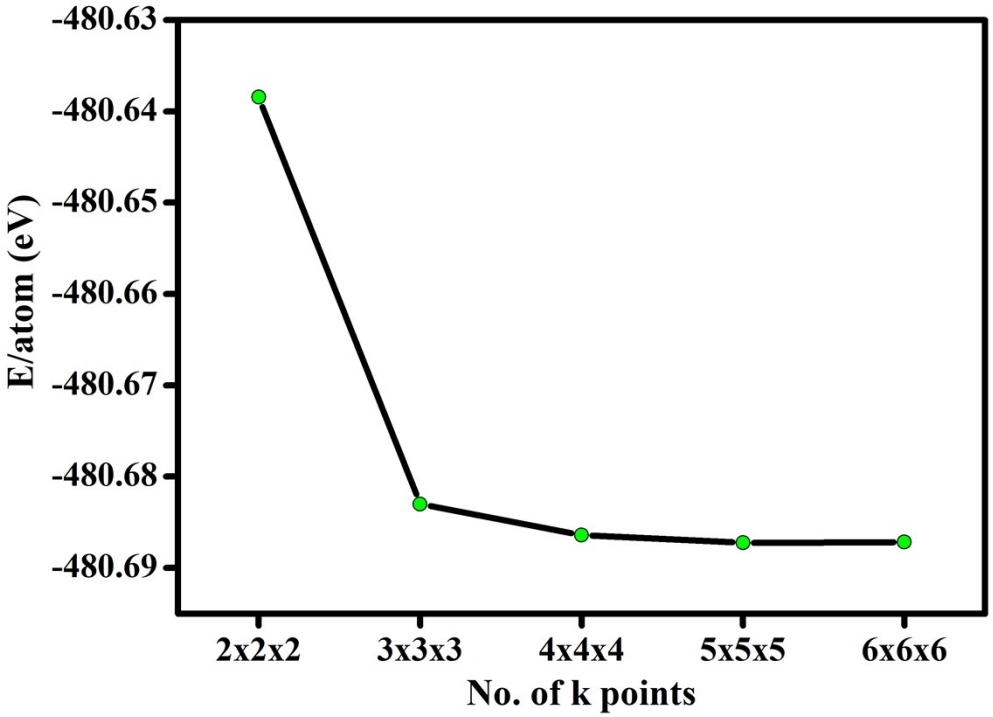


Figure. S10 k-point optimization of (ZnO)54 3 × 3 × 3 supercell.

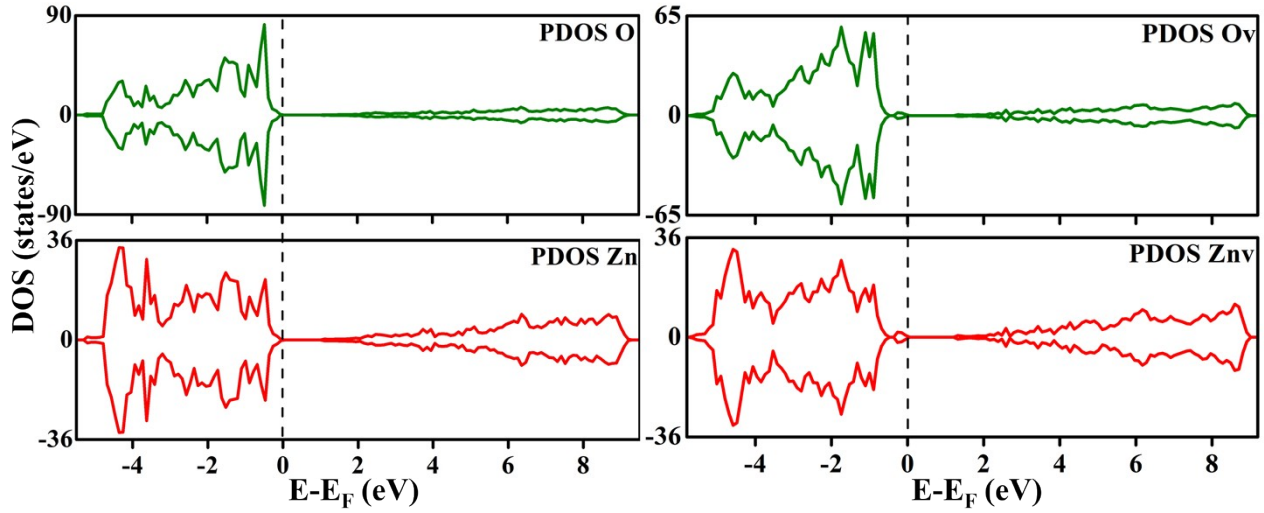


Figure. S11 The PDOS of Zn and O, making the **a)** ZnO and **b)** the ZnOv $(10\bar{1}0)$ surfaces.

Table S3. Comparison of the DFT calculated bond parameters (bond lengths and bond angles) of catechol with values from the literature.[1]

Atom	Present work	Experimental[2]	CG* method[3]	HF/6-31G(d,p)[4]	AMEOBA[5]	B3LYP[5]
Bond Length(Å)						
C-C	1.39(average)	1.40(average)	-	-	-	-
C1-O55	1.37	1.36	1.36	1.35	-	-
C2-O56	1.38	1.38	1.38	1.36	-	-
C-H	1.09	1.08	-	-	-	-
O55-H5	0.972	0.86	0.98	0.95	0.968	0.965
O56-H6	0.976	0.86	0.97	0.94	0.973	0.962
Bond Angle(°)						
C1-O55-H5	107	111	107.1	109.6	107.2	108.3
C2-O56-H6	109	108	111.3	111.4	110.8	110.5
C1-C2-O56	114.819	117.02	113.4	115.6	-	-
C2-C1-O55	120.121	121.06	-	-	-	-

Note: *Conjugated Gradient

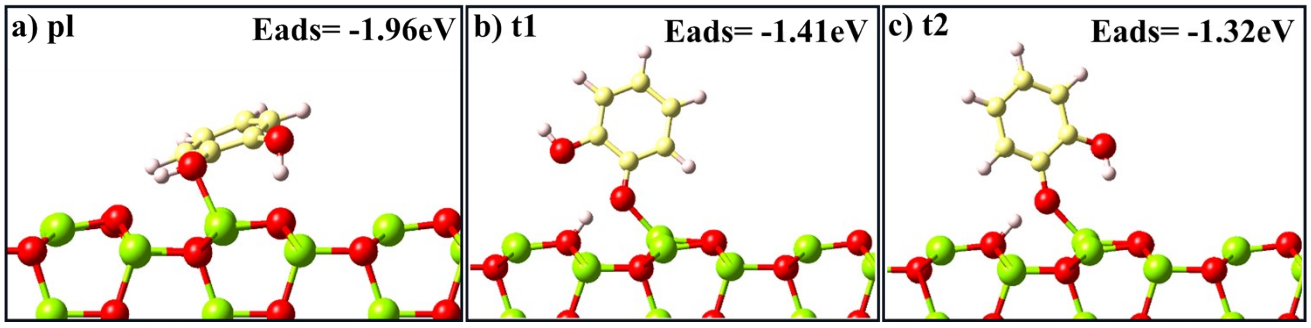


Figure. S12 Optimized configuration of catechol on ZnO surface a) pl, b) t1 and c) t2

Table S4. Bond lengths and bond angles before and after catechol adsorption in configuration 'pr'.

Name of Bond	Bond Length(Å)	
	Before Adsorption	**After adsorption**
C1-C4	1.39	1.41
C5-C4	1.39	1.39
C6-C5	1.39	1.39
C6-C3	1.39	1.39
C2-C3	1.39	1.39
C1-C2	1.40	1.41
C2-O56	1.38	1.40
C1-O55	1.37	1.36
O56-H6	0.97	1.03
O56-Zn9	-	**2.05**
O55-H5	0.97	-
O55-Zn27	-	**1.96**
H5-O21	-	**1.07**
Zn9-O7	1.90	1.98
Zn9-O25	1.90	1.97
Zn27-O25	1.90	2.00
Zn27-O43	1.90	2.00
Zn27-O27	1.83	1.96
Zn9-O9	1.83	1.86
	Bond Angle (°)	
	Before Adsorption	**After Adsorption**
C1-C2-O56	**114.82**	**121.60**
C2-C1-O55	120.12	122.61
Zn27-O55-C1	-	126.05
Zn9-O56-C2	-	128.47
Zn9-O25-Zn27	114.91	104.69

Table S5. A comparison of the adsorbent-adsorbate (metal oxide-catechol) interaction lengths and adsorption energies given in previously published studies with the current research. Column 3 provides the metal (on metal oxide)-oxygen (on the catechol) interaction lengths (Å) due to catechol adsorption on metal oxide. Column 4 of the Table displays the associated O_s-H_c interaction/bond length (O of metal oxide surface, and H of catechol), while column 5 shows the DFT calculated adsorption energy of catechol on metal oxide surface on different systems.

Material	Interaction/Bonding type	Bond length of Metal-O_c* (Å)	Bond length of O_s-H_c** (Å)	Eads (eV)	Reference
ZnO $(10\bar{1}0)$	Bidentate with dissociation of one	1.96 2.05	1.07	-2.14	This work

	hydrogen of catechol				
ZnO nanocluster (12 Zn and 12 O atoms)	Monodentate without dissociation of H	2.27	-	-3.45	ref[6]
ZnO/RGO	Bidentate without dissociation of H	1.96	-	-4.09	ref[6]
TiO_2 (anatase) (101) plane	Monodentate with dissociation of one H of catechol	1.94 2.33	0.972	0.810	ref[7]
TiO_2 (anatase) (101) plane	Bidentate with dissociation of both H of catechol	1.91 1.91	0.972 0.974	0.903	ref[7]
$H_2Ti_3O_7$	Monodentate with dissociation of one H of catechol	1.95	0.974	1.096	ref[7]
TiO_2(B)	Bidentate with dissociation of both H of catechol	1.92 1.92	0.976 0.976	-0.489	ref[7]

Note: *represents the bond length between the metal of the different metal oxides surface and the oxygen of catechol after adsorption.

**denotes the bond length between the oxygen of the metal oxide surface and the H of the catechol after adsorption.

Table S6. Change in bond length before and after adsorption of catechol on ZnOv

Name of Bond	Bond Length(Å)

	Before Adsorption	After adsorption
C1-C4	1.39	1.39
C5-C4	1.39	1.39
C6-C5	1.39	1.39
C6-C3	1.39	1.39
C2-C3	1.39	1.39
C1-C2	1.40	1.40
C2-O55	1.38	1.37
C1-O54	1.37	1.39
O55-H6	0.97	1.03
O55-Zn9	-	-
O54-H5	0.98	0.99
O54-Zn27	-	**2.31**
Zn9-O7	1.90	1.90
Zn9-O25	1.90	1.90
Zn27-O25	1.90	1.96
Zn27-O43	1.90	1.96
Zn27-O27	1.83	1.85
Zn9-O9	1.83	1.83
	Bond Angle (°)	
	Before Adsorption	**After Adsorption**
C1-C2-O55	114.82	118.49
C2-C1-O54	120.12	118.39
Zn27-O54-C1	-	126.35

Table S7. Bader charges on Zn and O atoms, making the ZnO and the ZnOv $(10\bar{1}0)$ slabs before and after the adsorption of catechol.

Atoms	ZnO before adsorption (*e*)	ZnO after adsorption (*e*)	ZnOv before Adsorption (*e*)	ZnOv after adsorption (*e*)
Zn1	1.2178	1.208	1.1971	1.2023
Zn2	1.1884	1.1851	1.1862	1.185
Zn3	1.1626	1.1764	1.1554	1.1699
Zn4	1.2066	1.2063	1.1879	1.1883
O1	-1.1998	-1.1898	-1.1857	-1.1902
O2	-1.2038	-1.2028	-1.2003	-1.1992
O3	-1.161	-1.1836	-1.1634	-1.1883
O4	-1.1988	-1.1985	-1.1973	-1.1975
Zn5	1.1912	1.1899	1.2035	1.2031

Zn6	1.1511	1.1525	1.1683	1.1686
O5	-1.1756	-1.1772	-1.1925	-1.1925
O6	-1.1667	-1.1668	-1.1641	-1.164
Zn7	1.2178	1.1754	1.1905	1.1911
Zn8	1.1884	1.1948	1.1835	1.1841
Zn9	1.1626	1.2307	1.1634	1.1558
Zn10	1.2066	1.2079	1.1906	1.1895
O7	-1.1998	-1.1715	-1.1757	-1.1787
O8	-1.2038	-1.1983	-1.1967	-1.1966
O9	-1.161	-1.1871	-1.1623	-1.1608
O10	-1.1988	-1.2012	-1.1965	-1.1967
Zn11	1.1912	1.1918	1.2036	1.2038
Zn12	1.1511	1.1512	1.1607	1.1609
O11	-1.1756	-1.1735	-1.1902	-1.1899
O12	-1.1667	-1.1656	-1.1581	-1.1582
Zn13	1.2178	1.2028	1.198	1.1978
Zn14	1.1884	1.1889	1.1833	1.1823
Zn15	1.1626	1.1624	1.1622	1.1621
Zn16	1.2066	1.2051	1.1873	1.1875
O13	-1.1998	-1.1862	-1.1815	-1.1802
O14	-1.2038	-1.2014	-1.1964	-1.1969
O15	-1.161	-1.1596	-1.1616	-1.1627
O16	-1.1988	-1.1981	-1.1964	-1.1966
Zn17	1.1912	1.1903	1.2013	1.2012
Zn18	1.1511	1.1501	1.1613	1.1611
O17	-1.1756	-1.1755	-1.1923	-1.1922
O18	-1.1667	-1.1682	-1.1571	-1.1577
Zn19	1.2178	1.1995	1.1948	1.1967

Zn20	1.1884	1.1869	1.174	1.175
Zn21	1.1626	1.2033	0.6113	0.6247
Zn22	1.2066	1.2066	1.1855	1.1855
O19	-1.1998	-1.1863	-1.1804	-1.18
O20	-1.2038	-1.2019	-1.1876	-1.1874
O21	-1.161	-1.2299	-	-
O22	-1.1988	-1.1981	-1.1983	-1.1983
Zn23	1.1912	1.19	1.1984	1.198
Zn24	1.1511	1.1526	1.1618	1.1618
O23	-1.1756	-1.1776	-1.182	-1.182
O24	-1.1667	-1.1668	-1.1591	-1.159
Zn25	1.2178	1.201	0.928	0.9341
Zn26	1.1884	1.1998	1.1736	1.1798
Zn27	1.1626	1.2042	1.1468	1.2077
Zn28	1.2066	1.2089	1.1685	1.1697
O25	-1.1998	-1.2012	-1.1843	-1.1946
O26	-1.2038	-1.1997	-1.1867	-1.1868
O27	-1.161	-1.158	-1.158	-1.1798
O28	-1.1988	-1.2011	-1.1826	-1.1834
Zn29	1.1912	1.1917	1.2041	1.2044
Zn30	1.1511	1.1504	1.1601	1.1601
O29	-1.1756	-1.1735	-1.1877	-1.1875
O30	-1.1667	-1.1655	-1.1585	-1.1585
Zn31	1.2178	1.1901	1.1955	1.1915
Zn32	1.1884	1.1887	1.1907	1.1893
Zn33	1.1626	1.163	1.1662	1.1621
Zn34	1.2066	1.2051	1.1818	1.1822
O31	-1.1998	-1.1671	-1.183	-1.172

O32	-1.2038	-1.2006	-1.2046	-1.2047
O33	-1.161	-1.165	-1.1579	-1.1562
O34	-1.1988	-1.1981	-1.1965	-1.1968
Zn35	1.1912	1.1902	1.2041	1.204
Zn36	1.1511	1.1504	1.1609	1.1607
O35	-1.1756	-1.1755	-1.1903	-1.1901
O36	-1.1667	-1.1685	-1.1586	-1.159
Zn37	1.2178	1.2068	1.1948	1.1939
Zn38	1.1884	1.1859	1.174	1.1747
Zn39	1.1626	1.1586	1.1554	1.1579
Zn40	1.2066	1.2063	1.1879	1.1881
O37	-1.1998	-1.193	-1.1804	-1.1781
O38	-1.2038	-1.2032	-1.1876	-1.1868
O39	-1.161	-1.1564	-1.1634	-1.1656
O40	-1.1988	-1.198	-1.1973	-1.1974
Zn41	1.1912	1.1902	1.2035	1.2031
Zn42	1.1511	1.1525	1.1618	1.1618
O41	-1.1756	-1.1772	-1.1925	-1.1924
O42	-1.1667	-1.1669	-1.1591	-1.1591
Zn43	1.2178	1.1963	0.928	0.9336
Zn44	1.1884	1.1941	1.1736	1.1806
Zn45	1.1626	1.1538	1.1634	1.1594
Zn46	1.2066	1.2095	1.1906	1.1909
O43	-1.1998	-1.183	-1.1843	-1.1872
O44	-1.2038	-1.1989	-1.1867	-1.1871
O45	-1.161	-1.1601	-1.1623	-1.1618
O46	-1.1988	-1.2001	-1.1965	-1.1969
Zn47	1.1912	1.192	1.2036	1.2039

Zn48	1.1511	1.1509	1.1601	1.1603
O47	-1.1756	-1.174	-1.1902	-1.1898
O48	-1.1667	-1.1655	-1.1585	-1.1585
Zn49	1.2178	1.1992	1.1955	1.1911
Zn50	1.1884	1.1889	1.1907	1.1888
Zn51	1.1626	1.1629	1.1622	1.1599
Zn52	1.2066	1.2047	1.1873	1.1875
O49	-1.1998	-1.1804	-1.183	-1.1716
O50	-1.2038	-1.2011	-1.2046	-1.2044
O51	-1.161	-1.1605	-1.1616	-1.1611
O52	-1.1988	-1.1978	-1.1964	-1.1966
Zn53	1.1912	1.1905	1.2013	1.2012
Zn54	1.1511	1.1502	1.1609	1.1607
O53	-1.1756	-1.1756	-1.1923	-1.1921
O54	-1.1667	-1.1683	-1.1586	-1.159
Total charge	0.108	0.146	0.1053	0.1586

Table S8. Bader charges on C, H, and O atoms constituting catechol before and after its adsorption to the $(10\bar{1}0)$ surfaces of ZnO and ZnOv.

Atom	Atomic charge on Catechol (*e*)	Atomic Charge (*e*)	
		$Catechol_{ZnO}$*	$Catechol_{ZnOv}$**
C1	0.4554	0.5824	0.3336
C2	0.4285	0.3964	0.5348
O55	**-1.1344**	**-1.189**	-1.1716
O56	**-1.1347**	**-1.1843**	-1.2221
H6	0.6151	0.6375	0.6444
H5	0.6367	0.6409	0.6052
C3	-0.0288	-0.0114	0.0026
C4	-0.0081	-0.0035	0.0017
C5	0.0448	-0.1382	-0.0415
C6	-0.064	-0.0054	-0.0189
H1	0.0683	0.0668	0.0667
H2	0.0669	0.0672	0.0986
H3	0.0524	0.0729	0.0667
H4	0.0627	0.0545	0.0694
Total charge	0.0608	-0.0132	-0.0304

*Charges on atoms of Catechol after adsorption to the surface of ZnO.

**Charges on atoms of Catechol after adsorption to the surface of ZnO_v.

Note: In case of $Catechol_{ZnOv,}$ O55 and O56 are numbered as O54 and O55, respectively.

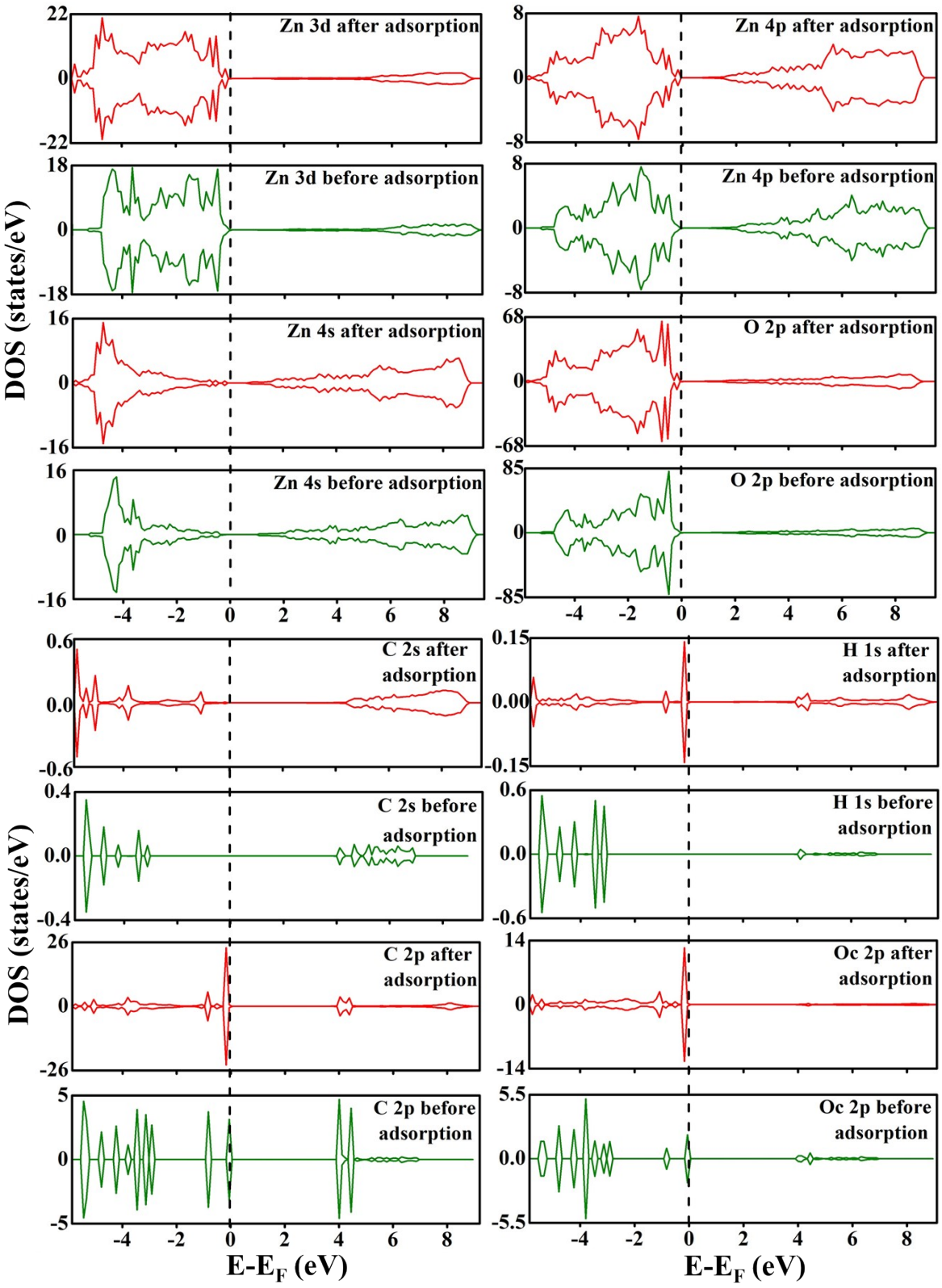


Figure. S13 Comparison of the PDOS of the orbitals of atoms in ZnO and catechol before and after adsorption (in the 'pr' configuration). The changes can be seen in the generation of new states as well as the variation in intensity.

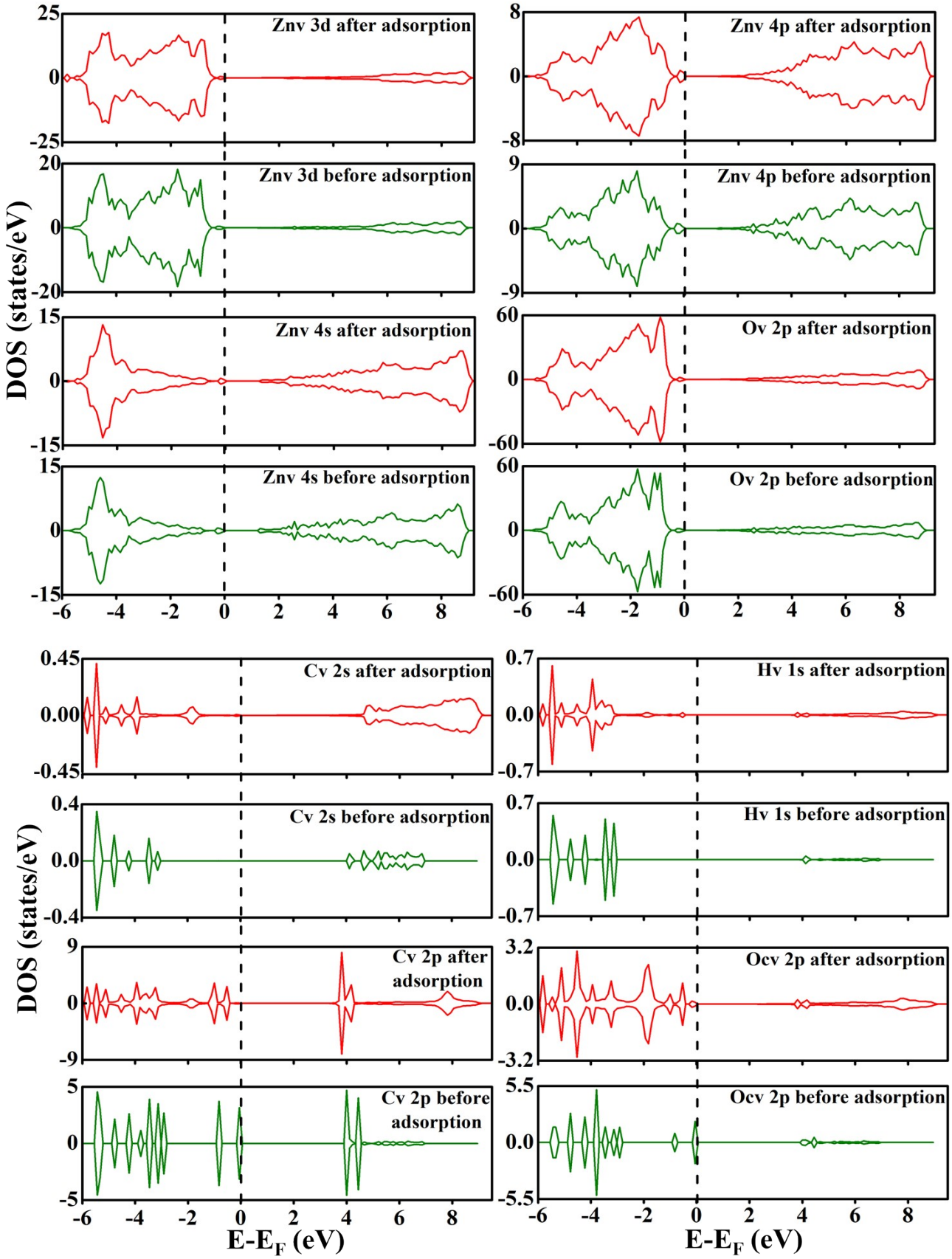


Figure. S14 Compares the PDOS of orbitals of atoms in ZnOv and catechol before and after adsorption (in the 'ovpr' configuration). The changes can be seen in the generation of a new state as well as the variation in intensity.

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