(Supplementary Information)

Enhanced d-d Transitions in HKUST/Bi_2WO_6 Nanocomposite Mediate Visible-Light Driven Selective Conversion of Benzyl Alcohol to Benzaldehyde

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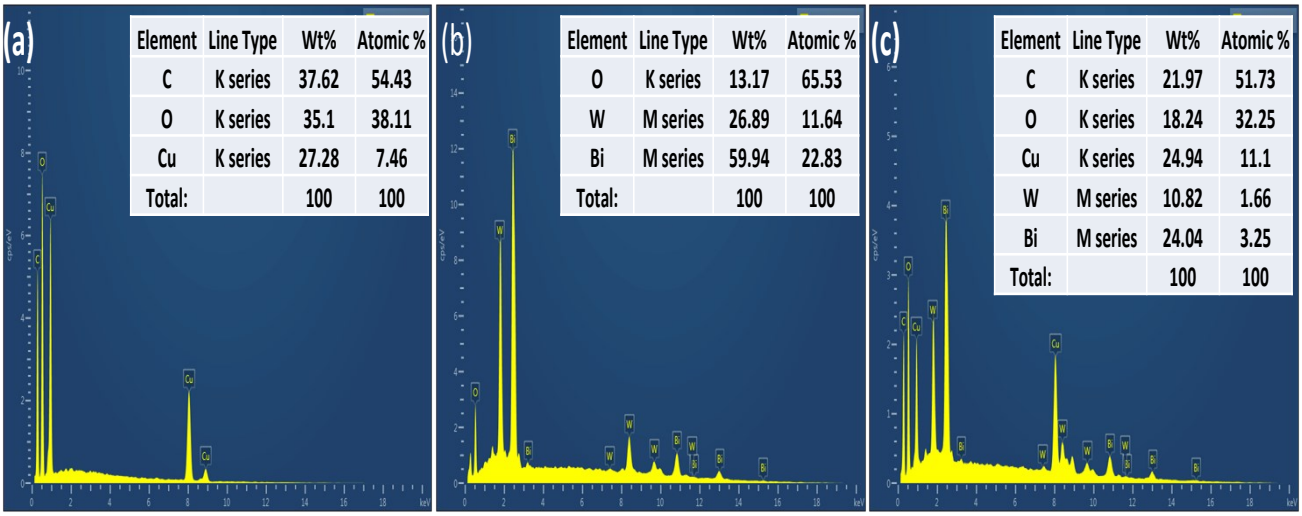

Figure S1 : EDX data of (a)HKUST MOF (b) Bi_2WO_6 (c) HKUST/Bi_2WO_6

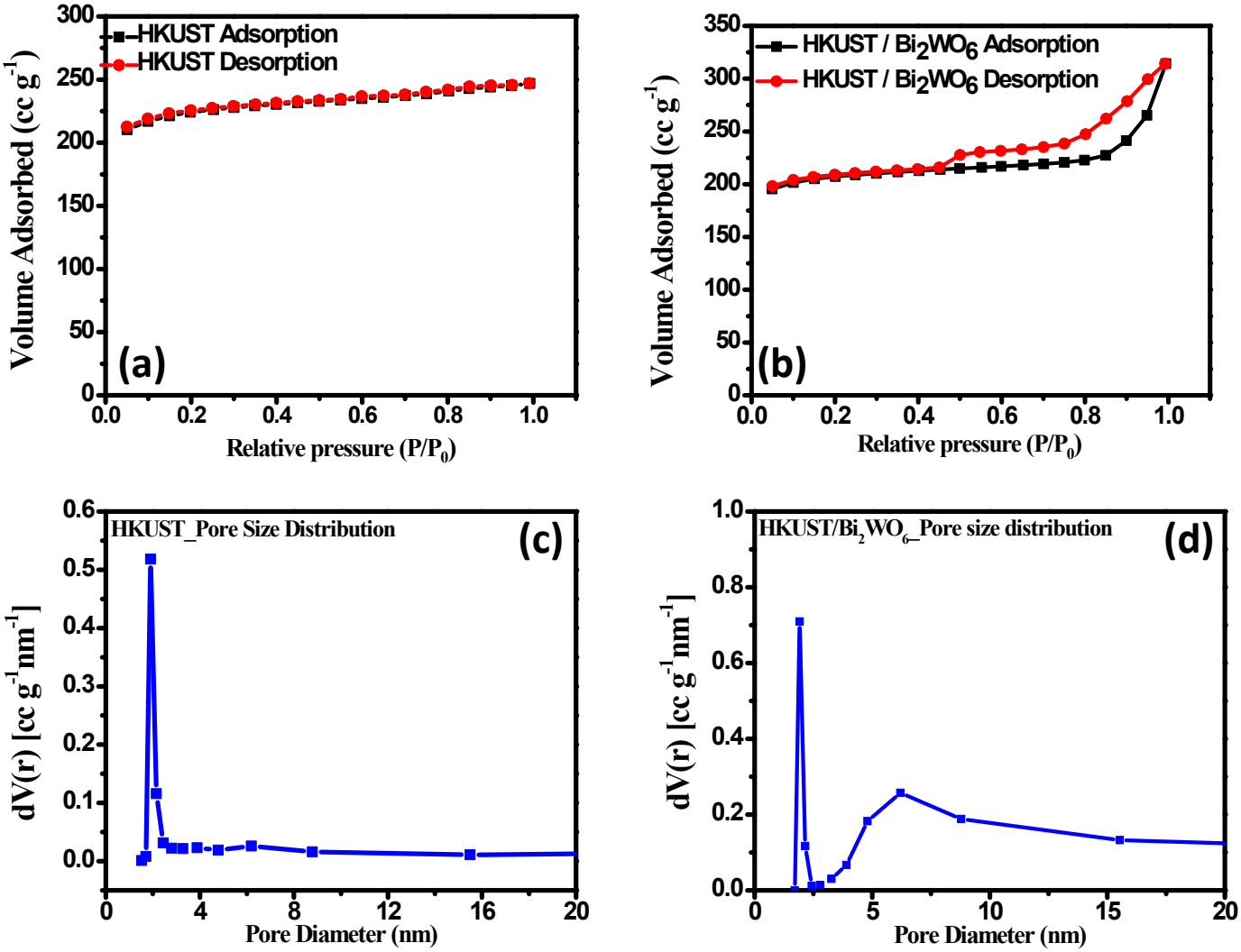

Figure S2. The N2 adsorption-desorption isotherms of (a)HKUST (b) HKUST/Bi_2WO_6 and BJH pore distributions plots of (c) HKUST(d) HKUST/Bi_2WO_6

Table S1. Solvent screening results for photocatalytic conversion of benzyl alcohol to benzaldehyde

S.NO.	Solvent	% conversion	% selectivity
1.	No solvent	**83**	**95**
2.	Water	**60**	**90**
3.	Methanol	**66**	**90**
4.	Xylene/Toulene	**84**	**95**

Calculations:

Band Gap calculations:

The optical band gap of samples was calculated from the following formula reported by Butler[1]

$$\alpha h\nu = A(h\nu - Eg)^{n/2} \quad (1)$$

where α, *h*, *v*, and Eg are absorption coefficient, Planck's constant, light frequency, and bandgap energy respectively. The value of n for semiconductor is determined by the type of transition (n=1 for direct transition and n=4 for indirect transition). The value of Eg for HKUST and **HKUST**/Bi_2WO_6 was determined from the plot of $(\alpha h\nu)^2$ vs $h\nu$) and was found to be 3.45 eV and 2.7 eV.

Band Potential calculations:

The relative position of the valence band of pristine HKUST and pure Bi_2WO_6 were further investigated to derive the flow chart of photogenerated electron-hole pairs. The valence band edge of HKUST-1 and Bi_2WO_6 was calculated by the empirical equation given below[2]

$$E_{VB} = X - E_e + 0.5\ E_g \quad (2)$$

Here X is the electronegativity of the semiconductor, expressed as the geometric mean of the absolute electronegativity of the constituent atoms. E_e is the energy of free electrons on the hydrogen scale (4.5 eV) and E_g is the band-gap energy. Given the equation above (2) the top of the valence band for pristine HKUST-1 and Bi_2WO_6 were calculated to be **3.11eV** and **1.77eV** respectively.

The relative position of the conduction band (CB) of HKUST-1 and Bi_2WO_6 were calculated using equation (3)

$$E_{CB} = E_{VB} - Eg \quad (3)$$

Using this equation, the E_{CB} for HKUST and Bi_2WO_6 was calculated to be **-0.33eV** and**-1.04eV** respectively.

Also, the position of d bands of HKUST MOF was calculated by using equations 2 and 3. The calculations yield the lower d orbitals potential of **2.21eV** and higher d orbitals potential of **0.65 eV.**

Reactions potentials vis-a-vis the band potentials

From the bandgap potential diagram, we see the feasible transitions finally promote electrons to CB of HKUST MOF having a potential of **-0.33eV**. As we have seen from scavenging experiments formation of ($\bullet O_2$) from O_2 is important for this reaction and in our case, this reduction reaction becomes highly feasible. The standard reduction potential for this rxn to happen is ($O2/\bullet O_2$) = **-0.28 eV**[3] VS SHE). The electrons in the conduction band of HKUST MOF can easily promote this reduction as they are at high potential i.e **- 0.33eV**. The holes generated are involved directly involved in the oxidation of benzyl alcohol as seen in the main script and also in the Mechanism.

BET Expalantion:

N2 adsorption-desorption measurements of HKUST and HKUST/Bi_2WO_6 composites were carried out to evaluate their surface properties the isotherms are displayed in Figure S2. HKUST

exhibited typical type I isotherm[4], which is an indication of microporous structure Fig.S2(a). The composite HKUST/Bi_2WO_6 revealed the combination of type I and type IV isotherms Fig.S2(b)as evidence for the existence of both micropores and mesopores. The pore size distribution of HKUST Fig S2(c) and HKUST/Bi_2WO_6 Fig S2(d) as evident from BJH pore distribution plots.The HKUST shows pores only in the range of ≤ 2nm indicating higher degree of microporosity ,While as the composite has pores both in the range of ≤ 2nm and also some pore intensity above 4nm indicating the presence of mesopores in the composite .The presence of mesopores in the composite are due to Bi_2WO_6 which possesses a mesoporous structure.

References:

[1] M. A. Butler, **2012**, *1914*.

[2] X. Zhang, L. Zhang, T. Xie, D. Wang, **2009**, 7371.

[3] J. Long, S. Wang, Z. Ding, S. Wang, Y. Zhou, L. Huang, X. Wanga, *Chem. Commun.* **2012**, *48*, 11656.

[4] F. A. Sofi, K. Majid, O. Mehraj, *J. Alloys Compd.* **2018**, *737*, 798.