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Supplementary Information

Photocatalytic degradation of methylene blue (MB) with Cu_1@ZnO single atom catalysts on graphene-coated flexible substrates

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Theoretical and Computational Methods

1. Formation Energy of Surface-Anchored Single Atom. The formation energy of doped Cu_1@ZnO was calculated by removing one surface Zn-atom and replaced by a Cu atom. Therefore, following thermodynamic definition, the formation energy of doped Cu_1@ZnO is defined as

$$\Delta E(doped) = E(Cu_1@\,ZnO) - E(Cu) - E(ZnO) + E(Zn)\,.$$

Considering the experimental synthesis condition of Cu-ZnO nanocluster, we approximatively calculated the formation Gibbs free energy of supported Cu_1/ZnO and doped Cu_1@ZnO at 298.15 K and 1 atm in the following way:

$$\Delta G(Cu_1@ZnO) = G(Cu_1@ZnO) - G(Cu^{2+}(aq)) - G(ZnO) + G(Zn^{2+}(aq))$$

$$\Delta G(Cu_1/ZnO) = G(Cu_1/ZnO) - G(Cu^{2+}(aq)) - E(ZnO)$$

Where the Gibbs free energy of Zn^{2+}(aq) and Cu^{2+}(aq) can be calculated through equation M(g) → M^{2+}(aq) + $2e^-$. That is,

$$G(M^{2+}(aq)) = E(M(g)) + \Delta G(0K \rightarrow 298.15K) + \Delta_f G^\circ(M^{2+}(aq)) - \Delta_f G^\circ(M(g)).$$

Where $\Delta_f G^\circ$ is the standard Gibbs energy of formation for Zn(g), Cu(g), Cu^{2+}(aq) and Zn^{2+}(aq)[1]. Only the single metal atom of Cu for Cu_1/ZnO and doped $Cu_1@ZnO$ models were relaxed when calculating the Gibbs free energy of Cu_1/ZnO and doped $Cu_1@ZnO$. Only the Zn atom to be replaced for ZnO model was relaxed when calculating the Gibbs free energy of ZnO. E(ZnO) is the quantum-mechanical electronic energy of pristine ZnO surface.

2. Charge Density Difference (CDD) and Bader Charge Analysis of Doped $Cu_1@ZnO$ Active Center. The Bader charge analysis and CDD calculations for $Cu_1@ZnO$ were done with VASP code. The Bader charges are +1.176 |e| for Zn, -1.177 |e| for O and +1.193 |e| for Cu, respectively, indicating Cu is slightly more positively charged than Zn when replacing the latter in ZnO surface. The calculated CDDs (Fig. S1) and Bader charge analysis of Cu_1/ZnO active site reveal that there is charge depletion at Cu-atom and charge accumulation at the equatorial and axial O-atoms. Upon light radiation with appropriate energy (hν), the non-bonding 2p lone-pair electron on surface O-atom will be excited to the Cu 3d empty orbitals through ligand-metal charge transfer (LMCT). This LMCT upon UV-radiation causes the electron-hole separation, which then respectively leads to reduction of O_2 by electron (e^-) and oxidization of H_2O (or organics) by hole (h^+).

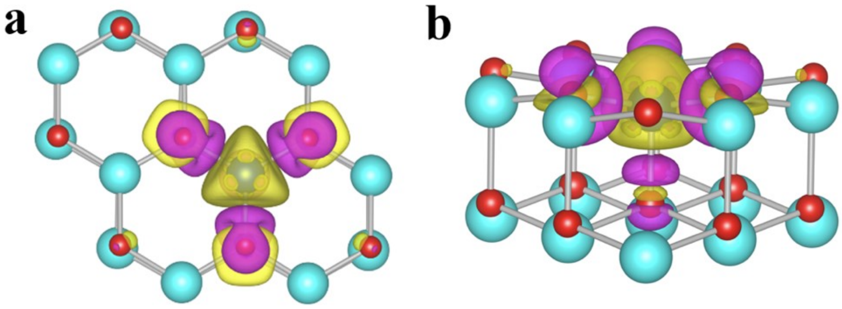


Figure S1. Charge density differences of $Cu_1@ZnO$: (a) top view, and (b) side view. The purple and yellow areas represent electron accumulation and depletion, respectively.

3. Adsorption of O_2, OH, and OOH on catalyst Cu_1@ZnO. The adsorption of oxidants O_2, OH, and OOH on catalyst Cu_1@ZnO is calculated. The adsorption geometries, quantum-mechanical (DFT) energies, and Gibbs free energies are summarized in the Table S1. The reaction Gibbs free energies for two possible reaction paths are listed in Table S2 and are summarized in the Figure S2 for comparison. These data are consistent with our explanation of the reaction mechanism.

Table S1 The adsorption geometries, DFT energies, and Gibbs free energies of O_2, OH, and OOH on catalyst Cu_1@ZnO

System	$d_{Cu\text{-}O}$ (Å)	$d_{O\text{-}O}$ (Å)	$d_{O\text{-}H}$ (Å)	ΔE (eV)	ΔG (eV)
$*O_2$	3.19	1.23	—	-0.07	-0.08
*OH	1.82	—	0.98	-1.24	-0.69
*OOH	2.14	1.37	0.99	-0.23	0.34

Table S2 The Gibbs free energies of reaction path 1 and path 2

Path-1	**ΔG (eV)**	**Path-2**	**ΔG (eV)**
$* + O_2 + e^- \rightarrow *OO$	-0.08	$* + O_2 + e^- \rightarrow *OO$	-0.08
$*OO + H^+ + e^- \rightarrow *OOH$	0.16	$*OO + H^+ + e^- \rightarrow *OOH$	0.16
$*OOH + H^+ + e^- \rightarrow *HOOH$	-1.23	$*OOH + H^+ + e^- \rightarrow *O + H_2O$	-0.62
$*HOOH + H^+ + e^- \rightarrow *OH + H_2O$	-2.75	$*O + H^+ + e^- \rightarrow *OH$	-2.75

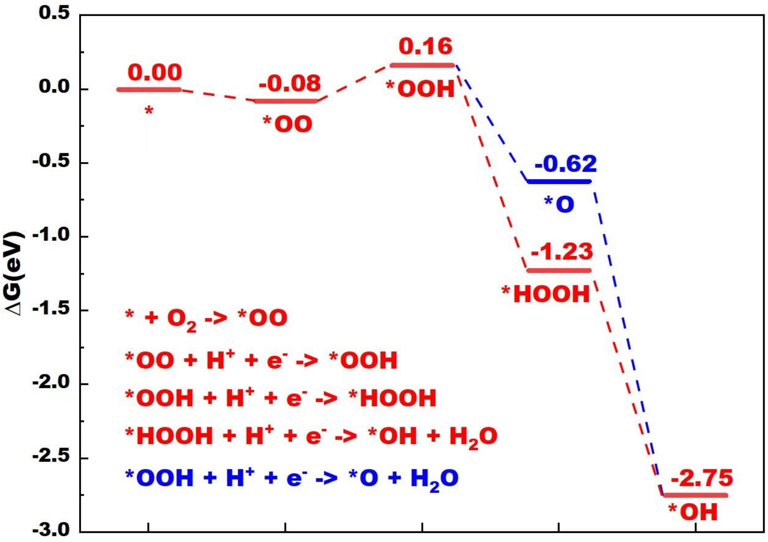


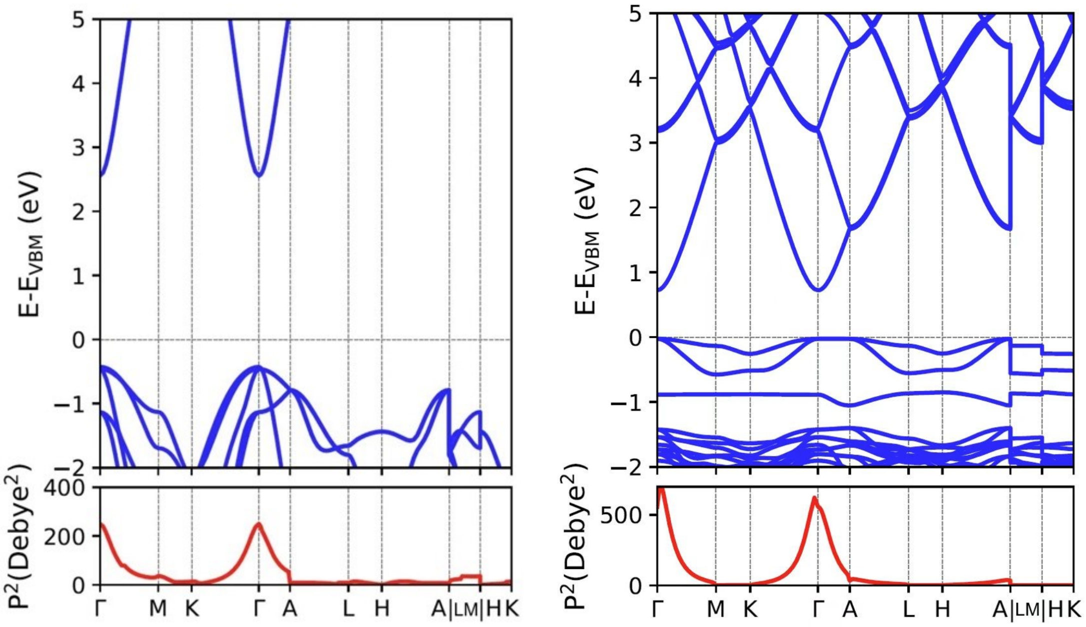
Figure S2. Reaction energy profile for O_2 activation, hydrogenation and decomposition

4. Transition Probabilities of Cu_1@ZnO. The transition dipole moment (TDM) for a transition between an initial state *i* and a final state *f* is the transition matrix element of the two states interacting via the electric dipole moment operator, with the square of the magnitude representing the strength of the interaction due to the distribution of charge within the system upon electric dipole transition[2, 3]. For a nonrelativistic single particle of mass *m*, the TDM in zero magnetic field can be written in terms of standard dipole-length approximation or alternatively dipole-velocity approximation via the momentum operator ($\hat{P} = -i\hbar\nabla$),

$$P_{i\to f} = \langle \Psi_i | \hat{r} | \Psi_f \rangle = i\hbar \frac{\langle \Psi_i | \hat{P} | \Psi_f \rangle}{(E_f - E_i)m} = i\hbar \frac{\sum_n C_{in} C_{fn} G_n}{(E_f - E_i)}$$

where Ψ_i and Ψ_f are energy eigenstates with energy E_i and E_f, and C_{in}, C_{fn} and G_n are plane-wave coefficients and reciprocal space vector with the same **k** vector, respectively, summed over the number of plane-waves ($n = 1, 2, \ldots n_{max}$). The total transition probabilities between the valence band (VB) and the conduction band (CB) equal to the calculated sum of the squares of TDM in unit of Debey[2].

The TDMs for undoped ZnO and Cu_1@ZnO were calculated using VASPkit code[4]. The calculated transition probabilities from the valence-band maximum to the conducting-band minimum along with the band structures of undoped ZnO and Cu_1@ZnO are shown in Figure S3.



(**a**) (**b**)

Figure S3. The calculated band structures and corresponding transition probabilities for the majority spin of undoped ZnO and doped Cu_1@ZnO using PBE functional.

References

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