Supplementary Information (SI) for Journal of Materials Chemistry A.

Cu-Decorated Sc_2CFN Monolayer for Efficient CO_2 Capture and Activation

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Supplementary data

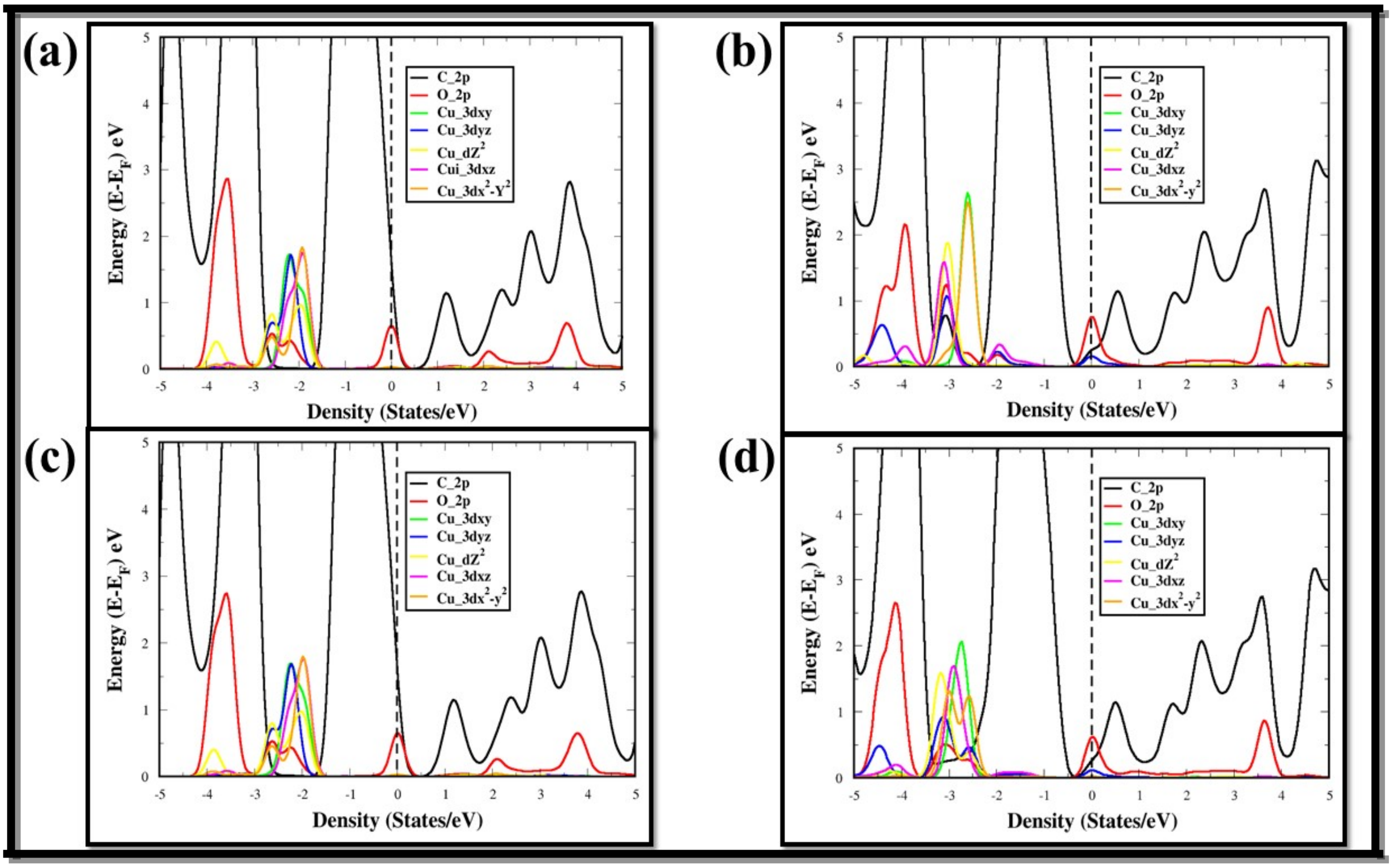

Figure S1. Shows Projected density of states (PDOS) showing the interaction between Cu 3d orbitals and CO_2 2p orbitals at different adsorption sites of Cu-decorated Sc_2CFN: (a) N, (b) F, (c) Sc+F, and (d) Sc+N. The strongest hybridization occurs at the N-site,

The orbital-resolved PDOS analysis (Figure S1) provides insight into the interaction mechanism between the Cu atom and CO_2 molecules adsorbed on different sites of the Sc_2CFN surface. In all cases, there is noticeable overlap between the **Cu 3d orbitals** and the **CO_2 O-2p states** in the energy range from –5 eV to 0 eV, confirming hybridization and charge transfer that contribute to CO_2 activation.

- At the **N-terminated site (Figure S1a)**, the **Cu $3d_{xz}$ and $3d_{yz}$ orbitals** exhibit the strongest overlap with the O-2p orbitals, consistent with the enhanced bending of CO_2 and higher adsorption energy.
- At the **F-terminated site (Figure S1b)**, the overlap is weaker and mainly involves the **Cu $3d_{xy}$ orbital**, leading to less pronounced CO_2 activation.
- For the **Sc+F site (Figure S1c)**, hybridization occurs through the **$3d_{xz}$/$3d_{yz}$ and $3d_{x^2-y^2}$ orbitals**, resulting in moderate CO_2 activation compared to the N-site.
- At the **Sc+N site (Figure S1d)**, partial contributions from **$3dz^2$ and $3d_{xz}$ orbitals** are observed, but the overlap is weaker compared to the N-site, consistent with lower activation strength.

Overall, these results confirm that the N-terminated Cu-decorated Sc_2CFN provides the most favourable orbital interactions for CO_2 activation, with the **Cu $3d_{xz}/3d_{yz}$ orbitals** playing the dominant role in hybridization with the O-2p orbitals of CO_2.

For the N-activated site, the adsorption is characterized by significant overlap between the C-2p/O-2p states of CO_2 and the Cu-d_{xz}/d_{yz} orbitals (–4.0 to –2.0 eV), with weaker contributions from Cu-dz^2. This indicates that CO_2 interacts preferentially through lateral d-orbitals when coordinated to N, contrasting with the F-activated site where the Cu-dz^2 orbital dominates.

The interaction between CO_2 and the F-activated Cu center is mediated primarily by the Cu-d_z^2 orbital, evidenced by its pronounced energy-aligned overlap with C-2p/O-2p features (≈–3.5 to –1.0 eV) and residual mixing around E_F, while dxz/dyz contribute weakly and dxy/dx^2–y^2 show minimal participation At the Sc+F co-doped site, the PDOS reveals that the Cu-dxz and dyz orbitals are primarily responsible for hybridization with the C-2p/O-2p states in the –4.5 to –2.5 eV region. In addition, weaker contributions from Cu-dz^2 and dx^2–y^2 are evident, suggesting a more complex multi-orbital interaction compared with the isolated F or N active sites For the Sc+N co-doped site, the interaction of CO_2 with the Cu center involves significant contributions from the in-plane Cu-dxy, dxz, and dyz orbitals, which overlap strongly with C-2p/O-2p states around –4.0 to –2.0 eV. Additionally, moderate involvement of Cu-dz^2 and dx^2–

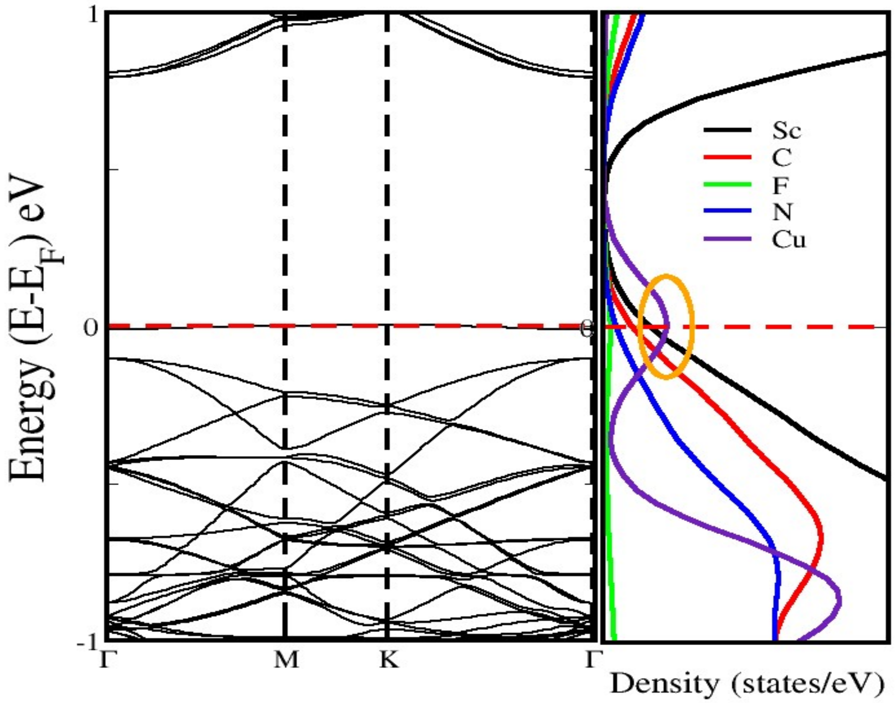

Figure S2. Electronic band structure and projected density of states (PDOS) of the Cu-doped Sc_2CFN monolayer. The Fermi level is set to zero (red dashed line). The system retains an indirect band gap nature, while the gap value is reduced due to Cu-induced states. Strong hybridization between Cu, Sc, and N orbitals near the Fermi level (highlighted region) indicates enhanced electronic interactions that narrow the band gap.

y^2 orbitals is detected, pointing to a more delocalized and multi-orbital hybridization mechanism than in either the F- or N-only sites

Here, in Figure S2 Shows the indirect nature of the band gap remains in the Cu-doped F-active site of Sc_2CFN monolayer, as the VBM and CBM still occur at different k-points. However, the band gap value is reduced (narrowed) compared to pristine Sc_2CFN, due to the Cu-induced states near the Fermi level. In fact, if the Cu contribution is strong enough, (shown in orange circle) the system can even approach semi metallic behavior depending on the doping concentration.

Table S1. Adsorption energies (Eads, in eV) of CO_2 on Cu-decorated Sc_2CFN monolayer for horizontal (HCO_2) and vertical (VCO_2) configurations at different adsorption sites.

Adsorption Site	**Eads (HCO_2) [eV]**	**Eads (VCO_2) [eV]**
F	**–0.60**	**–0.29**
N	**–0.92**	**–0.43**
Sc+F	**–0.83**	**–0.58**
Sc+N	**–0.59**	**–0.71**

Table S2. Adsorption energies (E_ads, in eV) of Cu on Sc_2CFN monolayer at different adsorption sites calculated with vdW correction

Adsorption Site	**Eads (eV)**
F	–0.67
N	–1.70
Sc+F	–1.27
Sc+N	–1.82

Table S3. Adsorption energies (Eads, in eV) of CO_2 on Cu-decorated Sc_2CFN monolayer at different adsorption sites, calculated with vdW correction

Adsorption Site	**Eads (eV)**
F	–2.49
N	–1.95
Sc+F	–1.89
Sc+N	–1.53

Table S4. Comparison of CO_2 adsorption energies (Eads, in eV) on different MXene systems from literature and this work.

MXene system	Eads (eV)	Reference	Ref.No
Ti_2CO_2	–0.45 to –1.10	CO2 abatement by two-dimensional MXene carbides	1
V_2CO_2	–0.60 to –1.30	CO2 abatement by two-dimensional MXene carbides	1
Mo_2CO_2	–0.50 to –1.20	Carbon dioxide adsorption of two-dimensional Mo2C MXene	2
W_2C, Cr_2C, Nb_2C (various)	–1.22 to –3.65	Carbon dioxide adsorption of two-dimensional Mo2C MXene	2
Ti_2C–Cu	–1.40 to –2.00	Ti2CMXene/activated carbon Nanocomposite for efficient CO2 capture: Insights into thermodynamics properties	3
V_2C–Cu	–1.60 to –2.20	Ti2C-MXene/activated carbon nanocomposite for efficient CO2 capture: Insights into thermodynamics properties	3
Sc_2CFN–Cu (this work)	**–1.53 to –2.49**	This work	

Table S4 compares our adsorption results with those of similar MXene systems reported in the literature. For pristine MXenes such as Ti_2CO_2 and V_2CO_2, CO_2 adsorption energies typically range from –0.45 to –1.30 eV, indicative of moderate chemisorption. Metal decoration, such as Cu on Ti_2C or V_2C, strengthens adsorption into the range of –1.40 to –2.20 eV. In our case, Cu-decorated Sc_2CFN exhibits adsorption energies between –1.53 and –2.49 eV (vdW corrected), which are in excellent agreement with reported Cu-decorated MXenes. Importantly, while Sc_2CFN–Cu demonstrates strong activation, the adsorption energies remain below the extreme values (≈ –3.65 eV) observed for some pristine MXenes, suggesting that CO_2 desorption remains feasible under photocatalytic conditions.

References

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