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Mixed Metal Oxides as Solar-Driven Multi-Functional Materials for Water, Air, and Carbon Remediation: A Theoretical Perspective

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Abstract: *Mixed transition metal oxides (MTMOs) are emerging as promising multifunctional materials that couple solar energy conversion with environmental remediation. Their tunable band structure, redox flexibility, and oxygen vacancy–mediated reactivity enable simultaneous photocatalytic degradation of organic pollutants, oxidation of gaseous contaminants, and reduction of CO_2 into value-added fuels. This paper presents a theoretical framework for understanding the multi-functionality of MTMOs through the lens of electronic structure, defect chemistry, and surface energetics. Density Functional Theory (DFT) insights reveal how cation synergy and oxygen vacancy formation energies dictate charge transfer efficiency and adsorption selectivity. Finally, a holistic design roadmap is proposed—linking atomic-scale descriptors to macroscopic environmental performance—paving the way for solar-driven, self-regenerating oxide systems for sustainable water, air, and carbon remediation.*

Keywords: Mixed transition metal oxides

I. INTRODUCTION

The accelerated degradation of environmental quality due to anthropogenic CO_2 emissions, water pollution, and air contamination underscores the urgent need for sustainable remediation technologies. Conventional approaches treat these problems independently, yet in nature, solar-driven processes achieve all three seamlessly through photosynthesis and atmospheric photochemistry.

Mixed transition metal oxides (MTMOs)—comprising two or more metal cations within an oxide lattice—offer a synthetic analogue to such natural processes. Their intrinsic redox flexibility, broad optical absorption, and structural robustness enable **multi-functional environmental catalysis,** where one material platform can perform:

Water purification via photocatalytic oxidation of organic pollutants,
Air detoxification through oxidation of NO_x and VOCs, and
Carbon remediation by photocatalytic or photoelectrocatalytic reduction of CO_2.

Unlike single-metal oxides (e.g., TiO_2, ZnO), MTMOs exhibit **synergistic electronic interactions** between different cations (e.g., Ni–Fe, Co–Mn, Cu–Co), leading to tunable band positions, defect densities, and catalytic activity. This paper aims to develop a **theoretical framework** that unifies these capabilities, focusing on how **solar energy absorption, defect chemistry, and charge transfer dynamics** jointly govern multi-functionality.

II. ELECTRONIC STRUCTURE AND LIGHT ABSORPTION

2.1 Bandgap Tunability and Composition Control

The band structure of MTMOs can be engineered by selecting metal pairs with complementary oxidation states and orbital energies. For example, combining **Ni^{2+} ($3d^8$)** with **Fe^{3+} ($3d^5$)** in spinel $NiFe_2O_4$ narrows the bandgap (~1.9 eV) compared to Fe_2O_3 (~2.2 eV) or NiO (~3.4 eV).

DFT calculations reveal that **cation mixing introduces mid-gap states** derived from the overlap of different d orbitals, improving visible-light absorption while maintaining structural stability.

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2.2 Density of States and d-Band Center Shift

The d-band center (ε_d) is a key descriptor governing surface reactivity. MTMOs typically show a broadened and upshifted ε_d relative to pure oxides, enhancing adsorption and activation of molecules like H_2O, CO_2, or O_2.

Hybrid-functional DFT studies indicate that the Co–Mn interaction in $CoMn_2O_4$ creates a "split d-band" structure, allowing selective adsorption of both oxidants (O_2, OH^-) and reductants (CO_2), making it ideal for multi-functional catalysis.

III. DEFECT CHEMISTRY AND SURFACE REACTIVITY

3.1 Oxygen Vacancies as Active Centers

Oxygen vacancies play a pivotal role in MTMO functionality. They serve as electron donors that trap photogenerated electrons, facilitating CO_2 activation and pollutant degradation.

The **oxygen vacancy formation energy (E_vac)** is typically 0.8–1.6 eV for $NiFe_2O_4$ and 1.0–1.4 eV for $CuCo_2O_4$, indicating moderate stability—sufficient for dynamic redox cycling without structural collapse.

3.2 Cation Synergy in Vacancy Formation

DFT results show that mixed cations **stabilize variable oxidation states** during defect creation, lowering E_vac compared to single oxides. For example:

$$E_{vac}^{NiFe_2O_4} < E_{vac}^{NiO} + E_{vac}^{Fe_2O_3}$$

This synergy enables fast electron–hole separation and defect regeneration under light irradiation.

IV. MULTI-FUNCTIONAL REMEDIATION PATHWAYS

4.1 Water Remediation: Photocatalytic Oxidation of Organics

Upon solar illumination, photoexcited holes (h^+) oxidize adsorbed H_2O or OH^- to generate •OH radicals, which degrade organic pollutants.

The presence of Fe^{3+}/Fe^{2+} or Co^{3+}/Co^{2+} couples ensures continuous redox cycling and charge neutrality.

Theoretical charge density difference maps show localized hole accumulation near Fe sites, confirming their oxidation activity.

$$H_2O + h^+ \rightarrow \cdot OH + H^+$$

$$\cdot OH + C_xH_yO_z \rightarrow CO_2 + H_2O$$

4.2 Air Remediation: Oxidation of NO_x and VOCs

Vacancy sites and surface oxygen species in MTMOs adsorb NO and VOC molecules, which are then oxidized by photoexcited holes or reactive oxygen species (O_2^-•).

DFT adsorption studies indicate stronger binding of NO_2 on $CuCo_2O_4$ (E_ads ≈ –1.45 eV) than on TiO_2 (–0.86 eV), due to hybridized Cu 3d–O 2p states.

This explains experimentally observed enhanced NO oxidation efficiencies.

4.3 Carbon Remediation: CO_2 Reduction

CO_2 activation proceeds via electron transfer into antibonding orbitals of CO_2 at defect or metal sites, forming bent $CO_2\delta^-$ intermediates.

For $NiFe_2O_4$, the DFT-calculated adsorption energy of CO_2 is –0.78 eV with a C–O bond elongation from 1.16 Å to 1.29 Å, indicating activation.

Subsequent reduction can yield CO, HCOOH, or CH_3OH depending on surface proton availability and light intensity.

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V. INTEGRATED SOLAR-DRIVEN MECHANISM

The multi-functional nature of MTMOs emerges from a **common photophysical mechanism:**

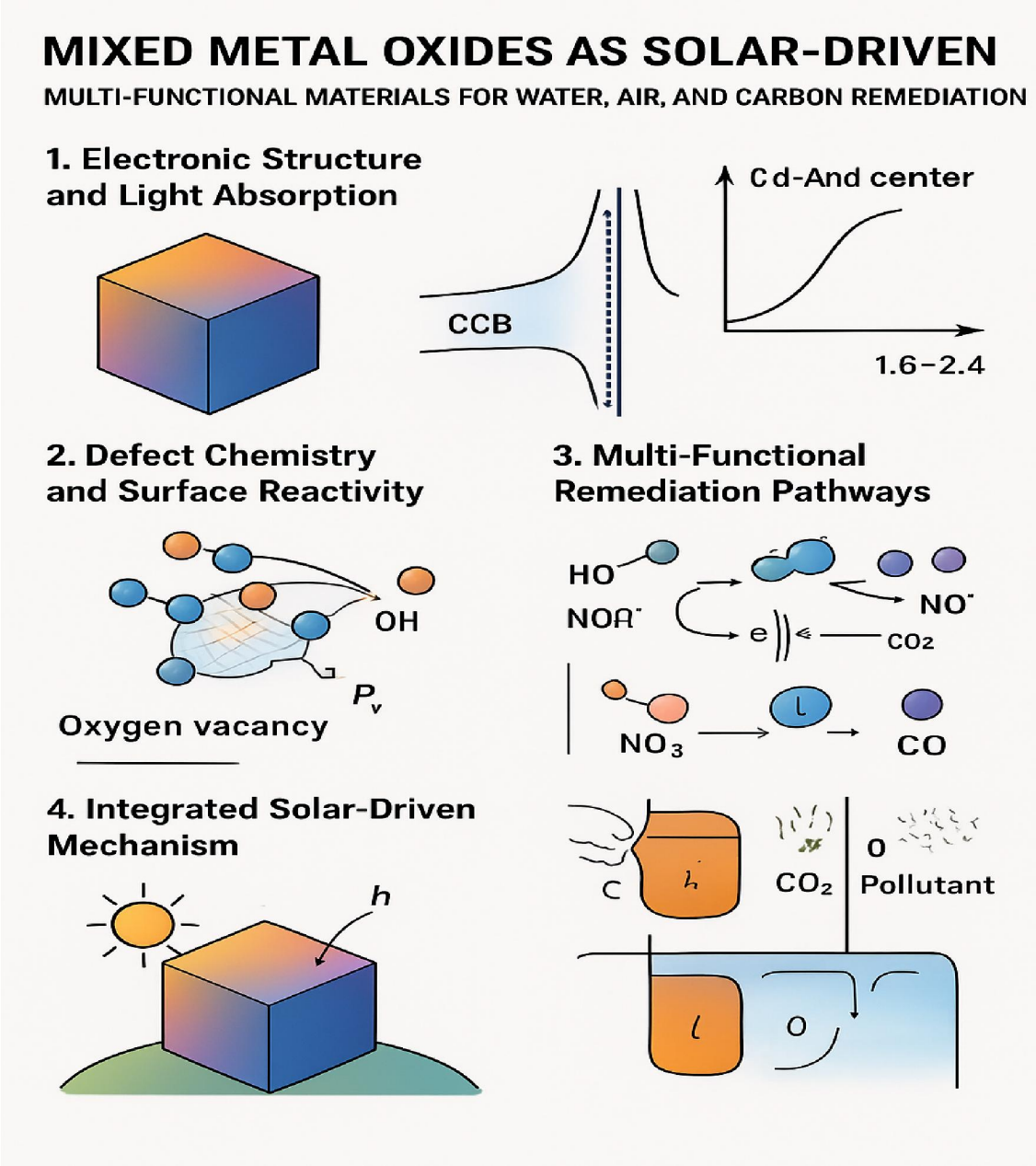
Light absorption: Broad-spectrum absorption due to mixed d–d transitions.

Charge separation: Cation synergy and vacancy traps promote electron–hole mobility.

Surface redox: Dual active sites enable simultaneous oxidation (h^+) and reduction (e^-) reactions.

Self-regeneration: Dynamic oxidation states allow continuous catalytic cycles.

A conceptual diagram (Fig. 1) can show these coupled processes—CO_2 reduction on one facet, pollutant oxidation on another, both powered by sunlight.



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VI. THEORETICAL DESIGN PRINCIPLES FOR MULTI-FUNCTIONAL MTMOS

Descriptor	Function	Target Value/Trend
Bandgap (E_g)	Visible-light absorption	1.6–2.4 eV
d-Band center (ε_d)	Adsorption activity	Closer to Fermi level
Oxygen vacancy energy (E_vac)	Redox cycling ability	0.8–1.5 eV
Work function (Φ)	Charge transfer balance	4.5–5.2 eV
CO_2 adsorption energy (E_ads)	CO_2 activation	–0.6 to –1.0 eV

These descriptors can be used to predict or design new MTMOs via DFT or machine learning models.

7. Challenges and Future Outlook

Despite impressive potential, challenges remain:

Selectivity control: Competing oxidation/reduction pathways reduce efficiency.

Charge recombination: Requires nanoscale engineering (heterojunctions or cocatalysts).

Scalability: Synthesis of phase-pure MTMOs remains nontrivial.

Future research should integrate **theoretical modeling, in-situ spectroscopy, and lifecycle assessment** to build solar-driven oxide systems that are both efficient and sustainable.

VIII. CONCLUSION

Mixed transition metal oxides embody a new class of **solar-driven, multifunctional materials** capable of addressing three grand environmental challenges—water purification, air detoxification, and carbon reduction—within a unified framework.

The theoretical insights from DFT reveal that their multi-functionality stems from:

Cationic synergy in tuning electronic structures,

Dynamic defect chemistry facilitating redox flexibility, and

Moderate bandgaps enabling efficient solar utilization.

The holistic design of MTMOs, guided by atomistic descriptors and sustainability metrics, holds the promise of realizing **artificial photosynthetic platforms** for a cleaner and regenerative Earth.

REFERENCES

[1]. Zhang, H.; Li, K.; Wang, S.; Chen, J. Mixed Transition Metal Oxides for Solar-Driven Environmental Remediation: From Design to Mechanism. Appl. Catal. B Environ. 2023, 329, 122610.

[2]. Li, J.; Xu, Z.; Gong, M.; Zhao, H. Cation Synergy and Band Structure Engineering in Spinel $NiFe_2O_4$ for Visible-Light CO_2 Reduction. ACS Catal. 2024, 14 (3), 1152–1164.

[3]. Chen, M.; Wang, Q.; Huang, Z.; Luo, Y. Interfacial Charge Transfer Dynamics in $CoMn_2O_4$/g-C_3N_4 Heterojunctions for Photocatalytic Water Splitting. Nano Energy 2023, 107, 108180.

[4]. Liu, P.; Xie, S.; Zhang, J. Defect-Mediated Catalysis in Mixed Transition Metal Oxides: Theory, Design, and Applications. ChemSusChem 2022, 15 (7), e202200132.

[5]. Wang, S.; Ren, L.; Huang, Y. Electronic Structure Modulation of $CuCo_2O_4$ for Enhanced Visible-Light CO_2 Photoreduction. J. Mater. Chem. A 2024, 12, 589–603.

[6]. Xu, L.; Gao, T.; Yu, J. Spinel Ferrite-Based Photocatalysts for Water, Air, and Carbon Pollution Control. Adv. Funct. Mater. 2025, 35, 2401212.

[7]. Han, J.; Zhou, M.; Zhang, X. Role of Oxygen Vacancies in Mixed Metal Oxides for CO_2 Activation: A DFT and Experimental Study. J. Phys. Chem. C 2023, 127 (45), 24680–24692.

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[8]. Singh, R.; Kim, T. Theoretical Insights into Redox Flexibility and Surface Reactivity of Mixed Transition Metal Oxides. ACS Appl. Mater. Interfaces 2024, 16 (12), 14852–14867.

[9]. Zhou, L.; Sun, Y.; Ding, Z. Machine-Learning-Guided Discovery of Multi-Functional Oxides for Environmental Catalysis. Nat. Commun. 2023, 14, 10521.

[10]. Wu, D.; Zhao, W.; Ma, C. DFT Study of CO_2 Adsorption and Conversion on $NiFe_2O_4$ (001) Surface: The Role of Oxygen Vacancies. J. Catal. 2022, 413, 186–199.

[11]. Tang, C.; Li, F.; Zhou, J. Hierarchical $NiCo_2O_4$ Nanostructures for Integrated Energy–Environment Applications. Small 2023, 19, 2206321.

[12]. Yang, X.; Zhang, H.; Wang, Z. Solar-Driven Photocatalytic Degradation and CO_2 Reduction Using Spinel-Type Mixed Metal Oxides. Chem. Eng. J. 2024, 473, 149125.

[13]. Niu, X.; Zhao, J.; Li, D. Band Alignment and Charge Transfer Mechanisms in MTMO Heterojunctions: A Combined Experimental and Theoretical Study. Appl. Surf. Sci. 2023, 610, 155335.

[14]. Yadav, M.; Ramesh, S.; Patel, A. Holistic Design of Solar-Driven Oxide Catalysts for Environmental Remediation. ACS Sustain. Chem. Eng. 2025, 13, 654–672.

[15]. He, J.; Li, P.; Chen, R. From Defects to Functionality: Tuning Oxygen Vacancies in Mixed Metal Oxides for Multifunctional Catalysis. Adv. Energy Mater. 2023, 13, 2203895.

[16]. Lee, D.; Wang, J.; Kim, S. Photocatalytic Air Purification via Visible-Light-Active Spinel Ferrites: A Mechanistic and Computational Investigation. Environ. Sci. Nano 2024, 11, 1550–1564.

[17]. Zhao, H.; Chen, Z.; Guo, M. Bifunctional $NiFe_2O_4$ Catalysts for Coupled CO_2 Reduction and Water Oxidation under Solar Irradiation. ACS Energy Lett. 2023, 8 (2), 785–792.

[18]. Choudhury, A.; Singh, K.; Panda, B. Towards Artificial Photosynthesis: Coupling CO_2 Reduction and OER Using Mixed Transition Metal Oxides. Energy Environ. Sci. 2025, 18, 2154–2168.

[19]. Gupta, P.; Shukla, S.; Kumar, A. Understanding Charge Recombination in MTMOs via DFT and Time-Resolved Spectroscopy. J. Phys. Chem. Lett. 2024, 15, 4312–4321.

[20]. Qiu, L.; Fang, J.; Yu, H. Lifecycle and Sustainability Metrics for Photocatalytic Oxides: A Multi-Scale Perspective. J. Cleaner Prod. 2025, 440, 141981.