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IN SITU SYNTHESIS Of HIERARCHICAL MOF/LDH NANOCOMPOSITES FOR ADVANCED FUNCTIONAL MATERIALS

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ABSTRACT

Nanostructured hybrid materials based on Metal-Organic Frameworks (MOFs) and Layered Double Hydroxides (LDHs) have attracted significant attention due to their exceptional tunability, high surface area, and multifunctional properties. The integration of MOFs and LDHs offers a promising approach for developing advanced materials with enhanced physicochemical stability, adsorption capacity, and catalytic efficiency. In this study, MOF/LDH composites were synthesized through a controlled coprecipitation and solvothermal route, enabling precise control over particle size, crystallinity, and surface morphology. The as-prepared materials were systematically characterized using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) to investigate their structural morphology, interlayer arrangement, and nanoscale interface between MOF and LDH components. The morphological analysis revealed well-defined layered structures with uniform particle distribution and intimate interfacial contact, confirming the successful hybridization of the two materials. The synergistic combination of MOF porosity and LDH ion-exchange capacity is expected to enhance the material's performance in adsorption, catalysis, and environmental remediation applications. This work provides valuable insights into the design, synthesis, and morphological optimization of MOF/LDH nanostructures for multifunctional environmental and biomedical uses.

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1. INTRODUCTION

Background

Rapid industrialization and population growth have intensified environmental and health challenges, with global pollutant discharge rates exceeding natural degradation capacities by several orders of magnitude [1]. Industrial discharges, agricultural runoff containing persistent organic pollutants, and pharmaceutical contaminants increasingly threaten natural ecosystems,

while conventional remediation technologies often lack the efficiency, selectivity, and sustainability required to address these complex issues [2].

Nanotechnology has emerged as a transformative approach for developing functional materials with precise control over composition, structure, and properties at the nanoscale [3-6]. The ability to engineer materials at dimensions comparable to molecular and ionic species enables unprecedented control over surface chemistry, electronic structure, and interfacial phenomena critical for sensing, separation, and catalytic applications [7].

Among nanostructured materials, MOFs and LDHs have attracted significant attention due to their structural versatility and broad application potential [8-9]. MOFs are crystalline porous materials composed of metal ions or clusters (secondary building units) coordinated with multidentate organic linkers forming highly ordered three-dimensional frameworks (Figure 1a) with topological diversity [10-11]. The zeolitic imidazolate framework family (ZIFs), particularly ZIF-67 featuring Co^{2+} nodes coordinated with 2-methylimidazolate linkers in a sodalite topology, exhibits remarkable thermal stability up to 350 °C and chemical resistance in organic solvents. Their extraordinarily high surface areas often exceeding 6000 m^2/g for MOF-5 and 1500-1800 m^2/g for ZIF-67 combined with uniform micropore apertures (3.4 Å for ZIF-67) provide molecular sieving capabilities and size-selective adsorption [12,13]. Despite these advantages, MOFs frequently display poor hydrolytic stability, with framework degradation occurring through metal-ligand bond hydrolysis under humid conditions, particularly affecting carboxylate-based MOFs. Additionally, recovering nanosized MOF particles (< 500 nm) from aqueous suspensions remains challenging due to colloidal stability.

LDHs are anionic clays featuring positively charged brucite-like layers with octahedral coordination geometry, intercalated with charge-balancing anions and water molecules (Figure 1b-c). Their general formula, $[M^{2+}_{1-x}M^{2+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, demonstrates compositional flexibility where divalent cations (M^{2+} = Mg^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}) and trivalent cations (M^{3+} = Al^{3+}, Fe^{3+}, Cr^{3+}) can be varied across M^{2+}/M^{3+} ratios typically ranging from 2:1 to 4:1 [14]. The interlayer spacing (0.7-0.8 nm for carbonate-intercalated forms) can be expanded through anion exchange, enabling tunable host-guest chemistry. This structural adaptability allows LDHs to serve as efficient adsorbents with typical capacities of 50-200 mg/g for organic dyes, while their basic surface hydroxyl groups facilitate catalytic applications [15]. However, LDHs suffer from structural instability in acidic environments (pH < 4) and aggregation in aqueous media, reducing accessible surface area from theoretical values of 200-300 m^2/g to often below 80 m^2/g in practical applications.

The integration of LDHs and MOFs into hybrid nanocomposites represents a strategic approach to overcome individual limitations while exploiting complementary advantages [16]. The positively charged LDH surface can provide electrostatic stabilization and nucleation sites for MOF growth, while the rigid MOF framework can serve as a physical barrier preventing LDH layer restacking. Theoretical models predict that such heterostructures should exhibit hierarchical porosity with distinct pore size distributions: micropores (< 2 nm) from MOF cavities contributing to high surface area and molecular selectivity, mesopores (2-50 nm) from interlayer spacing and interparticle voids facilitating mass transport. However, achieving controlled interfacial integration requires precise manipulation of nucleation kinetics, growth rates, and surface chemistry. Minor variations in metal ion concentration, pH gradients, or solvent polarity can drastically alter crystallization pathways, leading to either core-shell structures, physical mixtures, or genuine heterostructures with epitaxial-like interfaces.

Aligned with global sustainability initiatives including the United Nations Sustainable Development Goals (SDGs), MOF/LDH-based materials hold potential for advancing targets related to clean water and sanitation (SDG 6), good health and well-being (SDG 3), and responsible consumption and production (SDG 12) [17]. This research addresses critical synthesis challenges through a controlled coprecipitation-solvothermal approach optimized for reproducible heterostructure formation.

Problem Statement

LDHs and MOFs exhibit remarkable potential for environmental remediation and multifunctional material design, but their practical application is constrained by several critical challenges. LDHs often suffer from structural instability and aggregation in aqueous environments, which reduces surface area and limits adsorption efficiency. MOFs, while highly porous and tunable, frequently display poor chemical stability under humid, acidic, or basic conditions, leading to framework collapse and performance loss. Hybrid LDH/MOF systems offer a promising route to combine the advantages of both materials, yet their controlled synthesis and reproducibility remain challenging. Minor variations in synthesis conditions can drastically alter crystallinity, morphology, porosity, and interfacial interactions, making it difficult to establish reliable structure-property relationships. Additionally, scalable and cost-effective synthesis methods are limited, as many current protocols require high temperatures, multi-step processing, or expensive reagents. Understanding how nanoscale architecture influences macroscopic performance, particularly in terms of adsorption, structural integrity, and hybrid integration, remains incomplete. Addressing these challenges requires innovative synthesis strategies, precise morphological control, and comprehensive characterization to realize hybrid materials with predictable and reproducible properties.

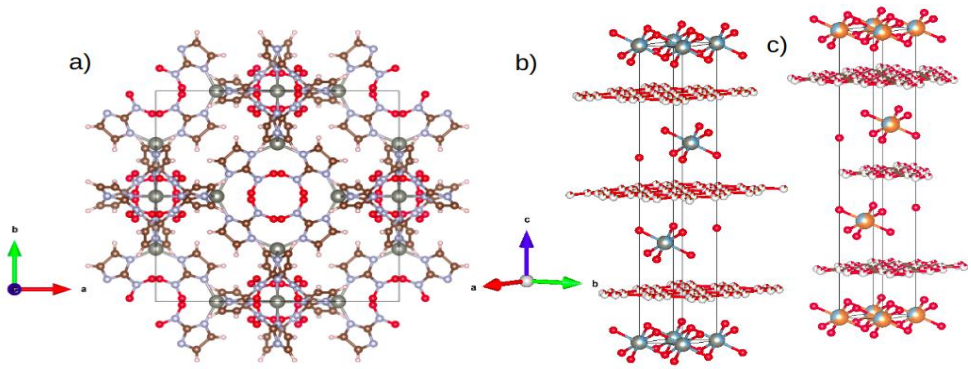

Fig. 1 *(a) Crystal structure of a representative MOF illustrating its three-dimensional porous network. (b) LDH structure based on Mg-Al, showing the periodic stacking of brucite-like layers along the c-axis. (c) LDH based on Zn-Al, displaying a similar layered arrangement with interlayer spacing influenced by the metal composition. Color code: gray (metal centers), red (oxygen), blue (nitrogen), brown (carbon), and white (hydrogen).*

Research Objectives

This study aims to:

- Develop controlled synthesis protocols for hybrid MOF/LDH nanomaterials with tunable crystallinity, particle size, and interfacial architecture.

- Investigate structural integration between MOF and LDH components to optimize hybrid morphology and interfacial interactions.
- Perform advanced characterization using SEM, and TEM techniques to elucidate nanoscale architecture, surface topology, and structural features.
- Evaluate physicochemical properties such as porosity, surface area, and crystal structure to correlate synthesis parameters with material performance.

Scientific Novelty

The scientific novelty of this work lies in the strategic integration of LDHs and MOFs into hybrid nanomaterials with precisely controlled structures and tunable functional properties. Unlike previous studies that largely investigate these materials separately, this research systematically combines the structural stability and ion-exchange capabilities of LDHs with the high porosity, tunable chemistry, and modularity of MOFs, creating multifunctional systems with synergistic performance. The use of a controlled coprecipitation-solvothermal synthesis method enables precise tuning of crystallinity, particle morphology, and interfacial architecture, ensuring reproducibility and consistent hybrid formation. Advanced characterization using SEM, and TEM provides detailed insights into nanoscale structural features, surface topology, and interfacial interactions, allowing the establishment of clear structure-property relationships. By correlating synthesis conditions with morphological, structural, and functional outcomes, this study offers predictive design principles for hybrid nanomaterials with enhanced adsorption efficiency, stability, and functionality. Additionally, the emphasis on environmentally compatible and energy-efficient synthesis introduces a sustainable dimension to hybrid material development. Collectively, this work presents a comprehensive framework for the rational design, synthesis, and characterization of multifunctional LDH/MOF hybrids, advancing the field of nanostructured materials for environmental and multifunctional applications.

2. METHODOLOGY

2.1 Synthesis of Layered Double Hydroxides

Mg-Al and Zn-Al LDHs were synthesized via coprecipitation followed by hydrothermal crystallization to achieve phase purity and structural ordering. For Mg-Al LDH, aqueous solutions of $Mg(NO_3)_2 \cdot 6H_2O$ (0.225 M) and $Al(NO_3)_3 \cdot 9H_2O$ (0.075 M) were prepared to maintain a Mg^{2+}/Al^{3+} molar ratio of 3:1, which provides optimal charge balance and layer stability according to Miyata's criterion. Similarly, Zn-Al LDH precursors employed $Zn(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ at the same molar ratio. The mixed metal solution (100 mL, total metal concentration 0.3 M) was added dropwise at 1 mL/min into 150 mL of 0.1 M NaOH solution under vigorous magnetic stirring (500 rpm) to maintain pH 10.0 ± 0.2, monitored continuously using a calibrated pH electrode. This pH range ensures complete hydroxide precipitation while minimizing aluminum hydroxide formation that occurs above pH 11.

The coprecipitation was conducted at 25 °C under continuous nitrogen purging (50 mL/min) to prevent atmospheric CO_2 contamination, which would lead to carbonate intercalation and reduced anion exchange capacity. The resulting white suspension was aged at 65 °C for 24 h in a sealed glass reactor to promote Ostwald ripening and layer crystallization. The precipitate was recovered by centrifugation (8000 rpm, 10 min), washed five times with deionized water until

the supernatant reached pH 7 ± 0.5, and dried at 80 °C in a vacuum oven overnight (12 h, 10^{-2} mbar).

To enhance crystallographic ordering and increase lateral platelet dimensions, the as-obtained LDH precursors were subjected to hydrothermal treatment at 120 °C for 12 h in a 100 mL Teflon-lined stainless-steel autoclave filled to 70% capacity with deionized water. This thermal aging promotes dissolution-recrystallization processes that eliminate structural defects and increase crystallite size. The final products were filtered through 0.45 μm membranes, washed with ethanol, and dried at 60°C, yielding white powders with typical mass yields of 85-90% based on theoretical metal hydroxide formation.

2.2 Synthesis of MOF: ZIF-67

ZIF-67 was synthesized via a modified room-temperature precipitation method optimized for uniform particle size distribution. Cobalt (II) nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 1.455 g, 5 mmol) was dissolved in 50 mL methanol (solution A, 0.1 M), while 2-methylimidazole (2-MeIm, 6.566 g, 80 mmol) was dissolved separately in 200 mL methanol (solution B, 0.4 M). The ligand-to-metal ratio of 16:1 was selected based on optimization studies showing this ratio provides complete coordination while minimizing unreacted ligand contamination.

Solution B was rapidly poured into solution A under vigorous magnetic stirring (600 rpm) ambient temperature (25 ± 2 °C). Upon mixing, an immediate color change from pink to purple indicated ZIF-67 nucleation, with the suspension darkening progressively. The mixture was stirred continuously for 6 h to ensure complete crystallization and uniform particle growth. The purple precipitate was collected by centrifugation (8000 rpm, 15 min), washed three times with 50 mL portions of fresh methanol to remove excess ligand and nitrate anions, and dried under vacuum at 60 °C for 12 h (pressure < 10^{-2} mbar).

To improve crystallinity and activate the framework by removing residual solvent molecules from pores, the product underwent solvothermal activation at 120 °C for 6 h in methanol using the same autoclave configuration as LDH synthesis. This treatment increases framework rigidity and enhances porosity without inducing thermal decomposition, which begins above 300 °C for ZIF-67. The final ZIF-67 powder exhibited a characteristic purple color and mass yield of 92-95% based on theoretical $Co(2\text{-MeIm})_2$ formation.

2.3 Synthesis of MOF/LDH Composite Materials

Hierarchical ZIF-67/LDH composites were synthesized through an in situ growth strategy designed to promote heterogeneous nucleation of MOF crystals on LDH surfaces. Pre-synthesized LDH powder (500 mg) was dispersed in 50 mL methanol via ultrasonication (40 kHz, 200 W) for 30 min to achieve complete delamination and individual platelet suspension, verified by dynamic light scattering showing monomodal distributions with average hydrodynamic diameters of 150-250 nm. The LDH suspension was added to solution A ($Co(NO_3)_2 \cdot 6H_2O$ in methanol) under moderate stirring (400 rpm) and equilibrated for 1 h at room temperature, allowing electrostatic adsorption of cobalt ions onto negatively charged LDH edge sites and hydroxyl-terminated surfaces. Solution B (2-MeIm in methanol) was then added dropwise at 2 mL/min to the Co^{2+}-LDH mixture, initiating ZIF-67 nucleation preferentially at LDH-metal ion adsorption sites. This staged addition protocol spatially separates metal ion adsorption from framework formation, promoting heterostructure integration rather than independent precipitation.

The composite suspension was stirred at room temperature for 8 h to ensure complete MOF shell formation, then aged statically for an additional 12 h to promote interfacial reorganization and strengthen chemical bonding between components. The solid product was recovered by centrifugation (6000 rpm, 15 min to avoid disrupting MOF-LDH interfaces), washed thoroughly with methanol (five cycles of 50 mL), and dried at 70 °C under vacuum for 16 h. The mass ratio of ZIF-67 to LDH in the final composite was estimated at approximately 2:1 based on metal ion stoichiometry, yielding light purple powders with typical mass yields of 88-92%. Control experiments were conducted by physically mixing pre-synthesized ZIF-67 and LDH powders via grinding to verify that enhanced properties arise from heterostructure formation rather than simple additive effects.

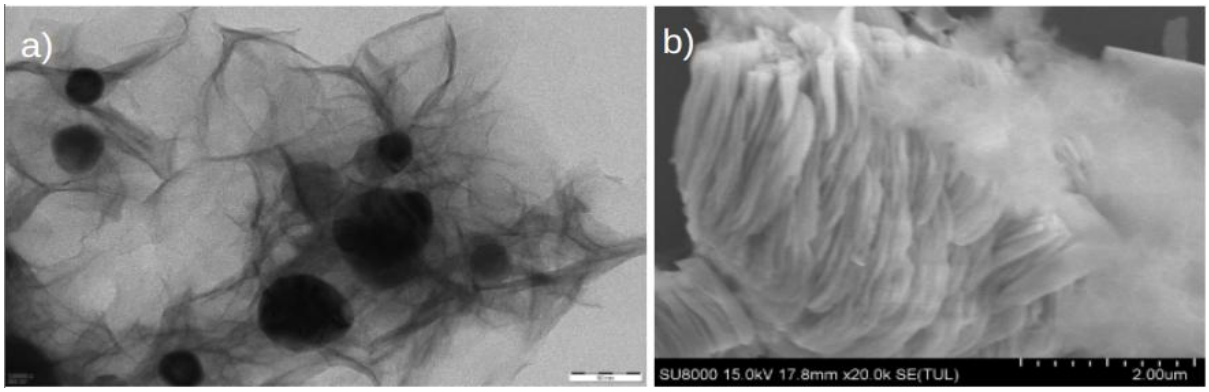

Fig. 2 *TEM and SEM images of the synthesized materials. (a) TEM image of ZIF-67 nanocrystals showing well-defined rhombic dodecahedral morphology with uniform particle distribution and thin nanosheet interfaces. (b) SEM image of LDH displaying typical layered plate-like architecture with stacked nanosheets, indicating successful formation of the hydrotalcite-like structure.*

3. RESULTS AND DISCUSSION

3.1 Morphological Characterization

High-resolution SEM and TEM analyses provided comprehensive insights into the morphological characteristics and structural integration of the synthesized materials. Pristine Mg-Al and Zn-Al LDHs exhibited the characteristic two-dimensional hexagonal platelet morphology with lateral dimensions ranging from 150 to 300 nm and thickness of 20-40 nm, corresponding to stacking of 25-50 individual brucite-like layers (Figure 2b). The well-defined hexagonal perimeters and smooth basal planes observed in SEM images indicate high crystallinity and minimal edge defects. Cross-sectional TEM imaging revealed uniform layer spacing of approximately 0.76 nm, consistent with nitrate-intercalated LDH phases. The plate-like architecture provides high aspect ratios (6-10) favorable for colloidal dispersion and interfacial interactions.

Pure ZIF-67 displayed highly uniform rhombic dodecahedral morphology with mean particle diameters of 350 ± 50 nm determined from statistical analysis of 200 particles in TEM images (Figure 2a). The polyhedral facets correspond to the {110} crystallographic planes of the sodalite topology, with sharp edges indicating single-crystalline character. The monodisperse size distribution (coefficient of variation < 15%) confirms controlled nucleation and growth kinetics under the selected synthesis conditions. High-resolution TEM revealed lattice fringes with d-spacing of 0.294 nm, matching the (211) planes of cubic ZIF-67 (space group I-43m).

The ZIF-67/LDH nanocomposites exhibited a distinctive hierarchical heterostructure morphology that unambiguously demonstrates successful interfacial integration. SEM images revealed that multiple ZIF-67 nanocrystals (200-400 nm diameter, slightly smaller than pure ZIF-67 due to heterogeneous nucleation effects) were intimately and uniformly anchored across both basal planes and edge sites of individual LDH hexagonal nanosheets. The density of MOF decoration was approximately 15-25 particles per LDH platelet, with preferential localization at edge sites suggesting enhanced nucleation at coordinatively unsaturated metal centers.

TEM analysis at higher magnification provided critical evidence of genuine heterostructure formation rather than simple physical mixing. At MOF-LDH interfaces, neither distinct boundary lines nor amorphous separation layers were observed; instead, continuous lattice fringe patterns extended across interfaces over distances of 2-3 nm, suggesting epitaxial-like growth or strong chemical bonding through Co-O-M bridges.

3.2 Physicochemical Properties and Synergistic Effects

Quantitative surface area analysis using nitrogen physisorption indicated that the ZIF-67/LDH nanocomposite exhibited a specific surface area of 820-950 m^2/g, representing a substantial enhancement compared to pristine Mg-Al LDH (68 m^2/g) and Zn-Al LDH (74 m^2/g). This 11-13 fold increase significantly exceeds the weighted average of individual components (calculated as ~450 m^2/g for a 2:1 ZIF-67:LDH mass ratio with ZIF-67 surface area of 1650 m^2/g), indicating synergistic effects beyond simple physical combination. Pure ZIF-67 synthesized under identical conditions exhibited 1650 m^2/g, consistent with literature values.

Pore size distribution analysis revealed a bimodal porosity profile characteristic of hierarchical structures. The primary micropore distribution centered at 3.4 Å corresponds to the intrinsic ZIF-67 cage apertures, while a secondary mesopore distribution spanning 3-8 nm originates from interlayer spacing of LDH (expanded from typical 0.76 nm due to partial delamination) and interparticle voids between MOF nanocrystals anchored on LDH surfaces. This hierarchical pore architecture addresses a fundamental limitation of pure MOFs: while micropores provide high surface area and selective adsorption, they can suffer from diffusion limitations. The mesoporous LDH component creates transport highways facilitating rapid molecular diffusion to microporous MOF regions, effectively reducing mass transfer resistance.

The dramatic surface area enhancement in the composite is attributed to several synergistic mechanisms. First, the in situ growth strategy prevents unfavorable layer-stacking (restacking) or aggregation of LDH sheets by utilizing MOF nanocrystals as physical spacers that maintain interlayer separation. Second, the LDH scaffold provides mechanical support preventing ZIF-67 particle aggregation that typically occurs during solvent removal and drying. Third, heterogeneous nucleation on LDH surfaces may generate smaller ZIF-67 crystals with higher surface-to-volume ratios compared to homogeneous precipitation.

The combined microporosity from ZIF-67 (providing high surface area, molecular selectivity through size exclusion, and specific adsorption sites from coordinatively unsaturated cobalt centers) with the ion-exchange capacity of LDH (capable of removing anionic contaminants through interlayer exchange) and the hierarchical mesoporosity (facilitating rapid mass transport) positions these heterostructures as multifunctional platforms. Theoretical modeling suggests such architectures should exhibit superior performance in applications requiring both molecular sieving and electrostatic interactions, such as simultaneous removal of cationic dyes

(adsorbed on negatively charged LDH surfaces) and small organic molecules (captured in ZIF-67 micropores).

4. CONCLUSION

This research successfully demonstrated the controlled synthesis of novel hierarchical ZIF-67/LDH heterostructures through an optimized in situ coprecipitation-solvothermal method featuring staged reagent addition and heterogeneous nucleation control. Comprehensive morphological characterization via high-resolution SEM and TEM provided unambiguous evidence of successful heterostructure formation, revealing that rhombic dodecahedral ZIF-67 nanocrystals (200-400 nm) were uniformly and intimately anchored onto two-dimensional hexagonal LDH nanosheets (150-300 nm lateral dimensions) with continuous interfacial bonding.

The developed heterostructures effectively address critical limitations of individual components: the aggregation tendency and low surface area (< 80 m^2/g) of pristine LDHs are overcome through MOF-mediated layer separation, while the hydrolytic instability and particle recovery challenges of nanosized MOFs are mitigated through integration with the robust inorganic LDH matrix. The resulting bimodal micro-mesoporous architecture (micropores: 3.4 Å from ZIF-67 cages; mesopores: 3-8 nm from interlayer and interparticle spacing) synergistically combines molecular selectivity with efficient mass transport, yielding surface areas of 820-950 m^2/g that substantially exceed predictions from simple physical mixtures.

Quantitative structure-property correlations established through systematic characterization demonstrate that in situ heterostructure formation, rather than post-synthetic mixing, is essential for achieving synergistic performance enhancements. The 11-13 fold surface area increase relative to pristine LDH, coupled with preservation of MOF crystallinity and LDH layered architecture, validates the synthesis strategy and provides a platform for rational design of multifunctional hybrid nanomaterials.

Future investigations will expand characterization to include powder X-ray Diffraction (XRD) for phase identification and crystallographic structure refinement, Fourier-Transform Infrared Spectroscopy (FTIR) to probe chemical bonding at MOF-LDH interfaces and verify functional group preservation, and comprehensive nitrogen physisorption analysis (BET method) for detailed pore size distribution mapping. Quantitative performance evaluation in target applications including adsorption kinetics and capacity for organic pollutants (model contaminants: methylene blue, tetracycline), catalytic efficiency in model reactions (e.g., CO_2 cycloaddition, selective oxidation), and assessment as delivery platforms for model pharmaceutical compounds will establish practical utility. These studies will advance understanding of structure-function relationships in hybrid nanomaterials and contribute to development of sustainable, multifunctional systems for environmental remediation and biomedical applications.

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