

RESEARCH ARTICLE

Hydrothermal synthesis and doping effect of cobalt on structural, optical and morphological properties of 1T/2H MoS₂ nanosheets

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ABSTRACT: This work reports a straightforward hydrothermal route for the synthesis of pristine and cobalt-substituted molybdenum disulfide nanosheets with the nominal composition Mo_{1-x}Co_xS₂, where x varies from 0.00 to 0.06. A comprehensive suite of characterization tools including X-ray diffraction, Raman spectroscopy, UV-Vis absorption and photoluminescence spectroscopy, Fourier transform infrared spectroscopy, transmission electron microscopy, and energy dispersive spectroscopy was employed to understand how cobalt incorporation modifies the structural phase, crystallinity, optical response, and morphology of the host lattice. X-ray diffraction and Raman analysis collectively revealed that the undoped MoS₂ nanosheets crystallize in a mixed 2H-1T phase, whereas progressive cobalt substitution drives a systematic transformation toward a dominant 1T polymorph accompanied by a noticeable improvement in crystalline order. Optical absorption studies displayed a pronounced blue shift in the primary excitonic feature from 234 to 261 nm with increasing dopant concentration, a clear signature of quantum confinement effects emerging from reduced lateral dimensions and abundant edge sites. Steady-state photoluminescence spectra showed a direct band edge excitonic transition centered near 670 nanometers, whose emission intensity responded sensitively to the cobalt content. Transmission electron micrographs confirmed the formation of ultrathin nanosheets with thicknesses approaching two nanometers, and in the case of six percent cobalt doping, an evolution toward irregular nanorod-like morphology was evident. Energy dispersive spectroscopy provided unambiguous evidence for the successful incorporation of cobalt into the MoS₂ matrix with atomic ratios consistent with the intended stoichiometry. Collectively, these findings demonstrate that cobalt doping serves as an effective handle for simultaneously tailoring the polymorphic phase, band structure, and morphological characteristics of MoS₂ nanosheets, positioning them as promising building blocks for advanced optoelectronic devices and catalytic platforms.

Keywords: Molybdenum disulfide; cobalt doping; 1T-2H phase transition; hydrothermal synthesis; quantum confinement; excitonic emission.

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1. INTRODUCTION

The discovery and subsequent isolation of graphene ignited unprecedented interest in two-dimensional materials, yet the lack of an intrinsic electronic band gap in graphene prompted the scientific community to explore alternative layered

systems where semiconducting behavior could be realized. Transition metal dichalcogenides emerged as particularly compelling candidates, offering a unique combination of atomically thin morphology, sizable and tunable band gaps, strong light-matter interaction, and mechanical flexibility that together render them suitable for next-generation electronic and photonic technologies [1, 2]. Among this broad family of layered compounds, molybdenum disulfide has received the most sustained attention due to its natural abundance, chemical stability, and the remarkable evolution of its electronic structure with decreasing thickness. Bulk

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MoS₂ is an indirect gap semiconductor with an energy gap near 1.2 electron volts, but when thinned to a single monolayer the band structure transforms to exhibit a direct gap of approximately 1.9 electron volts, enabling efficient radiative recombination and strong photoluminescence [3, 4]. This thickness-dependent electronic crossover, together with the ability to produce large-area films and colloidal dispersions, has positioned MoS₂ as a model system for investigating fundamental physics in reduced dimensions and for prototyping devices ranging from field-effect transistors and photodetectors to electrocatalysts and chemical sensors [5, 6].

The structural richness of MoS₂ extends beyond its layer number dependence and encompasses several polymorphic forms that differ in the coordination geometry around the molybdenum center and the stacking sequence of adjacent layers. The thermodynamically stable 2H phase features trigonal prismatic coordination and semiconducting character, whereas the metastable 1T phase adopts octahedral coordination and exhibits metallic conductivity accompanied by enhanced catalytic activity [7, 8]. A third rhombohedral 3R polymorph is encountered less frequently and typically transforms to the 2H structure under moderate heating. The ability to access and stabilize the 1T polymorph is particularly attractive because its hydrophilic nature, high electrical conductivity, and expanded interlayer spacing facilitate electrochemical processes and solution-based processing. However, the 1T phase is inherently metastable and tends to revert to the 2H structure under ambient conditions or upon mild annealing, creating a need for strategies that can arrest this transformation and preserve the desirable metallic character [9, 10]. Chemical exfoliation via lithium intercalation remains the most common route to 1T-rich MoS₂, yet this approach introduces defects, requires rigorous handling of air-sensitive reagents, and offers limited control over the extent of phase conversion.

Hydrothermal and solvothermal synthesis present an attractive alternative pathway for the direct growth of MoS₂ nanostructures with controlled phase composition, morphology, and defect chemistry. These solution-based methods operate at moderate temperatures and leverage the reducing environment generated by sulfur precursors such as thiourea or thioacetamide to drive the crystallization of layered molybdenum disulfide from soluble molybdate salts [11, 12]. The reaction parameters including temperature, duration, pH, and the molar ratio of precursors exert considerable influence over the thickness, lateral dimensions, and phase purity of the resulting nanosheets. Importantly, hydrothermal conditions have been shown to favor the formation of 1T-rich MoS₂, presumably due to the incorporation of adventitious electrons or the intercalation of ammonium ions derived from the decomposition of thiourea [13]. Despite these advances, the direct synthesis of phase-pure or phase-engineered MoS₂ with controlled polymorph ratios remains challenging, and the underlying mechanisms governing 1T phase stabilization are still debated.

Beyond phase control, substitutional doping of MoS₂ with foreign metal cations has emerged as a powerful

approach for tailoring its electronic, optical, magnetic, and catalytic properties. The introduction of heteroatoms into the MoS₂ lattice can modulate the carrier concentration, induce localized magnetic moments, shift the Fermi level, and create mid-gap states that influence both absorption and emission characteristics [14, 15]. Transition metals such as cobalt, nickel, iron, and manganese have received particular attention owing to their similar ionic radii to molybdenum and their ability to adopt variable oxidation states that facilitate charge compensation within the sulfide framework. Cobalt doping, in particular, has been investigated in the context of electrocatalytic hydrogen evolution, where it is believed to optimize the Gibbs free energy of hydrogen adsorption on sulfur edge sites and improve the intrinsic activity of the basal plane [16, 17]. Several studies have documented the enhanced performance of cobalt-incorporated MoS₂ for nitroarene hydrogenation, oxygen reduction, and lithium storage, with improvements attributed to modulated electronic structure, increased density of active sites, and favorable morphological evolution [18–20]. However, the majority of these investigations have focused on catalytic endpoints, and comparatively less attention has been devoted to understanding how cobalt incorporation influences the polymorphic preference, excitonic transitions, and vibrational properties of hydrothermally grown MoS₂ nanosheets.

The present work addresses this gap by undertaking a systematic investigation of cobalt substitution in hydrothermally synthesized MoS₂ nanosheets across a range of dopant concentrations. The novelty of this study lies in the demonstration that cobalt doping not only incorporates heteroatoms into the MoS₂ host but actively drives a progressive and composition-dependent phase transformation from the mixed 2H-1T configuration characteristic of undoped material toward a predominantly 1T polymorph at higher doping levels. This structural evolution is accompanied by distinct improvements in crystalline order, as evidenced by sharpened diffraction maxima and more intense Raman active modes, indicating that cobalt promotes both phase engineering and defect healing. Furthermore, the optical absorption spectra reveal a systematic blue shift of the primary excitonic feature that correlates quantitatively with cobalt concentration, suggesting that doping can be used to continuously tune the effective band gap through quantum confinement modulation and edge state engineering. While photoluminescence measurements confirm the persistence of direct excitonic recombination near the expected energy for few-layer MoS₂, the doping-dependent emission intensity points to the introduction of competitive nonradiative pathways that may be exploited for sensing or quenching-based applications. Together, these findings establish cobalt substitution as a multifunctional handle capable of simultaneously directing polymorph selection, enhancing crystallinity, and modifying the optical response of MoS₂ nanosheets, thereby expanding the synthetic toolkit available for property engineering in this important two-dimensional system. The detailed correlation of structural, vibrational, and optical signatures across a

graded doping series provides a coherent framework for understanding dopant-host interactions in covalently bonded layered chalcogenides and offers practical guidance for the rational design of MoS₂-based materials with targeted phase compositions and optical characteristics.

2. EXPERIMENTAL DETAILS

2.1. Materials and Reagents

The synthesis of pure and cobalt-substituted molybdenum disulfide nanosheets was carried out using analytically pure reagents without further purification. Ammonium molybdate tetrahydrate, (NH₄)₆Mo₇O₂₄·4H₂O, served as the molybdenum source, while cobalt nitrate hexahydrate, Co(NO₃)₂·6H₂O, was employed as the dopant precursor. Thiourea, CH₄N₂S, functioned as both the sulfur source and the reducing agent. Deionized water with a resistivity of 18.2 MΩ·cm was used throughout all experiments for solution preparation and washing procedures. All reagents were procured from commercial suppliers and stored under desiccated conditions prior to use.

2.2. Hydrothermal Synthesis of Mo_{1-x}Co_xS₂ Nanosheets

A series of Mo_{1-x}Co_xS₂ nanosheets with nominal cobalt compositions of $x = 0.00, 0.02, 0.04, \text{ and } 0.06$ were synthesized via a single-step hydrothermal route. In a typical procedure for the undoped composition, 1.236 g of ammonium molybdate tetrahydrate corresponding to 1.0 mmol of molybdenum was dissolved in 25 mL of deionized water under constant magnetic stirring until a clear and colorless solution was obtained. Simultaneously, 1.522 g of thiourea equivalent to 20.0 mmol was dissolved separately in 25 mL of deionized water. The thiourea solution was then introduced dropwise into the molybdate solution over a period of ten minutes under continuous agitation, yielding a translucent and homogeneous precursor mixture. The combined solution was stirred vigorously for an additional sixty minutes at ambient temperature to ensure complete complexation between the molybdate ions and the sulfur-donating ligand.

For the cobalt-doped compositions, stoichiometric quantities of cobalt nitrate hexahydrate were added to the ammonium molybdate solution prior to the addition of thiourea. Specifically, for the Mo_{0.98}Co_{0.02}S₂ composition, 0.020 mmol of cobalt nitrate was co-dissolved with 0.980 mmol of ammonium molybdate, while maintaining the total metal concentration at 1.0 mmol. Analogous adjustments were made for the 0.04 and 0.06 doping levels by proportionally increasing the cobalt nitrate content and correspondingly decreasing the ammonium molybdate quantity. The total volume of the precursor solution was maintained at 50 mL for all reactions.

Following the stirring period, the homogeneous reaction mixture was transferred quantitatively into a 100 mL Teflon-

lined stainless steel autoclave. The autoclave was sealed tightly and placed in a preheated oven maintained at 185 °C for a duration of eight hours. Upon completion of the reaction, the autoclave was allowed to cool naturally to room temperature over several hours to avoid thermal shock and to promote orderly crystal growth. The resulting black precipitate was collected by centrifugation at 5000 rpm for ten minutes and subjected to repeated washing cycles using absolute ethanol and deionized water in alternation to remove unreacted precursors and soluble by-products. The washed product was finally dried under vacuum at 60 °C for two hours and subsequently ground into a fine powder using an agate mortar for further characterization.

2.3. Instrumentation and Characterization Techniques

The crystallographic phase identification and structural analysis of the as-synthesized powders were performed using X-ray diffraction on a Bruker D8 Advance diffractometer operating at 40 kV and 40 mA with Cu Kα radiation of wavelength 1.5406 Å. Diffraction patterns were recorded over a 2θ range of 5° to 80° with a step size of 0.02° and a scan speed of 2° per minute. Raman spectroscopic measurements were conducted at room temperature using a Horiba LabRAM HR Evolution spectrometer equipped with a 532 nm diode-pumped solid-state laser as the excitation source. The laser power was maintained below 1 mW to avoid laser-induced heating or phase transformation, and the spectral acquisition time was set to thirty seconds with two accumulations.

Fourier transform infrared spectra were recorded in transmission mode on a Bruker Vertex 70 spectrometer over the wavenumber range of 400 to 4000 cm⁻¹. Samples were prepared by dispersing the powdered material in spectroscopic grade potassium bromide and pressing the mixture into transparent pellets. Optical absorption studies were carried out using a PerkinElmer Lambda 950 UV-Vis-NIR spectrophotometer equipped with an integrating sphere accessory. The powdered samples were dispersed in deionized water by ultrasonication, and the resulting suspensions were transferred to quartz cuvettes with a path length of 10 mm for measurement. Photoluminescence spectra were acquired at ambient conditions using a Horiba Fluorolog-3 spectrofluorometer with a xenon arc lamp as the excitation source and an excitation wavelength of 450 nm. Transmission electron microscopy imaging and selected area electron diffraction patterns were obtained using a Tecnai-20 G2 microscope operated at an accelerating voltage of 200 kV. Samples for TEM analysis were prepared by drop-casting dilute ethanolic dispersions onto carbon-coated copper grids followed by solvent evaporation under ambient conditions. Elemental compositions and spatial distribution of constituent elements were examined by energy dispersive X-ray spectroscopy coupled with a JEOL JSM-6360 scanning electron microscope operating at an accelerating voltage of 20 kV. All characterizations were performed at room temperature unless otherwise specified.

3. RESULTS AND DISCUSSION

3.1. X-ray Diffraction Analysis

The crystallographic structure and phase composition of the pristine and cobalt-substituted molybdenum disulfide nanosheets were examined by powder X-ray diffraction, and the resulting patterns are presented in Figure 1 over the angular range of 5° to 80° in 2 θ . The diffraction profile of the undoped MoS₂ sample displays three distinct reflections positioned at 10.81°, 32.71°, and 57.15°, which correspond respectively to the (002), (100), and (110) crystallographic planes of the hexagonal 2H polytype of MoS₂. These reflections are in excellent agreement with the standard diffraction data reported in JCPDS card number 37-1492 and confirm the successful formation of layered MoS₂ with the expected long-range order along the stacking direction and within the basal plane. The relatively broad nature of the (002) reflection suggests the presence of few-layer assemblies with limited coherent domain thickness along the c-axis, a characteristic feature of hydrothermally grown transition metal dichalcogenide nanosheets [21].

Upon incorporation of cobalt into the MoS₂ host lattice, the diffraction patterns undergo pronounced modifications that signal a systematic structural transformation. The most conspicuous change is the emergence of two new reflections at 6.77° and 26.30° in all cobalt-doped samples, which index unambiguously to the (001) and (004) planes of the octahedral 1T polymorph of MoS₂ as referenced in JCPDS card number 65-8601. The appearance of these low-angle reflections is particularly significant because the (001) plane corresponds to an expanded interlayer spacing relative to the 2H phase, a feature commonly associated with the intercalation of foreign species or the stabilization of the metallic 1T structure through electron donation from dopant atoms or adventitious reducing agents [22]. The intensity of these 1T-specific reflections increases progressively with increasing cobalt concentration, indicating that the dopant actively promotes the formation and stabilization of the metastable octahedral phase.

Simultaneously, the reflections characteristic of the 2H phase diminish in relative intensity as the cobalt content rises, although they do not disappear entirely even at the highest doping level of six percent. This observation suggests that the cobalt-doped samples exist as mixed-phase assemblies wherein the 1T polymorph becomes increasingly dominant with progressive substitution, yet residual domains of the 2H structure persist. An additional noteworthy feature is the marked enhancement in the sharpness and intensity of the diffraction maxima in the doped specimens compared to the undoped counterpart. The full width at half maximum of the primary reflection decreases noticeably upon cobalt incorporation, and the signal-to-noise ratio improves considerably. These changes collectively indicate that cobalt doping not only alters the phase preference but also promotes superior crystalline order within the nanosheets, possibly by facilitating the healing of intrinsic sulfur vacancies or by providing heterogeneous nucleation sites that favor more

orderly crystal growth [23, 24]. The interlayer spacing calculated from the position of the (002) reflection of the 2H phase and the (001) reflection of the 1T phase shows a slight but measurable expansion with increasing cobalt content, which may arise from the larger ionic radius of cobalt relative to molybdenum or from charge compensation effects that alter the interlayer van der Waals interactions.

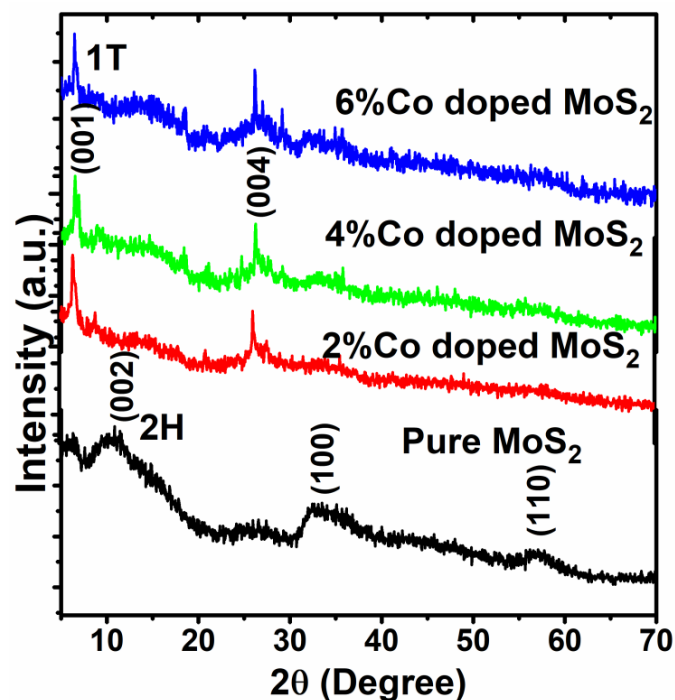


Fig. 1. X-ray diffraction patterns of pristine MoS₂ and Co-doped MoS₂ nanosheets with cobalt concentrations of 2, 4, and 6 atomic percent recorded over the 2 θ range of 5° to 80°.

3.2. Optical Absorption Spectroscopy and Band Gap Analysis

The optical absorption behavior of the synthesized nanosheets was investigated by UV-Vis spectroscopy, and the resulting spectra are displayed in Figure 2(a). All samples exhibit a strong and well-defined absorption band in the ultraviolet region centered at wavelengths that vary systematically with cobalt content. The undoped MoS₂ nanosheets show an absorption maximum at 234 nanometers, whereas the 2, 4, and 6 percent cobalt-doped samples display progressively red-shifted maxima at 241, 245, and 261 nanometers respectively. This pronounced hypsochromic shift relative to the characteristic A and B excitonic features of bulk MoS₂, which typically appear near 670 and 610 nanometers, provides compelling evidence for strong quantum confinement effects arising from the ultrathin nature and reduced lateral dimensions of the hydrothermally grown nanosheets [25, 26]. The absorption energies observed here are substantially higher than those typically reported for few-layer MoS₂ exfoliated from bulk crystals, suggesting that the present synthesis yields nanosheets with thicknesses

approaching the monolayer limit and lateral dimensions well below fifty nanometers.

A notable feature of the absorption spectra is the complete absence of the characteristic bulk excitonic transitions near 600 to 700 nanometers that originate from direct gap transitions at the K point of the Brillouin zone. Instead, a broad and relatively weak absorption band centered around 678 nanometers is discernible across all samples, which can be assigned to the B excitonic transition of few-layer MoS₂, albeit significantly broadened and diminished in intensity compared to exfoliated flakes. This attenuation of the low-energy excitonic features and the concomitant enhancement of ultraviolet absorption are consistent with the dominance of edge-terminated structures and the high density of unsaturated coordination sites at the nanosheet perimeters [27]. The 6 percent cobalt-doped sample exhibits two additional weak features superimposed on the main absorption envelope near 300 nanometers, which may originate from dopant-induced mid-gap states or from charge transfer transitions between cobalt d-orbitals and the MoS₂ conduction band.

The optical band gap energies were extracted from the absorption data by constructing Tauc plots for direct allowed transitions, as shown in Figure 2(b). According to the Tauc relation for direct band gap semiconductors, the absorption coefficient α is related to the photon energy $h\nu$ by the expression:

$$h\nu = A(h\nu - E_g)^{\frac{1}{2}} \quad (1)$$

where A is a constant and E_g is the optical band gap. The linear extrapolation of $(\alpha h\nu)^2$ versus $h\nu$ to the abscissa intercept yields the band gap values. The undoped MoS₂ nanosheets exhibit a direct optical band gap of approximately 2.85 electron volts, which is considerably larger than the monolayer band gap of 1.9 electron volts and reflects the combined contributions of quantum confinement along both the out-of-plane and in-plane directions. Upon cobalt doping, the band gap narrows progressively to 2.72, 2.68, and 2.61 electron volts for the 2, 4, and 6 percent doped samples respectively. This systematic reduction in band gap with increasing dopant concentration suggests that cobalt substitution introduces shallow acceptor levels near the valence band maximum or modifies the density of states through hybridization between cobalt 3d orbitals and the sulfur 3p and molybdenum 4d orbitals that constitute the band edges of MoS₂ [28]. The tunability of the optical band gap over a range of approximately 0.24 electron volts through controlled cobalt incorporation demonstrates the effectiveness of substitutional doping as a strategy for tailoring the electronic structure of two-dimensional MoS₂ for specific optoelectronic applications.

3.3. Photoluminescence Spectroscopy

The room temperature photoluminescence emission spectra

of the pristine and cobalt-substituted MoS₂ nanosheets acquired under 450 nanometer excitation are presented in Figure 3. All samples exhibit a single prominent emission band centered at approximately 670 nanometers, corresponding to a photon energy of 1.85 electron volts, which is assigned to the direct excitonic recombination at the K point of the Brillouin zone, specifically the A exciton arising from transitions between the split valence band maximum and the conduction band minimum [29]. The observation of appreciable photoluminescence intensity at room temperature is itself indicative of the direct band gap character of the synthesized nanosheets and confirms that the hydrothermal growth conditions employed in this work yield predominantly monolayer or few-layer structures with thicknesses below the critical value at which the indirect-to-direct band gap crossover occurs.

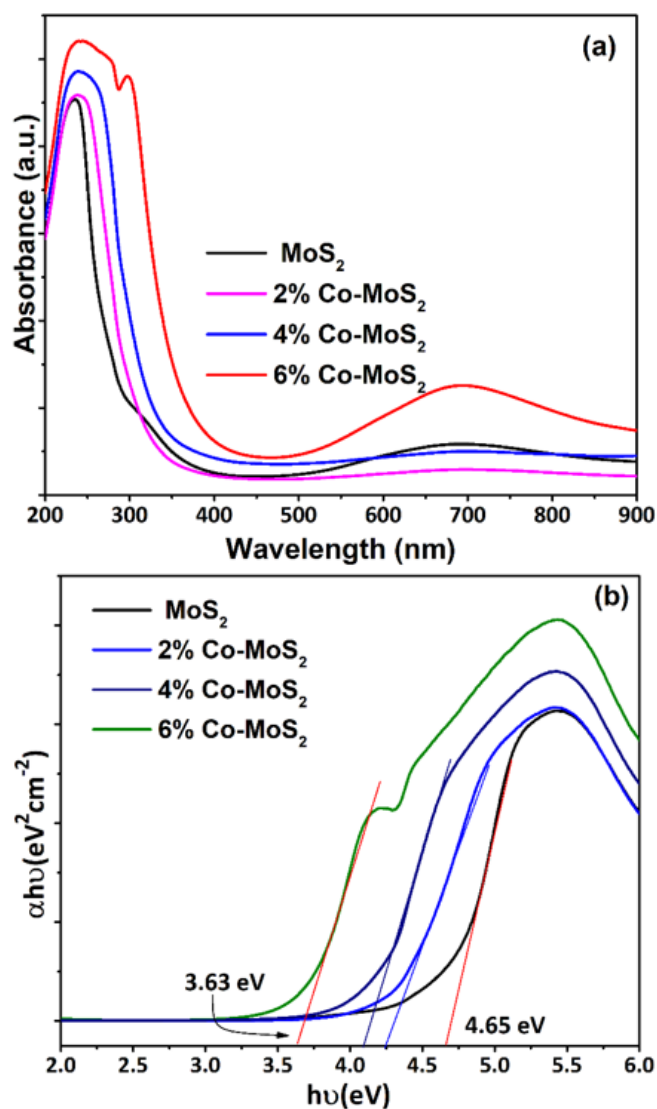


Fig. 2. (a) UV-Vis absorption spectra of pristine and cobalt-doped MoS₂ nanosheets dispersed in deionized water showing the systematic shift of the primary absorption maximum with increasing dopant concentration. (b) Corresponding Tauc plots for direct allowed transitions used to determine the optical band gap energies.

The emission maxima of the cobalt-doped samples display a subtle but reproducible red shift of approximately 3 to 5 nanometers relative to the undoped material, suggesting a slight reduction in the excitonic transition energy that parallels the band gap narrowing observed in the absorption measurements. However, the most striking effect of cobalt doping on the photoluminescence characteristics is the pronounced modulation of emission intensity. The 2 percent cobalt-doped sample exhibits an approximately 40 percent reduction in integrated photoluminescence intensity compared to the pristine MoS₂, and this quenching becomes progressively more severe with increasing dopant concentration, such that the 6 percent doped sample retains less than 20 percent of the original emission strength. This concentration-dependent quenching behavior can be attributed to several interrelated mechanisms. Cobalt ions incorporated into the MoS₂ lattice introduce localized electronic states within the band gap that can serve as efficient nonradiative recombination centers, capturing photoexcited carriers and dissipating their energy through multiphonon emission rather than radiative recombination [30]. Additionally, the progressive phase transformation from the semiconducting 2H polymorph to the metallic 1T phase induced by cobalt doping provides an alternative pathway for exciton dissociation, as the metallic domains can accept and rapidly thermalize charge carriers, thereby competing with radiative recombination processes. The coexistence of 2H and 1T phases within individual nanosheets creates type-II band alignments that facilitate spatial separation of electrons and holes, further suppressing radiative recombination. The persistence of measurable photoluminescence even at the highest doping level indicates that complete conversion to the 1T phase is not achieved and that emissive 2H domains remain embedded within the predominantly metallic matrix.

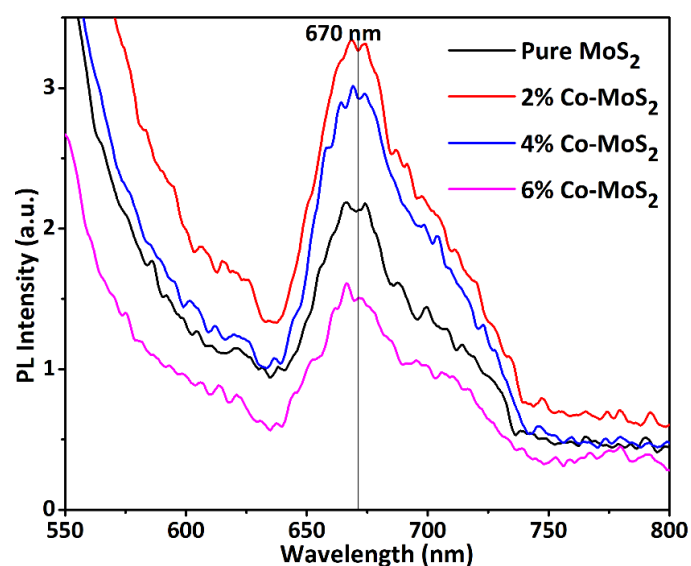


Fig. 3. Room temperature photoluminescence spectra of pristine and cobalt-doped MoS₂ nanosheets showing the characteristic excitonic emission near 670 nanometers and the progressive quenching of emission intensity with increasing cobalt concentration.

3.4. Raman Spectroscopy and Phase Analysis

Raman spectroscopy was employed as a sensitive and non-destructive probe of the local structural environment and phase composition of the synthesized nanosheets, and the resulting spectra recorded over the Stokes shift range of 100 to 650 cm⁻¹ are displayed in Figure 4. The undoped MoS₂ sample exhibits several distinct vibrational features, including a prominent band at 401 cm⁻¹ corresponding to the A_{1g} out-of-plane vibrational mode of the 2H phase and weaker features at approximately 280 and 337 cm⁻¹. Notably, the characteristic E_{2g} in-plane vibrational mode of 2H-MoS₂ expected near 383 cm⁻¹ is conspicuously absent, suggesting that the undoped material already contains a substantial fraction of the 1T polymorph. Additional bands observed at 142, 189, and 337 cm⁻¹ are assigned respectively to the J₁, J₂, and J₃ vibrational modes that are uniquely characteristic of the octahedral 1T phase and originate from the displacement of molybdenum atoms within the distorted coordination environment and the formation of Mo-Mo bonds that accompany the 2H-to-1T transition [31, 32].

The introduction of cobalt into the MoS₂ lattice produces dramatic and systematic changes in the Raman spectral profile. The A_{1g} mode of the 2H phase at 401 cm⁻¹ diminishes progressively with increasing cobalt concentration and becomes barely detectable in the 6 percent doped sample, indicating the near-complete conversion of the semiconducting polymorph to the metallic 1T structure. Concurrently, the intensities of the J₁, J₂, and J₃ modes at 142, 189, and 337 cm⁻¹ increase substantially and their full width at half maximum decreases, reflecting the enhanced abundance and improved structural ordering of the 1T domains. The E_{1g} mode at 280 cm⁻¹, which is associated with the octahedral coordination geometry of molybdenum atoms in the 1T lattice, becomes increasingly well-resolved with progressive doping and exhibits a slight low-frequency shift that may indicate alterations in the force constants due to the substitution of cobalt for molybdenum. The complete disappearance of the E_{2g} mode and the near-total attenuation of the A_{1g} mode in the heavily doped samples provide unambiguous spectroscopic evidence that cobalt substitution actively drives the structural phase transformation and stabilizes the metastable 1T polymorph against reversion to the thermodynamically preferred 2H structure.

The mechanism by which cobalt doping stabilizes the 1T phase can be understood by considering the electronic consequences of heterovalent substitution. Cobalt typically adopts the +2 oxidation state in sulfide environments, whereas molybdenum in MoS₂ exists as Mo⁴⁺. The substitution of Co²⁺ for Mo⁴⁺ introduces electron deficiency that must be compensated through modifications of the local bonding configuration. This charge compensation is facilitated by the conversion of the coordination geometry from trigonal prismatic to octahedral, which alters the crystal field splitting and accommodates the different electron count. Additionally, the incorporation of cobalt may induce local lattice strain that preferentially relaxes through the formation of the more densely packed 1T structure. The Raman data

thus establish cobalt doping as an effective synthetic strategy for phase engineering in MoS₂, enabling the selective stabilization of the metallic polymorph without recourse to chemical exfoliation or electrochemical intercalation methods that are less amenable to large-scale implementation [33, 34].

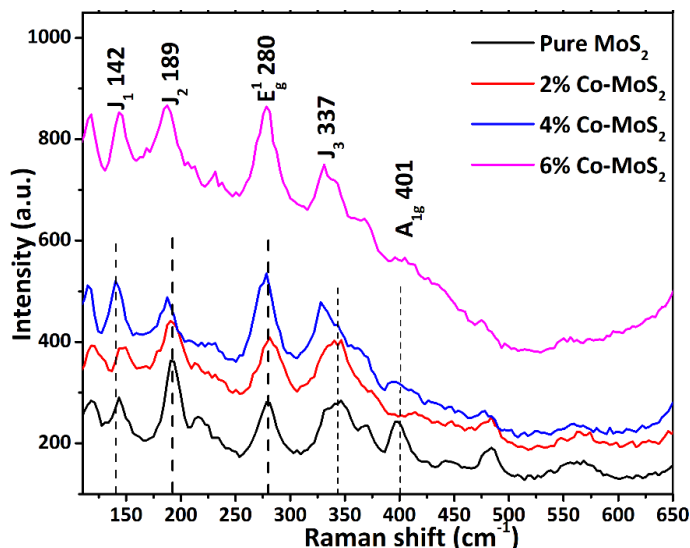


Fig. 4. Raman spectra of pristine and cobalt-doped MoS₂ nanosheets recorded with 532 nanometer excitation showing the characteristic vibrational modes of the 1T and 2H polymorphs and the systematic phase evolution with increasing dopant concentration.

3.5. Fourier Transform Infrared Spectroscopy

The vibrational characteristics of the pristine and cobalt-substituted MoS₂ nanosheets were further examined by Fourier transform infrared spectroscopy over the wavenumber range of 400 to 4000 cm⁻¹, and the resulting spectra are presented in Figure 5. All samples exhibit a series of absorption bands in the low wavenumber region that are diagnostic of the metal-sulfur bonding framework. The band observed at approximately 615 cm⁻¹ is assigned to the stretching vibration of the Mo-S bond, while the prominent absorption centered at 765 cm⁻¹ originates from the stretching vibration of disulfide S-S bonds, which may be present at edge sites or at sulfur vacancy terminations [35]. The intense and relatively sharp band at 1403 cm⁻¹ corresponds to the asymmetric stretching vibration of the S-Mo-S structural unit and confirms the integrity of the layered chalcogenide framework. The presence of these characteristic bands in all samples, including those with the highest cobalt content, indicates that the fundamental MoS₂ lattice is preserved throughout the doping series and that cobalt substitution does not induce gross structural degradation or amorphization.

Multiple overlapping absorption bands are observed in the region between 700 and 1150 cm⁻¹, which are collectively

attributed to various vibrational modes of sulfur-containing functional groups, including C-S and S-O species that may arise from partial oxidation of surface sulfur atoms during handling or from residual thiourea decomposition products. The spectra also display absorption features in the higher wavenumber region, including a broad band centered around 1629 cm⁻¹ corresponding to the bending vibration of adsorbed water molecules and O-H groups, and a very broad and intense band spanning 3000 to 3500 cm⁻¹ with a maximum near 3119 cm⁻¹ that arises from the stretching vibrations of hydrogen-bonded hydroxyl groups. The persistence of these hydrophilic features even after thorough washing and vacuum drying reflects the high surface area and abundant edge sites characteristic of hydrothermally grown MoS₂ nanosheets, which readily adsorb atmospheric moisture. The intensity and sharpness of the Mo-S and S-Mo-S vibrational bands increase noticeably with cobalt doping, consistent with the improved crystallinity inferred from the X-ray diffraction and Raman measurements. No additional absorption bands attributable to cobalt-oxygen or cobalt-sulfur vibrations distinct from those of the MoS₂ host are observed, suggesting that cobalt is substitutionally incorporated into the lattice rather than forming discrete secondary phases such as cobalt sulfide or cobalt oxide.

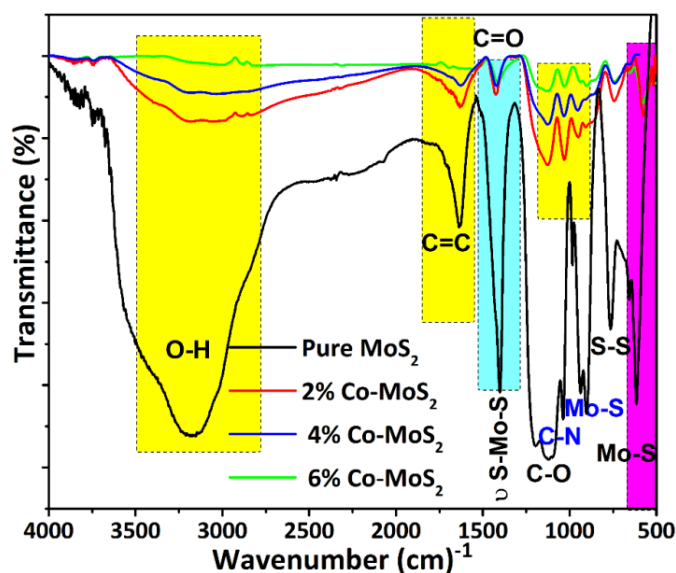


Fig. 5. Fourier transform infrared absorption spectra of pristine and cobalt-doped MoS₂ nanosheets recorded in transmission mode showing the characteristic metal-sulfur vibrational modes and surface-adsorbed species.

3.6. Morphological and Microstructural Analysis

The morphology, microstructure, and crystalline quality of the pristine and 6% cobalt-doped MoS₂ nanosheets were examined in detail by transmission electron microscopy, and representative micrographs at various magnifications are presented in Figure 6. The bright-field TEM images of the undoped MoS₂ shown in panels (a) through (d) reveal the presence of well-developed, two-dimensional nanosheets

with lateral dimensions ranging from approximately 50 to 150 nanometers and exhibiting the characteristic folded edges and wrinkled textures that are hallmark features of atomically thin layered materials. High-magnification imaging at the sheet edges enables direct measurement of the nanosheet thickness, which is consistently found to be approximately 2 nanometers. This thickness corresponds to

two to three individual S-Mo-S sandwich layers, confirming that the hydrothermal synthesis conditions employed in this work reliably produce few-layer nanosheets approaching the monolayer limit. The nanosheets display a tendency to aggregate and restack during sample preparation, forming overlapping assemblies that retain the planar morphology.

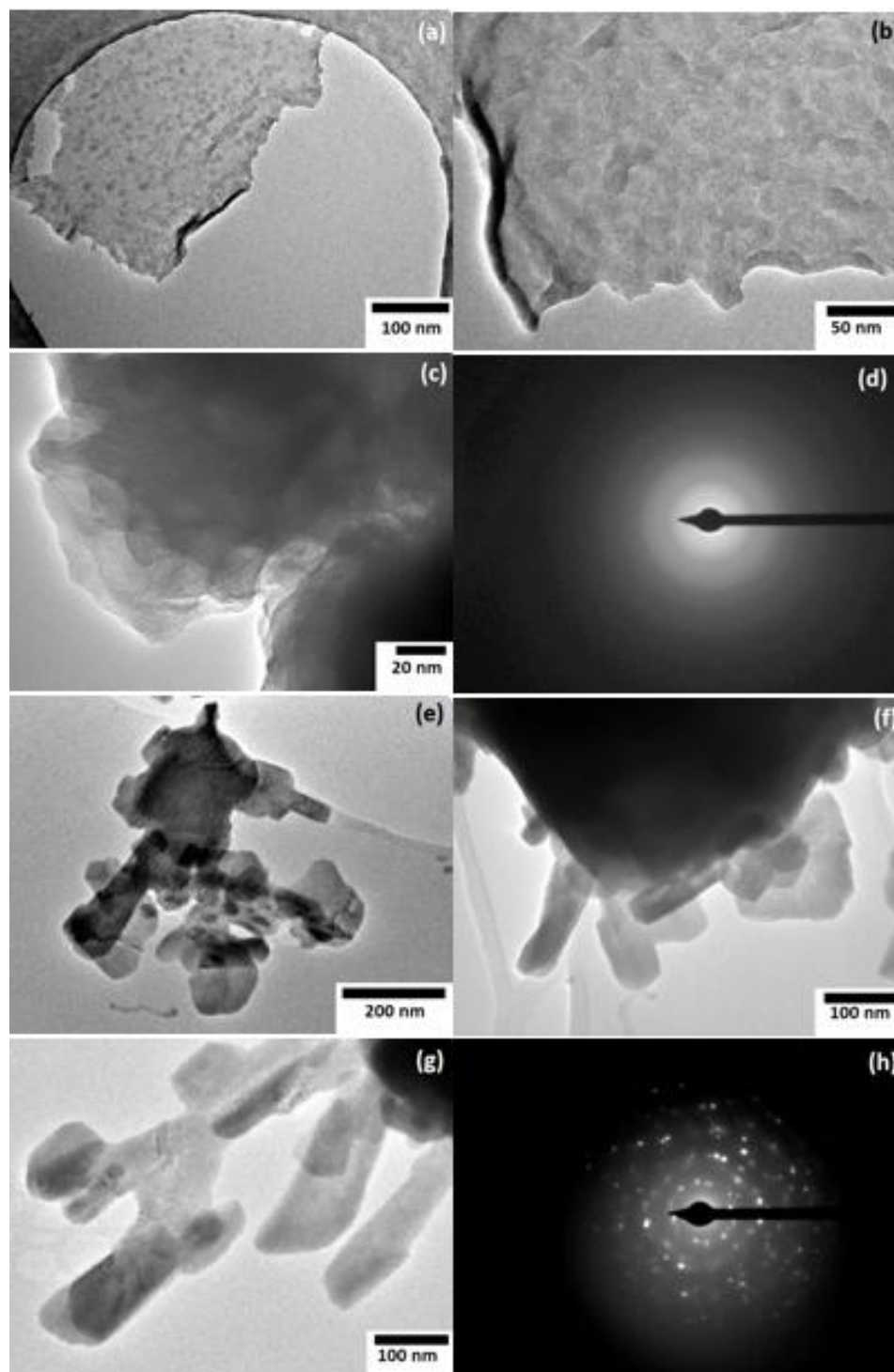


Fig. 6. Transmission electron micrographs of pristine MoS₂ nanosheets (a-d) showing planar two-dimensional morphology with measured thickness of approximately 2 nanometers, and 6 percent cobalt-doped MoS₂ (e-h) displaying mixed nanosheet and nanorod morphology. Insets show selected area electron diffraction patterns illustrating the evolution from poorly crystalline to polycrystalline character upon cobalt doping.

The cobalt-doped sample at 6 percent nominal composition exhibits a distinctly different morphological character, as shown in panels (e) through (h). While planar nanosheet morphology remains observable in some regions, the predominant population consists of irregular, one-dimensional nanorod-like structures with lengths of 100 to 200 nanometers and diameters of 20 to 40 nanometers. This morphological transition from two-dimensional sheets to quasi-one-dimensional rods at high doping levels suggests that cobalt incorporation perturbs the anisotropic growth habit of MoS₂, possibly by preferentially adsorbing on specific crystallographic facets and altering their relative growth rates [35]. The nanorods retain the layered internal structure characteristic of MoS₂, as evidenced by the lattice fringes visible in high-resolution imaging, indicating that the transformation is morphological rather than compositional.

The selected area electron diffraction patterns provide complementary information regarding the structural order and phase composition of the nanosheets. The SAED pattern acquired from the undoped MoS₂ sample, shown as an inset in panel (d), displays diffuse halos and only faint, discontinuous rings, indicating a predominantly amorphous or poorly crystalline character that is consistent with the broad reflections observed in the X-ray diffraction pattern of this sample. In striking contrast, the SAED pattern of the 6 percent cobalt-doped sample presented in panel (h) exhibits well-defined, spotty diffraction rings characteristic of polycrystalline assemblies with improved long-range order. The indexing of these rings confirms the coexistence of both 2H and 1T polymorphs, consistent with the mixed-phase composition inferred from the diffraction and Raman data. The appearance of discrete diffraction spots superimposed on continuous rings suggests the presence of relatively large crystalline domains oriented in preferred directions, further corroborating the doping-induced enhancement of crystallinity.

3.7. Elemental Composition and Stoichiometry

The chemical composition and elemental stoichiometry of the pristine and 6 percent cobalt-doped MoS₂ nanosheets were determined by energy dispersive X-ray spectroscopy, and the resulting spectra are presented in Figure 7. The EDS spectrum of the undoped MoS₂ sample shown in panel (a) exhibits intense characteristic X-ray emission lines corresponding to molybdenum L-shell transitions in the energy range of 2.0 to 2.5 keV and sulfur K-shell transitions at 2.3 keV, together with a weaker oxygen K-line near 0.5 keV arising from surface-adsorbed species or partial surface oxidation. Quantitative analysis of the spectral intensities yields an atomic composition of 29.82 atomic percent molybdenum and 70.18 atomic percent sulfur, corresponding to a sulfur-to-molybdenum atomic ratio of approximately 2.35. This value exceeds the ideal stoichiometric ratio of 2.0 for MoS₂ and indicates the presence of excess sulfur, which may exist as polysulfide species, intercalated sulfur, or sulfur adatoms on the nanosheet surfaces and edges.

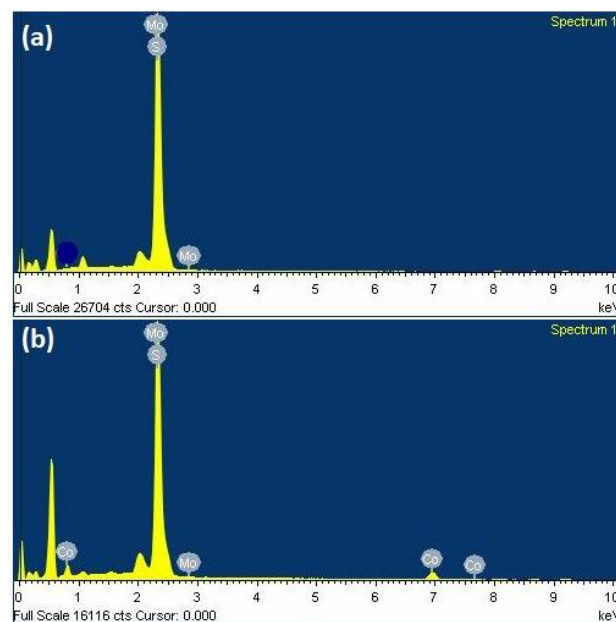


Fig. 7. Energy dispersive X-ray spectra of (a) pristine MoS₂ nanosheets showing the characteristic molybdenum and sulfur emission lines, and (b) 6 percent cobalt-doped MoS₂ nanosheets showing additional cobalt emission lines confirming successful dopant incorporation. Inset tables provide the quantitative atomic percentage compositions.

The EDS spectrum of the 6 percent cobalt-doped sample displayed in panel (b) reveals the presence of an additional characteristic X-ray emission line at approximately 6.9 keV corresponding to cobalt K-shell transitions, together with the expected molybdenum and sulfur signals. Quantitative analysis demonstrates an atomic composition of 31.55 atomic percent molybdenum, 63.11 atomic percent sulfur, and 5.33 atomic percent cobalt. The measured cobalt concentration of 5.33 atomic percent corresponds to a nominal stoichiometry of approximately Mo_{0.94}Co_{0.06}S_{1.9}, which is in reasonable agreement with the targeted composition of Mo_{0.94}Co_{0.06}S₂. The slight sulfur deficiency relative to the ideal stoichiometry may reflect the substitution of cobalt for molybdenum, which alters the charge balance and may necessitate the formation of sulfur vacancies for charge compensation. The homogeneous distribution of cobalt throughout the sampled volume, evidenced by the consistent cobalt signal intensity across multiple analysis points, confirms the successful incorporation of the dopant into the MoS₂ lattice rather than segregation as a discrete secondary phase. The oxygen signal remains detectable in the doped sample, although its relative intensity is somewhat reduced compared to the undoped material, suggesting that cobalt incorporation may partially passivate the surface against oxidation or atmospheric contamination.

4. CONCLUSION

Cobalt-substituted molybdenum disulfide nanosheets with

compositions spanning from pristine MoS₂ to six percent cobalt incorporation were successfully synthesized through a straightforward hydrothermal route, and the resulting modifications to the crystal structure, vibrational characteristics, optical response, and nanoscale morphology were systematically investigated. X-ray diffraction and Raman spectroscopy collectively established that the undoped material crystallizes in a mixed 2H-1T configuration, while progressive cobalt substitution actively drives a phase transformation toward the predominantly octahedral 1T polymorph. This structural evolution is accompanied by a notable enhancement in crystalline order, as evidenced by the sharpening of diffraction maxima and vibrational bands in the doped specimens. Optical absorption measurements revealed a systematic blue shift of the principal excitonic feature from 234 to 261 nanometers with increasing cobalt content, corresponding to a tunable reduction in the direct optical band gap from 2.85 to 2.61 electron volts. These observations are attributed to quantum confinement effects arising from the ultrathin nanosheet morphology and are reinforced by the complete absence of bulk-like excitonic transitions. Room temperature photoluminescence spectra displayed the characteristic A exciton emission near 670 nanometers, the intensity of which undergoes progressive quenching with increasing dopant concentration due to the introduction of nonradiative recombination centers and the growing fraction of metallic 1T domains. Transmission electron microscopy confirmed the formation of nanosheets with thicknesses approaching two nanometers, while the six percent cobalt-doped sample exhibited an additional population of irregular nanorod-like structures, indicating that heavy doping perturbs the anisotropic growth habit. Selected area electron diffraction patterns demonstrated the evolution from poorly crystalline to polycrystalline character upon cobalt incorporation, corroborating the improved structural order inferred from diffraction and Raman data. Energy dispersive spectroscopy quantitatively verified the presence of cobalt within the MoS₂ lattice at levels consistent with the nominal stoichiometry. Collectively, these findings establish cobalt doping as an effective and versatile strategy for simultaneously controlling the polymorphic phase, crystalline perfection, optical band gap, and emission characteristics of MoS₂ nanosheets through a single synthetic parameter. This capability for correlated property engineering provides a foundation for the rational design of two-dimensional transition metal dichalcogenides tailored for advanced optoelectronic devices, photocatalytic systems, and electrochemical energy storage applications.

DECLARATIONS

Ethical Approval

We affirm that this manuscript is an original work, has not been previously published, and is not currently under consideration for publication in any other journal or

conference proceedings. All authors have reviewed and approved the manuscript, and the order of authorship has been mutually agreed upon.

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Availability of data and material

All of the data obtained or analyzed during this study is included in this paper.

Conflicts of Interest

The authors declare that they have no financial or personal interests that could have influenced the research and findings presented in this paper. The authors alone are responsible for the content and writing of this article.

Author's contribution statement

All authors have contributed equally to the research and preparation of this work.

Data availability statement

The data supporting the findings of this study are available from the corresponding author upon reasonable request.

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