Superlative Photoelectrochemical Properties of 3D MgCr- LDH Nanoflowers influencing towards Photoinduced Water Splitting Reactions

susanginee nayak

Institute of Technical Education and Research (ITER), Siksha 'O' Anusandhan Deemed to be University

Kulamani M. Parida (✉ paridakulamani@yahoo.com)

Institute of Technical Education and Research (ITER), Siksha 'O' Anusandhan Deemed to be University

Research Article

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Abstract

Layered double hydroxides (LDHs) are competent photocatalysts for water splitting reactions, vital to produce solar fuels, but their restricted available reactive sites, slow mass and charge transfer, are yet remain a challenge. To surmount these lacunas, Nanoflowers-like three-dimensional (3D) open structure of MgCr-LDH have been designed in a substrate-free path by one-step formamide assisted hydrothermal treatment followed by visible light irradiation and utilized as efficient photocatalysts for the H₂ and O₂ production. The structural, morphological, optical and photoelectrochemical (PEC) properties of the MgCr-LDH nanoflowers were extensively examined, by various physico-chemical characterization techniques. Moreover, the well-designed 3D MgCr-LDH nanoflowers with open structure were formed by a stacking of numerous 2D nanosheets, which inherently triggered with magnificent PEC properties, including high current density of 6.9 mA/cm², smallest arc of the Nyquist plot (59.1 Ω cm⁻²) with photostability of 6000 s thereby enhancing the photocatalytic water splitting activity along. Moreover such a perfectly self-stacked 2D nanosheet in 3D MgCr-LDH possess defect sites as enriched 50% oxygen vacancy resulting a good contact surface within the structure for effective light absorption and easy electron and hole separation, facilitates the adsorption of protons and intermediate of water oxidation. Further, the doped Cr³⁺ pull up electrons from water oxidation intermediates, thereby displaying superior photocatalytic H₂ and O₂ production activity of 1315 μ mol/h and 579 μ mol/h, respectively. Favorable oxygen vacancy type defect surface with Cr³⁺ dopant in MgCr-LDH triggers significant PEC properties, which influences the easy charge transfer and separation mechanism and robustly enhance the photocatalytic performance of the nanoflower.

Introduction

In progress of time, the rapid and massive exhaustion of traditional fuels, such as crude petroleum oil, coal, and natural gas, accelerates the high demand in the advancement of sustainable energy resources to meet up the adequate requirements¹. And it is quite imperative to enlarge the green and clean energy sources such as solar energy, H₂ energy, hydrothermal energy, wind energy, tidal energy, and geothermal energy, etc., to lessen the environmental majors²⁻⁴. Opportunely, photocatalytic (PC) or PEC water splitting to produce H₂ and O₂ is considered as one of the most superfluities of green technological approaches to indulge the solar-to-chemical energy conversion for addressing the worldwide energy shortage^{5,6}. The hydrogen evolution reaction (HER), and oxygen evolution reaction (OER), has been investigated for decades and regarded as a vital energy conversion reaction, as in water electrolyzers^{7,8}. However, the slow OER kinetics, including the 4 electron transfer to form O₂ requires a potent catalyst, which could minimize the overpotentials required in water splitting^{9,10}. Since from the foremost invention of PEC water splitting on TiO₂ photoelectrode by Fujishima and Honda¹¹, diverse low-cost, abundant and renewable photocatalytic materials such as Bi₂WO₆^{12,13}, g-C₃N₄¹⁴⁻¹⁸, CdS^{19,20}, MoS₂^{21,22}, graphene²²⁻²⁴, MXene²⁵⁻²⁷, graphdiyne²⁸, etc., have been developed for their sustainability, suitability and efficiency for water splitting reactions.

Especially, layered double hydroxides (LDHs), represented by their molecular formula of $[M^{2+}_{1-x} M^{3+}_x(OH)_2] [A^{n-} x/n \cdot mH_2O]$, where M^{2+} and M^{3+} represents divalent and trivalent metal cations, and A^{n-} is an anion, regarded as a multifaceted 2D layered positively charged nano-photo/electrocatalysts, which have triggered extensive consideration owing to their unique structure, and exceptional properties such as tunable band gap, tailored compositions and availability of suitable surface area leading to a varied range of possible LDH nanostructures for PC and PEC application²⁹⁻³⁷. For illustration, the author, Nayak and Parida et al. has modified NiFe-LDH^{16, 17, 21, 38, 39}, MgAl-LDH^{40, 41}, MgCr-LDH^{42, 43}, based nanohybrid for significant application in PC water splitting along with environmental pollutant abatement purposes. Nevertheless, pristine LDH generally manifests feeble quantum efficiency in the presence of solar irradiations as a result of sluggish carrier charge mobility and speedy recombination of excitonic charge pairs that is linked with the deficit of suitable band structure, light absorption tendency, which question about their effectiveness in becoming a robust photocatalyst⁴⁴. Mostly, less exposed reactive sites are associated with the interlayer of pristine LDH for fast adsorption of reactive intermediates and transfer of electrons to reach at the reaction site to promote water splitting. Another subject is that pristine LDHs might undergoes self-degradation of surfaces reactive sites under oxidative conditions^{45, 46}. Accordingly, novel kind of materials, offering rich reactive sites, fast adsorption of reactive intermediates on defect sites, which draw electrons from intermediates for fast charge separation and providing significant stability throughout the reaction, would symbolize as advancement in water splitting reactions^{47, 48}. In this regard, numerous strategies has been developed so far accounting lattice doping of metal cation⁴⁹, introducing guest entities into the interlayer⁵⁰, and heterostructure nanohybrid formation of LDH with other semiconductor photocatalysts^{16, 17, 21, 38}. Though, these advanced nanohybrid materials displayed outstanding photocatalytic activities as verified in ZnCr-LDH⁴⁴, NiAl-LDH⁵¹, CoAl-LDH⁵³, NiFe-LDH¹⁶, NiCo-LDH⁵⁴, CoFe-LDH⁵⁵, but there is certain room for development in terms of insufficient interaction among counter photocatalysts, undesired active site coverage or blockage, meager excitonic isolation, reduced recyclability etc. In recent times researchers are looking for a way to overcome these hurdles of nanohybrid photocatalysts nanomaterials has put an immense demand for single component LDH based photocatalysts.

Alternatively, an intriguing feature of LDH material is their inherent properties of exfoliation into critical anisotropic 2D nanocrystalline structure of uni/multi-lamellar nanosheets (NS), which composed of ~ 1–10 stacked layers controlled by their synthesis methods and unusual structural features that could be used as building blocks for diverse functional materials⁵⁶. Importantly, during the exfoliation of pristine LDH to nanosheets, oxygen vacancies might be generated which induces the formation of low coordination metallocentres that causes the formation of active catalytic sites of metal oxides/hydroxides/oxyhydroxides for triggering the water splitting reactions^{47, 48}. It is further noted that numerous exfoliated LDHs having divalent metal cations and abundant metalloactive sites, such as MgCr-LDH⁴³, ZnCr-LDH⁵⁷, CoFe-LDH⁵⁸, NiTi-LDH⁵⁹, and TbZnCr-LDH⁶⁰, have been researched to refine the PEC properties and photocatalytic performances. Besides other exfoliated LDH systems have been established but rarely explored their performances such as MgAl-LDH nanosheets⁶¹, CoAl-LDH⁶², etc. In

these aspects, combination of Mg^{2+} cation with insertion of Cr^{3+} cation as dopant in MgCr-LDHs are significant as Cr^{3+} ions in partial substitution to the octahedral sites of Mg^{2+} cation layers could behave as reactive sites to promote water splitting, while Mg ions offer structural stability of LDHs. In addition, the incorporation of doped Cr^{3+} metal cation into the lattice of MgCr-LDH hold an electronic configuration of $t_{2g}^3 e_g^0$, in which the vacant e_g orbital could be favorable for the capture of electron from the defect sites and corresponding carrier charge transfer process stabilized the system by enhancing the kinetics of water splitting reactions ⁶³.

Motivated by the promising properties of exfoliated LDH nanosheets, in this context, we fabricated 3D hierarchal binary MgCr-LDH nanoflower assembled with 2D nanosheets and oxygen vacancy defect sites by a mild hydrothermal strategy followed by visible light irradiation, which established these materials as a highly active photocatalytic water splitting catalyst with enhanced photoelectrochemical properties for future PEC photoanode materials. To the best of our knowledge, these 3D MgCr-LDHs as model systems possessing excellent PEC properties have not conducted earlier concerning photocatalytic water splitting reactions. These kind of 3D binary MgCr-LDH nanoflower assembled with 2D nanosheets and oxygen vacancies as defect sites provides many advantages in variety of ways: (i) superior electronic transportation, (ii) augmentation of the synergic effects amongst Mg, and Cr, and (iii) presence of Cr^{3+} as dopant, behaves as a pool of electrons by pulling electrons from the oxygen vacancies which used for trapping of electrons, thus swiftly regenerate the active sites for effective water splitting reactions, (iv) As is known, $\text{Mg}(\text{OH})_2$ is almost inactive under visible light and causes negligible carrier charge excitation through water splitting process and from an elemental perspective, the Cr^{3+} cation presents in the MgCr-LDH reveals its special electronic configuration of vacant e_g orbitals, which facilitates the electronic charge transfer process, thus anticipated to augment the conductivity and certainly promote the boosting of reaction performances and reusability of the photocatalyst. Moreover, the fabricated bimetallic MgCr-LDH acts as a versatile solitary photocatalyst, by providing depth insight into the role of oxygen vacancies type defect sites, doped Cr^{3+} ions and open 3D flower like structure for enhancing PEC properties together with promoting charge transfer process for photocatalytic water splitting performances of the LDH layer, whose mechanistic insight has been discussed in detail.

Results And Discussion

Corroboration of Perception

Engineering of the morphological features to refrain the existing active sites with creation of new defect sites plays an utmost vital role for an effective excitonic partition and electronic channelization in light driven catalytic reactions ⁶⁴. Apart this, the development of green and cost-effective photocatalytic system in terms of substrate-free particulate 3D binary MgCr-LDH flowers via a combination of simplistic hydrothermal technique followed by visible light illumination could be regarded as a novel approach towards sustainable energy utilization ⁶⁵. This type of 3D binary MgCr-LDH nanoflower assimilated by 2D

nanosheets propose assured advantages without complex pre/post-treatments together with an effective amalgamation of pre-existing active sites of $\text{Cr}(\text{OH})_3$ and oxygen related defect sites for effective electronic transportation resulting out magnificent PEC properties towards photoinduced water splitting reactions^{66,67}. This resourceful practice certifies single-step synthesis of colloidal MgCr-LDH NSs and thanks to the oxygen vacancies on the MgCr-LDH NSs which mostly provided active sites for further nucleation and crystallization process. The growth process of the 3D MgCr-LDH nanoflower structures could be described as follows (Figure 1); a significant and time-saving methodology has been adopted to deliver the significant structural transformation of exfoliated MgCr-LDH NSs to hierarchal 3D structure of MgCr-LDH matrix. Firstly, the well-controlled growth of MgCr-LDH NSs from MgCr-LDH PSs was accomplished by the use of hydrolyzing agent HCHO⁶⁸, together with OH^- following a coprecipitation and dispersion by sonication process⁶⁹. Mostly, hydrolysis of HCHO liberate solvation energy⁷⁰, which could be utilized in making the $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ solution more alkalinity and triggers nucleation and growth of MgCr-LDH NSs owing to restricted access to nutrients in a confined area. At some point in the reaction process, HCHO acts as a ligand binding Mg^{2+} and Cr^{3+} cations to produce metal complexes in aqueous medium through H-bonding; and causes the complex configuration of polyoxometalate cluster. Thirdly, at mild hydrothermal process of 80 °C, these metal cluster complex shape into 1D sequence using hydrolysis reaction; and chain segments are united to form supramolecular units. Under such instance, the nucleation and growth process of LDH in the successive reaction with OH^- and HCHO could be hindered so causes the formation of MgCr-LDH NSs. With continuous heating at 80 °C for 12 h, the incremental thickness of the interconnected NSs crystallizes into fully-fledged NSs. However, after a visible light irradiation of about 30 min, the exfoliated NSs entangled and folded to self-stack and cluster shape of 3D nanoflowers. However, the transition state of the MgCr-LDH/NS happened through an unusual route, with advancement of a porous 3D MgCr-LDH medium. The morphological alteration from 2D nanosheets to 3D nanoflower formed by aggregation, self-assembly, and Ostwald process⁶⁵. Further decomposition of HCHO release formate together with slow liberation of NH_3 , CO_2 , H_2 and H_2O in a restrained gap⁴³, but ensure for the porosity and floppiness in the material. In the interim, several H_2O molecules also penetrate into the interlayer^{42,43}. The main reaction steps of MgCr-LDH/NS to MgCr-LDH/NF transformation are given below.

Morphological Features Analysis

The field emission scanning electron microscopy (FESEM) techniques were used to reveal the morphologies of the as-synthesized MgCr-LDH/NF. Figure 2 (a, b) indicates the FESEM morphological analysis results of MgCr-LDH/NF, representing the creation of a normal 3D flower-like architecture contented with abundant hexagonal nanosheets. Specifically, with the addition of 20 mL of HCHO and mild hydrothermal treatment of 80 °C and visible light exposure of 30 mins, hexagonal NSs as visualized in Figure 2(a), which self-stacked to shape into cluster and further looks like a 3D nanoflowers structure consisting of 2D nanosheets as MgCr-LDH/NF (Figure 2(b), average $d = 50 \text{ nm}$,). Apparently, HCHO control the LDH morphology, and coordinated the CHO^- ligand to the metal cations, plus the regulation of pH by release of H^+ and OH^- from NaOH. The Mg^{2+} ions precipitate rapidly ($K_{\text{sp}} = 1 \times 10^{-12}$) by adding solution associated with OH^- and NO_3^{2-} , forming Mg(OH)_2 that offer the nucleation site for Cr^{3+} ions to precipitate ($K_{\text{sp}} = 1.6 \times 10^{-30}$) as Cr(OH)_3 . Though, Mg^{2+} and Cr^{3+} ions coordinated with CHO^- ions and generate the $[\text{Mg}(\text{CHO})_x]^{2-x}$ and $[\text{Cr}(\text{CHO})_y]^{3-y}$ intermediates, and the H^+ and OH^- ions neutralize to fix the solution pH at 7. In these circumstances, nucleation and growth process of LDH by reacting with OH^- and NO_3^{2-} could be arrested, leading to the creation of MgCr-LDH nanosheets. The MgCr-LDH /NF would be generated by self-assembly of freshly created MgCr-LDH NS (Figure 2(a)) on the previously formed layers (Figure 2(b)). As discussed, the layered 2D MgCr-LDH NSs interconnected to create 3D nanoflowers consisting of 2D NSs with an open structure; besides, these kind of morphological aspects furnish an enormous amount of available surface, which manifest enrich photo/electroactive sites for the water redox reaction, and open space for ion pooling for escalating the kinetics of diffusion barrier within the electrode/electrolyte interface ⁷¹.

Following the FESEM analysis, the structural aspects of the 3D MgCr-LDH nanoflowers, could be well-recognized vide transmission electron microscopy (TEM) and high resolution-TEM (HR-TEM) analyses. TEM images of MgCr-LDH NS (Figure), and MgCr-LDH/NF (Figure 2(c)) elucidate the effect of HCHO induced mild hydrothermal treatment and visible light irradiation on structures and morphologies of materials. Figure 2(c-e) exemplified the distinct and fluffy nature of the characteristic 3D MgCr-LDH materials. Further the TEM image also illustrates the consistency of dense and thin 2D nanosheets (Figure S1), in typical 3D MgCr-LDH nanoflower⁷². The free and exposed 2D NSs surface ease out catalyst reactions and triggers the photocatalytic water splitting activities of binary MgCr-LDHs ⁷³. Furthermore, the obscure part appeared owing to the dense stacking, and distortion of the NSs and these properties could also be identified in graphene and analogous materials ⁷⁴. The high resolution-transmission electron microscopy (HR-TEM) images of MgCr-LDH/NF (Figure 2(f)) offer a distinct view of

lattice distance ~ 0.26 nm, represented by dotted lines, which is approximately matching with the typical (012) plane in 2D MgCr-LDH NSs. The particle diameter of MgCr-LDH/NF is assumed to be average distance of 20-50 nm. A similar morphological pattern is also detected in NiAl LDHs,⁴⁷ etc. The inset selected area electron diffraction (SAED) pattern (Figure 2(f)) also confirms the (003), and (012) planes of the LDH fully matching with the X-ray diffraction (XRD) pattern (Figure 3). These results signify the polycrystalline nature of the NSs in the flowery like binary LDHs⁴⁷. Furthermore, sharp contrast elemental mapping of the Mg, Cr, and O together with the energy dispersive X-ray spectroscopy analyses (EDX) spectral plot clearly specify the uniform allocation of constituent elements in MgCr-LDH/NF (Figure S2 (a-d)).

Structural and valence state features of binary MgCr-LDHs (3:1)

The solid state crystallographic planes of MgCr-LDHs (3:1) based samples were characterized through powder XRD patterns and the entire diffraction pattern could be resemble into a hexagonal crystal phase with a space group R3m and rhombohedral symmetry of hydrotalcite like materials (Figure 3). The diffraction pattern of MgCr-LDH/PS (Figure 3(a)), consisting of three main peaks at $2\theta = 10^\circ$, 19.2° , and 34.5° ascribed to the phase reflection of the (003) and edge plane of (012) along with the peak at is indexed to the (110) edge plane⁷⁵. These (012) and (110) edge planes in XRD pattern of LDH are previously considered as the main exposed planes of LDHs and match up to the cationic and anionic distances within the layered structure. The peak index of the (110) reflection approximately at $2\theta = 56.2^\circ$ (for Cu-K α target) evidence the retaining of the LDH layered structure⁷⁶. The d-spacing value of MgCr-LDH/PS related to (110) plane was calculated to be 1.63 Å, which is typical characteristic of NO₃⁻ intercalated LDH materials. The lower shift of the (006) and loss of (003) basal reflection planes suggest a change in the unit cell parameter and a decline in the periodicity of basal plane. This is related to the H₂O content from the interlayer LDH galleries. In PXRD pattern of MgCr-LDH/NS (Figure 3(a)), reveals broad and symmetrical basal reflections at lower $2\theta = 33^\circ$ with little spike type of asymmetrical reflections at higher $2\theta = 56^\circ$, correspondingly. The significant lower shifting of the (012) and (110) planes of MgCr-LDH/NS in comparison to MgCr-LDH/PS, indicating with the interlayer height differences, an change in basal spacings and stacking disorder of discrete nanosheets. The other intense peaks of the (003) and (006) planes were missing in the MgCr-LDH, which notify the variation in water contents during the formation of delaminated MgCr-LDH/NS under the influence of HCHO^{69,70}. Similarly, the d-spacing value of MgCr-LDH/NS related to (110) plane was calculated to be 1.6324 Å. In disparity, the MgCr-LDH/NF (Figure 3(b)), exhibits sharp and broad reflection planes of the main planes of (003), (012) and (110) at $2\theta = 12.6^\circ$, 35.4° and 61.2° , respectively. The relatively shifting of the intense and broad reflections peaks of MgCr-LDH/NF to higher 2θ angle quite indicative of the decrease in the interlayer distance, which is an indicative of the assembling of the nanosheets and corresponding evolution of the flower like structure. This consequences are further verified by the decrease in interlayer distance of

1.5110 Å relative to the (110) basal planes. Furthermore, the missing of the (006) basal reflection planes demonstrate a reduction in periodicity of basal reflection plane owing to the association of nanosheets in nanoflowers. This implies that the crystal sizes are reduced in both lattice parameter a ($a = 2d(110)$) and c ($c = 3d(003)$) directions, indicative of self-stacking thickness of LDH nanosheets in nanoflowers. The variations in crystallographic information of MgCr-LDH based samples are included in Table S1.

The Fourier transform infrared (FT-IR) spectroscopy (Figure S3) also explicates the alteration of molecular units during the formation of MgCr-LDH/NF. In the matter of MgCr-LDH/NS, the broad shoulder band identified at 3800 cm^{-1} and 2600 cm^{-1} was merged into an intense and weak broad band approximately at about 3500 cm^{-1} and 3000 cm^{-1} , respectively ⁷⁷. The strong and wide band located at exactly 3500 cm^{-1} corresponded to the superposition of -OH stretching mode of vibrations, underneath the subsistence of -OH functional group of metal hydroxide layers ^{16, 21}. The extremely weak broad band located at approximately 3000 cm^{-1} is accredited to the existence of hydrogen bonds among H_2O molecules residing in the interlayer and -OH group of metal hydroxide layers ⁷⁸. In addition; an additional absorption band at 1650 cm^{-1} corresponded to the deformation of H_2O molecules ⁷⁹. Similarly, the distinct bands at 1639 cm^{-1} , allocated to the stretching mode of metal-oxygen (M-O) i.e., Mg-O vibration. The band located at 1348 cm^{-1} can be derived from the stretching mode of vibrations of NO_3^- group; and the insignificant bands at 652 cm^{-1} collectively with the band at 1440 cm^{-1} are related with the overlapped NO_3^- bending mode of vibration with the unwanted carbonate groups perhaps contaminated from the CO_2 gas of air ⁸⁰. Mostly absorption bands beneath 800 cm^{-1} can be accredited to M-O bending and stretching mode of vibrations. In the interim, the FT-IR spectra of MgCr-LDH/NF signifies that the broad shoulder peak among 3800 and 2600 cm^{-1} is related to -OH ions is removed, demonstrating that the coordinated -OH ions with the metal cation exist in different phase (Fig. 2D). Furthermore, the decrease of the peaks intensity in between 1500 and 1440 cm^{-1} signifies that NO_3^{2-} and CO_3^{2-} anions are completely eliminated after a hydrothermal treatment and light irradiation ⁷⁹. Mostly absorption bands beneath 800 cm^{-1} can be accredited to the M-O bending and stretching mode of vibrations. As the LDH layered structure is stabilized by the electrostatic interactions among the hydroxide layer and intercalated anions; so the elimination of NO_3^{2-} anion by stumbling of formamide assisted hydrothermal and light treated exfoliation usher to diminish their interactions, which in succession causes delamination of cationic layers and further self-assembled to prosper like a nanoflower, as confirmed from TEM analyses of material structure.

The X-ray photoelectron spectra (XPS) elucidate the surface elemental composition and surface states of binary MgCr-LDH based catalysts and the presence of Mg, Cr, O and C elements were noticeable on the XPS surface survey spectra (Figure S4). Figure 4 represent the deconvoluted Gaussian-fitted XPS spectra of Mg 2p, Mg 1s, Cr 2p, O 1s and C 1s in the modified MgCr-LDH/NS and MgCr-LDH/NF based materials. In an illustration, Mg 2p XPS spectra of MgCr-LDH/NS and MgCr-LDH/NF are shown in Figure 4(a). In

MgCr-LDH/NS, for the Mg 2p_{3/2} spectrum (Figure 4 (a)), peak located at 49.8 eV reveals the occupancy of Mg(OH)₂ in the MgCr-LDH/NS and correspond to the main Mg²⁺ cationic states in the material ⁴⁰. Moreover, peak fitted Mg 2p_{3/2} spectrum of MgCr-LDH/NF shows the states of Mg-phase after the structural transformation into flowery shaped materials (Figure 4(a)). The corresponding Mg 2p_{3/2} peaks of MgCr-LDH/NF were blue-shifted towards a higher binding energy 50.1 eV (difference in energy shifting ~0.3 eV). The fitting XPS spectrum of Mg 2p in MgCr-LDH/NF reveals the existence of bivalent Mg²⁺ in material. In Figure 4(b), the appropriate binding energy of Mg 1s peak was identified at 1302. 9 eV ⁴², whereas the Mg 1s peak at 1303.1 eV in MgCr-LDH/NF, which denotes the absolute continuation of Mg²⁺ in MgCr-LDH. In Figure 4(c), the energy level fitting peaks of Cr 2p_{3/2} and Cr 2p_{1/2} appear at 576.4 and 586.5 eV in the XPS spectrum of Cr 2p of NiFe-LDH/NS, respectively ⁴². The binding energy of Cr 2p peak at 576.4 eV denotes the creation of Cr–O bond ⁶³. Similarly, in case of NiFe-LDH/NF, the core-level Cr 2p spectrum could be fitted into two spin-orbit doublets, which correspond to peaks of Cr 2p_{1/2} and Cr 2p_{3/2} for the presence of Cr³⁺ cation ⁶⁷. The binding energy of Cr 2p at 577.2 and 586.5 eV is accredited to Cr 2p_{3/2} and Cr 2p_{1/2} states, which verified the trivalent nature of Cr ions. The binding energy of Cr 2p at 577.2 eV proposes the generation of Cr–OH bond. These results suggested that the metal cations associated with MgCr-LDH/NF preserved the unusual valence state after the hydrothermal and light treatment. As illustrated in Figure 4(c), in comparison to the two peaks of Cr 2p in MgCr-LDH/NS, the Cr 2p peaks in MgCr-LDH/NF slightly shifted towards higher binding energy. These results might be attributed to the successful introduction of Cr³⁺ with empty electron orbitals, which adjusts the electronic structure of the catalyst. Figure 4(d). displays the O 1s XPS spectra of MgCr-LDH/NS and MgCr-LDH/NF. The high resolution O 1s XPS spectrum of MgCr-LDH/NS could be deconvoluted into three peaks at 530.8, 531.3 and 531.6 eV, which are assigned for lattice oxygen linked with Mg and Cr metal, surface hydroxyl bonded to metal centers and oxygen vacancies (V₀) or under-coordinated lattice oxygen vacancies ⁴². Moreover, in comparison to the O1s spectrum of MgCr-LDH/NS, the approximate peaks identified in MgCr-LDH/NF includes 529.7, 530.5, 531.3, and 531.6 eV which is associated for water molecules, lattice oxygen, surface–OH group, and oxygen vacancies (V₀), respectively ⁶⁶. Moreover, the more prominent oxygen vacancies (V₀) peak in MgCr-LDH/NF, signifies the subsistence of oxygen vacancies related defects type owing to existence of delaminated MgCr-LDH during the hydrothermal process and further light irradiation causes aggregation of the nanosheets to produce MgCr-LDH/NF containing oxygen vacancies sites. Figure 4(d), shows that the hydrothermal treatment enhances the intensity of the M–OH bond, and formation of oxygen vacancies on assembly of nanosheets in MgCr-LDH/NF becomes more favorable at an optimal light exposure time of 30 mins. The percentages of V₀ as determined from the fitted peak area of O 1s spectra are 25% and 50% for MgCr-LDH/NS, and MgCr-LDH/NF samples. Further hydrothermal treatment with light exposure causes appearance of new peaks attributed to the formation of adsorbed water peaks at 529.7 eV ⁶⁶. In addition, the positively shifted Cr 2p_{3/2} peak of MgCr-LDH/NF (~ 577.2 eV), demonstrating the decreases in electron density around Cr and electron clouds are inclined towards the Mg (OH)₂ surface owing to the formation of oxygen vacancies. Additionally, the C 1s XPS spectrum of MgCr-LDH/NF (Figure 4(e)) reveals the existence of C 1s main

peak with a high binding energy at 289 eV corresponds to O–C=O linkage. The other binding energy peaks at 287.9, 286.7, and 284.5 eV corresponds to C–O–C, C–OH, C–C linkage, respectively¹⁷. All of these characteristic features substantiate that hydrothermal treatment of formamide treated bulk MgCr-LDH could lead to the removal of gaseous products like NO₂ from the interlayer of LDH and causes structural twist towards nanosheets with oxygen vacancies and further exposure with visible light resulted with self-aggregation and removal of other gaseous products like CO₂, H₂, and H₂O in a sintered confinement, thereby leading to flower like MgCr-LDH/NF containing exfoliated nanosheets with enriched oxygen vacancies. Hence togetherness of hydrothermal and visible light treatment has dramatic effect on structural twist from bulk MgCr-LDH to nanoflower through nanosheets for significant photoinduced water splitting reactions.

PEC properties studies of the MgCr-LDH material

The magnificent PEC photocurrent properties of the pristine MgCr-LDH and the corresponding MgCr-LDH nanosheets and hierarchical 3D flower like MgCr-LDH structure were investigated using LSV studies obtained under dark and visible light illumination in order to legacy the function of photoinduced excitonic charge separation to intensify the net photocurrent as shown in Figure 5 (a, b). The photocurrent measurement studies of the series of MgCr-LDH materials were recorded in a potential panel of -1.0 to 1.2 V *versus* Ag/AgCl reference electrode using 0.1 M Na₂SO₄, at scan rate of 10 mV·s⁻¹ and converted to reversible hydrogen electrode (RHE) according to the Nernst equation.

$$E(\text{RHE}) = E_{\text{Ag/AgCl}} + 0.197 + 0.059 \text{ pH. (4)}$$

Figure 5(a, b), shows pristine MgCr-LDH/PS could able to produce the linear current density of 0.06 $\mu\text{A}/\text{cm}^2$ at potential of 1.19 V under light exposure, which is much lower than MgCr-LDH/NS and MgCr-LDH/NF. In particular, the enhancement in photocurrent jumped to 6.9 mA/cm^2 at 1.10 V for MgCr-LDH/NF from MgCr-LDH/NS 0.12 $\mu\text{A}/\text{cm}^2$ at 1.20 V, and 0.06 $\mu\text{A}/\text{cm}^2$ for MgCr-LDH/PS electrode at 1.19 V under scan rate of 10 mV/s with an augmentation factor of 57.5 and 2.0 fold times, respectively. Meanwhile, the formation of nanosheets assembling in MgCr-LDH/NS at a hydrothermal treatment of 80 °C and further assembling of the nanosheets to flower like 3D structure under light treatment for 30 mins intensify the effective active sites for water oxidation thus suggesting the synergistic effect of structural evolution of hierarchical nanostructures together with the beneficial role of the Cr dopant and oxygen related defect sites for effective charge separation and incremental current density of the MgCr-LDH/NF⁴⁷. At the meantime, the dark current response was considered as negligible for MgCr-LDH/NF photoelectrode. The onset potential is determined by the junction point of the I-V curve and the dark current density curve⁸¹ The onset potential of MgCr-LDH/NF is greatly decreased through the structural transition of bulk to nanosheets, and then to nanoflower, which is indicative of the amalgamation of oxygen vacancies related defect sites with the structural transition from nanosheets to 3D morphological features for easy charge tunneling and fast separations of excitonic charge pairs for enhanced

photocatalytic water oxidation performances. The Tafel slope is mostly utilized to authenticate the superior OER properties of various binary LDH, which is considered as the rate determining step in the water splitting process; and is deliberate by below equation ⁸²:

$$\eta = a + b \log(j) \quad (5)$$

where η , a , b , and j correspond to the overpotential, constant, Tafel slope, and current density. The Tafel slopes were determined from LSV plots by plotting V versus $\log j$ and calculated to be 239, 192, and 82 mV/decade for MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF, respectively (Figure 5(c)). It was found that morphological variation from bulk to nanosheets and further nanoflower like assembly decreases the Tafel slopes and the smallest slope was tenable for MgCr-LDH/NF, confirming the highest current density and faster kinetics towards water splitting reactions. Normally, lower overpotential and smaller Tafel slopes constituted better catalytic water splitting performance and well-recognition to the fast electron-hole transfer and separation process owing to extraneous and uncovered active sites in 3D MgCr-LDH/NF, ^{82, 66}. To further scrutinize the transient PEC response of MgCr-LDH-based photoelectrode, chopped light on and off irradiation with a cycle of 30 s recorded a polarization curves as shown in Figure 5(d), All the photoelectrode exhibit rapid transient responses in the illuminated on and off cycle, accompanying a faster photoinduced excitonic charge carrier generation route. It is recognized that photocurrent density quickly shows incremental in current density and then maintains it till the light source switched off and then suddenly falls to a steady value.

The electrochemical impedance spectroscopy (EIS) measurements studies were executed to investigate the charge-transfer resistance properties among the interface of photocatalysts/photoelectrode and electrolyte for the advancement in the expedition process of the kinetics of electrode (solid)-electrolyte (liquid) reactions along with stability measurement of the MgCr-LDH electrode. The electrochemical results of MgCr-LDH based samples have been analyzed and are described in the Nyquist plot as shown in Figure 6. All EIS data's were fitted with the equivalent circuit as displayed in upset image of Figure 6. The Nyquist plot of MgCr-LDH based sample is depended on series resistance (R_1) and is linked with the charge-transfer resistance (R_{ct}) during the interfacial contact area of the electrode/electrolyte interface at high frequency region of the minor semicircle. The semicircle in the mid frequency zone is denoted as the charge-transfer resistance (R_2) across the electrode-electrolyte interface of the MgCr-LDH, The CP1 with CP2 and W_1 corresponds to the chemical capacitance and Warburg impedance, respectively. Normally, the electrochemical model circuit suggested that the minor semicircle portion is related to the charge transfer resistance (R_{ct}) and the major straight line is relevant to the mass transfer resistance (R_m) at low frequency ⁸³. The as obtained fitted values of R_{ct} for MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF photoelectrodes were found to be 129.18, 80.80 and 59.17 $\Omega \text{ cm}^{-2}$, respectively. To the MgCr-LDH/NF displays the smallest R_{ct} and R_m values among the three types of MgCr-LDH-based photoelectrode, which indicate the efficient dynamics of carrier charge separation and rapid surface redox kinetics occurred on the MgCr-LDH/NF photoelectrode and electrolyte interface. Moreover, the stability of the

photoelectrode is highly necessary to secure high PEC efficiency of the materials. The stability of the MgCr-LDH/NF photoanode samples was tested performing chronoamperometric J - T curve measurements by applying a constant potential of 0.5 V to overcome the Ohmic losses in the electrolyte and metal contacts under visible light exposure for 6000 s (Figure S5). Interestingly, rational photocurrent stability preservation over a suitable period was exemplified for the MgCr-LDH/NF nanostructure photoelectrode.

The M-S plots were acquired for pristine MgCr-LDH/PS and nanostructure MgCr-LDH photoelectrode samples indicating the reversed sigmoid plots resembling to n-type semiconductors (Figure 7). A flat band potential (V_{fb}) of an electrode could be calculated by following Mott–Schottky equation ⁴⁷,

$$\frac{1}{C^2} = \left(\frac{2}{q\epsilon_0\epsilon N_d} \right) \left(V_{app} - V_{fb} - \frac{kT}{q} \right)$$

6

Where ϵ = dielectric constant, N = the charge carrier density, C = space charge layers capacitance, V_a = applied potential, e = electron charge, and ϵ_0 = permittivity of vacuum. The estimated V_{fb} value recedes in the potential edge of CB (E_{CB}) of n-type semiconductors versus RHE. Furthermore, the carrier charges density (N_d) found from the Mott-Schottky plots is used to estimate the alteration in carrier charge concentration. The theoretical equation calculating N_d of semiconductor is as follows.

$$N = (2/q\epsilon_0\epsilon)[d(1/C^2)/dV]^{-1} \quad (7)$$

Importantly, the flat band potential of MgCr-LDH/NF indicates a decrease in band bending and higher slope assigned to the increased in carrier density, which is attributed to the defect-sites allowed to the charge transfer process among the electrode and electrolyte. Hence, the significant charge transfer rate in MgCr-LDH/NF photoelectrode is a synergistic result of 3D flower like structure containing 2D nanosheets and oxygen related defect sites. The cathodic shift of conduction band edge of the MgCr-LDH/NF offers significant potential for water redox reaction under visible light exposure.

Photocatalytic Water Splitting Activity

The capability of the MgCr-LDH based samples to decompose water under visible light, have been tested for a series of H_2 and O_2 production performance using a home-made quartz cell test reactor closed with 125 W medium pressure Hg lamps emitting visible light with 1 M $NaNO_2$ as UV cut off filter to expose light of $\lambda \geq 400$ nm and Julabo based chiller under similar experimental conditions ^{16, 17, 21}. A power

density of 100 mW cm^{-2} was precise for the visible light approach on the quartz chamber and the average light flux was $\sim 2890 \text{ Lx}$. The dark experiment reveals no substantial H_2 or O_2 production either in the lack of catalyst or light, which notify that photocatalytic water splitting reaction is dependent on both catalyst and light. Firstly, the 0.03 g of MgCr-LDH/PS catalysts, MgCr-LDH/NS and MgCr-LDH/NF catalysts were tested for H_2 and O_2 evolution using 30 mL of $10 \text{ vol\%}$ aqueous solutions of CH_3OH and AgNO_3 as sacrificial agents. In Figure 8(a), it is found that as the structural transformation increases from the bulk phase to nanosheets and gradually increases towards nanoflower, the H_2 and O_2 production shows a volcanic trend. The enhanced water splitting activity of binary MgCr-LDH/NF might be owing to the distinctive structural features (3D flowers stacked with 2D nanosheets) and the synergistic effects among the dispersion of Mg , and Cr atoms as found from TEM results. Figure 8(a), shows the maximum hydrogen production of MgCr-LDH/NF reached $1315 \mu\text{mol/h}$, which was 1.8 and 4.3 times of MgCr-LDH/NS ($726 \mu\text{mol/h}$) and MgCr-LDH/PS ($300 \mu\text{mol/h}$) under visible-light irradiation. This might be the results of the increase of electronegativity of MgCr-LDH/NF owing to the generation of oxygen vacancies. The exfoliation of MgCr-LDH under mild hydrothermal condition, generates uncoordinated metallocentres and dense amount of free atoms at the edge sharing hexagon, responsible for oxygen related vacancies and causes intersection of the NS for enhancing light harvestation ability of the materials and corresponding exciton separation efficiency directly or indirectly responsible for the water splitting reactions⁴⁷. This is also reflected in the XPS spectra and impedance plots of the magnificent PEC properties, and the formation of flower structure is more conducive to H_2 production because of the special structure of the layered 2D nanosheets inside the 3D flower offers added active phases, which amplify the excitonic separation process, so facilitates quick redox reaction. The existence of inconsistent oxidation states in the binary LDH (Mg^{2+} and Cr^{3+}), due to the inclusion of Cr^{3+} in the framework, charge transfer, conductivity and electron capture hastily followed to facilitate the H_2 production. Furthermore, the fabricated photocatalysts were also examined towards O_2 evolution reaction ($E^0 \text{ O}_2/\text{H}_2\text{O} = +1.23 \text{ V vs. RHE}$), under 250 W visible light emitting Hg-lamp for a period of 1 h ⁸⁴. It was found from Figure 8(b) that the MgCr-LDH/NF shows the highest O_2 production activity of $579 \mu\text{mol/h}$ followed by the MgCr-LDH/NS of $356 \mu\text{mol/h}$ and MgCr-LDH/PS of $254 \mu\text{mol/h}$. The enhanced production capacity of MgCr-LDH/NF is due to the similar reason as explained for H_2 production, i.e., owing to the presence of rich defect site related to oxygen vacancies trap out more photoexcited electrons which will be available over CB of LDH matrix and separating out holes at the VB of LDH under visible light illumination which are then effectively channelized by the composed 2D nanosheets in the hierarchal 3D structure of MgCr-LDH/NF ⁸⁵. Moreover, the 3D structures intimately allocate the 2D active nanosheets, which could render additional active sites, and assist excitonic charge transportation and release of gaseous products in the 3D nanoflower architecture. The addition of Cr^{3+} cations is supposed to be potentially redox active sites in the MgCr-LDH OER catalyst.

In order to measure the photostability of the H_2 and O_2 evolution performance of the MgCr-LDH/NF catalyst, a cyclic H_2 and O_2 evolution experiment was carried out at $10\% \text{ CH}_3\text{OH}$ and AgNO_3 aqueous solution (Figure 8(c, d)). Each cycle experiment is 125 mins , and a total of 4 cycles are performed. In the

3rd and 4th cycle, the H₂ and O₂ production gradually decreases due to the consumption of sacrificial reagents. The H₂ and O₂ evolution shows that the MgCr-LDH/NF photocatalyst has good catalytic stability. In addition, XRD patterns were executed on the catalysts before and after the cycle of hydrogen production, as shown in Figure S6. It was found that the XRD patterns of the catalyst before and after the cycle of hydrogen production did not change significantly, except a little reduction in peak intensity which may be due to loss in catalyst handling, surface blocking by the sacrificial reagents and may be corrosion of catalysts surface during the catalytic reaction. These features indicate that the MgCr-LDH/NF catalyst has excellent water splitting activity.

Additionally, the H₂ production experiment of MgCr-LDH/NF was carried out under the presence of different sacrificial agent (10% lactic acid solution, 10% methanol, 10% triethanol amine (TEOA)) under similar experimental condition as shown in Figure 9 (a). The sacrificial based water splitting reaction depends upon various factors such as the oxidation potential of the reagent, polarity, chain length, side-product formation, adsorption on catalyst surface, number of hydroxyl groups etc. Experiments show that the highest hydrogen production is in the 10% CH₃OH aqueous solution. This is because of the easy electron donor in the reaction system, and more electrons are generated and transferred to the active part of the photocatalyst for H₂ generation reaction, further the reagent oxidized by photogenerated holes in the VB of LDH to CO₂. The detailed of the mechanism are as predicted in the following equations.

Further, scavenger experiment was performed to trace out the active species responsible for water oxidation by using different sacrificial agents such as AgNO₃, isopropyl alcohol (IPA), ethylenediamine tetraacetic acid (EDTA-2Na) as displayed in Figure 9(b). It was pragmatic that the O₂ formation activity is maximum in case of AgNO₃, whereas on addition of IPA, and EDTA-2Na (hole scavenger), the reduction performance increases which indicates the active role of hole in the water oxidation process. Yet again,

for quantifying the efficiency of the photocatalyst towards O₂ production, the apparent conversion efficiency, was measured to be for photocatalytic O₂ evolution by MgCr-LDH/NF system under visible light irradiation. Considering this results, the •OH radical formation was experimented over different as-synthesized samples (MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF) and the results depict the highest possible formation of •OH radical, signifying the most resolute photoluminescence (PL) peak of the terephthalic acid (TA)-OH complex over MgCr-LDH/NF as shown in Figure 9 (c). The •OH formation ability of the MgCr-LDH/NF could be regarded as the effective separation of excitonic pairs via appropriate amount of oxygen vacancies and Cr³⁺ dopant for enhancing the kinetics of water oxidation leading to greater accumulation of highly oxidizable holes in the VB of the concerned material. Moreover, the calculated VB potential of MgCr-LDH/NF is approximately 2.0 eV vs. NHE, which is quite sufficient enough to generate •OH radical (OH/•OH = 1.99 eV vs. NHE). Hence the formation of e⁻, h⁺ and •OH radical is quite feasible over the surface of MgCr-LDH/NF for superior photocatalytic water splitting performances.

Insight into the possible photocatalytic mechanism of charges separation

Ultraviolet (UV) - Visible (Vis) diffuse reflectance spectra (UV-Vis-DRS) and PL spectra were analyzed to explore the electronic charge transfer path within the MgCr-LDH/NF photocatalyst^{16,17,21}. The optical absorption properties of a photocatalyst/photoanode are an important phenomenon, which directly affect their photocatalytic performances⁸⁶. The optical properties of the MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF photocatalyst are investigated by UV-vis absorption spectrometry as shown in Figure 10(a). All MgCr-LDH based samples exhibits strong optical absorption in the range of 200-350, 400-500, and 550–700 nm wavelength range, and thereby possess the properties to behave as photocatalysts under visible light exposure. Most-importantly, MgCr-LDH/PS display strong absorption band at 211 and 235 nm in the UV zone, which might be attributed to the charge transfer from ligand to metal cation

(LMCT) within the matrix of MgO_6 and CrO_6 octahedron in the lattice of MgCr-LDH i.e. $\text{O-2p} \rightarrow \text{Mg-2p/Mg-1s}$ orbital and $\text{O-2p} \rightarrow \text{Cr-3d}_{t_{2g}}$ transition in octahedron surroundings⁴². The rest of the absorption band in the spectral region of approximately 470-700 nm arises from the causes of charge transfer from d-d transition of Cr i.e. $3d_{t_{2g}} \rightarrow 3d_{e_g}$ orbital of which occupied with unfilled high energy $3d_{e_g}$, and under the exposure of visible light, triggers the electronic transfer from partial filled $3d_{t_{2g}}$ orbitals to the $3d_{e_g}$ orbitals, sequentially⁴⁴. Interestingly, MgCr-LDH spectra hump from 450 to 750 nm, which could be accredited to the metallic-green color of MgCr-LDH. The UV-Vis-DRS spectrum of MgCr-LDH/NS catalysts, which reveals a more intense hump at 378 nm, and 578 nm, verified with the excitonic transition band, and d-d transition band in the excitonic states of $4A_{2g} \rightarrow 4T_{2g}$ (F), respectively. The red shifted and intense absorption edge of MgCr-LDH/NS in comparison to MgCr-LDH/PS resulted owing to the reduced thickness of the exposed atomic sites of the nanolayers that reduced the electron transfer distance and formation of oxygen vacancies as verified from XPS spectra allowed for dense concentration of electron clouds over the nanosheets with enhanced conductivity for photoinduced catalytic performances.

Intriguingly, MgCr-LDH/NF, owing to the dynamics in structure with more defect sites endorsed numerous lights to scattered inside the folded nanosheets to strengthen the optical path, and the most interesting findings of red-shifted maximum light absorption capacity was noticed as compared to that of MgCr-LDH/NS and MgCr-LDH/PS based samples. Moreover, intense defect site in terms of oxygen vacancies in MgCr-LDH/NF, amplify the absorption of light intensity in the wider visible zone for finer photocatalytic performances. As displayed in Figure 5a, the optical absorption shoulder of MgCr-LDH/NF was situated in the UV-Vis region. Normally, MgCr-LDH/NF displayed two types of absorption band i.e. inherent LMCT band among $\text{O-2p} \rightarrow \text{Mg-2p/Mg-1s}$ and $\text{O-2p} \rightarrow \text{Cr-3d}_{t_{2g}}$ transition within 200–390 nm, d–d transitions of Cr^{3+} charge transfer in the band region of 400–712 nm. The d–d transitions of Cr^{3+} ion (d^3 electronic arrangement) is comprises of $4A_{2g} \rightarrow 4T_{1g}$ (F) and $4A_{2g} \rightarrow 4T_{2g}$ (F) which were associated to the absorption peaks at 410 and 570 nm, respectively^{38, 88}. The predominant band of CrO_6 absorption peak in the MgCr-LDH/NF arises because of the atomic level variation among MgO_6 than CrO_6 with defects riched self-assembled MgCr-LDH nanosheets,⁸⁷. This intrinsic absorption band indicates the existence of lately twisted energy levels owing to oxygen vacancy among the conduction band (CB) and valence band (VB) in the MgCr-LDH/NF.. The missing of surface oxygen encourage the easy charge pair transfer and separation as verified from the improved PEC properties, which results in enhanced photocatalytic water splitting performances of MgCr-LDH/NF materials.

Figure 10(b-d), shows the band gap value of MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF as obtained in reference to Kubelka Munk function: $\alpha h\nu = A (h\nu - E_g)^{1/2}$. LDHs appeared to have a multifaceted band structure and composed of several optical absorption bands^{16, 17, 21, 38}. Similar structure was identified in MgCr-LDH, howbeit it displayed two bandgap related to two absorption bands and accounts for directly allowed transition. The band gap value of MgCr-LDH/NF was obtained as 2.20 (E_{g1}), 3.12 eV (E_{g2}) and the band gap value of MgCr-LDH/NS and MgCr-LDH/PS were 2.27 (E_{g1}), 3.54 eV (E_{g2}) and 2.37 (E_{g1}), 3.89 eV (E_{g2}), respectively. Mostly, the E_{g1} could be allocating to the transition of

$O2p \rightarrow Crnd$ levels and the $E_g/2$ could be set for the electronic transition from $O2p \rightarrow Mgns/np$. Hence, the band gap alteration of the as synthesized MgCr-LDH nanoflower is influenced by the defect site specific to oxygen vacancies, which could enhance the light absorption intensity in the visible zone for significant photocatalytic performances.

PL spectral technique is a fundamental tool to analyze the transfer and separation efficacy of photoinduced excitonic charge pairs in various semiconductor photocatalytic materials^{16, 17, 21, 38}. When the molecule absorbs light energy, first it will become in excited state. However, the electrons in excited state have a short lifespan. If they do not react in time, they will be dissipated in the form of fluorescence and heat and the utilization rate of visible light of the catalyst is reduced. The faster the quenching of molecules in excited state electrons, the higher the steady-state fluorescence emission peak intensity of molecule in Figure 11. The weaker PL signal signifies the higher lifetime of photogenerated charge carriers in semiconductor photocatalyst. Herein, PL was used to investigate charge transfer behavior of structurally evolved MgCr-LDH based materials starting from the bulk phase to nanosheets and then nanoflowers at an excitation wavelength of 320 nm as shown in Figure 11³⁸. The main peak of MgCr-LDH/PS is centered at approximately $\lambda = 374$ to 410 nm, which is associated with the typical photoemission of MgCr-LDH, approximately close to the bandgap energy of 3.7 eV ($E_g/2$)⁴². The emission peak at 400-410 nm in MgCr-LDH/PS is due to the vacancies in MgO_6 octahedron, which acts as recombination sites and used to trap holes. The emission peaks at 459 nm could be linked to the radiative recombination of surface trapped localized excitonic charge carriers. The large decrease in PL intensity for MgCr-LDH/NF indicated that the recombination of photogenerated exciton pairs is significantly quenched owing to the large density of formation of defect sites and oxygen vacancies after the structural evolution from bulk to nanosheets and then self-assembling of the nanosheets led to the formation of nanoflowers^{85, 88}. This is related to the dynamic of charge transfer within the MgCr-LDH/NF matrix, which could be helpful to stimulate the PEC properties and corresponding water splitting reaction. The PL spectra of MgCr-LDH/NS and MgCr-LDH/NF also reveals three types of characteristic emission band comprising of vacancies exist in MgO_6 octahedron of the $Mg(OH)_2$ layers, localized surface defect, and oxygen vacancy. The localized defect state and oxygen vacancies in MgCr-LDH/NS arises owing to the presence of uncoordinated metal centers during the formation of nanosheets and triggers charge transfer inside the $Mg(O)_6$ octahedron and towards the $Cr(O)_6$ octahedron. However, the rich defects sites and oxygen vacancies peaks of MgCr-LDH/NF was identified at 500 nm and 524 nm, respectively, which was due to the occupancy of the numerous folded nanosheets during the secondary growth period of nanoflower structure to reduce their surface energy, and release of the strong stress, under exterior forces for instance electrostatic, van der Waals forces, and hydrogen bonds in which twisted nanosheets self-assembled into stable and irregular 3D nanostructures⁸⁵. MgCr-LDH/PS displays the strongest PL peak signifying higher efficiency of excitonic recombination process. The most diminished PL peak of MgCr-LDH/NF at about 373–500 nm reveals the lower recombination rate of photoinduced excitonic pairs. Hence, the suppression in excitonic charge pairs in MgCr-LDH/NF is associated with electron and hole trapping sites, which increases the fate of electronic charge pairs for triggering superior water splitting

performances. Generally, the smaller the impedance arc radius, the faster the charge carriers separation. The radius corresponding to the above sample Nyquist circle is MgCr-LDH/PS > MgCr-LDH/NS > MgCr-LDH-NF. In summary, the MgCr-LDH-NF combination can not only use the internal oxygen vacancy and Cr³⁺ dopant as barrier for the electron-hole recombination to accelerate the separation of carriers, but also build an effective electron transfer channel, accelerate electron transfer, and improve the charge trapping ability.

In general, photocurrent response is used to reveal the phenomenon of photogenerated electrons generated by photoexcitation of photocatalyst. As we all know, the higher the photocurrent response value, the higher the excitation rate of photo-induced exciton pairs, and minimize the electrons and holes recombination rate. The transient photocurrent responses of three working electrodes under visible light exposure are revealed in Figure 5(d). It could be identified that after structural transformation into MgCr-LDH/NF, the catalyst formed successfully constitutes a dense of nanosheets containing oxygen related defect sites, and the MgCr-LDH/NF working electrode shows a significant increase in photocurrent density. An internal interface is formed within the nanoflower structure where oxygen vacancies and Cr³⁺ involved in the multi electron process for effective trapping of the electrons separating out from the photogenerated holes for superior water splitting reactions.

In order to further analyze the electron transfer within the catalysts, Mott-Schottky curves and UV-DRS plots were correlated to calculate the CB and VB edges, respectively. The flat band (E_{fb}) of n-type semiconductor is close to the conduction band^{17, 21}. Therefore, the E_{CB} of MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF can be calculated in RHE as -0.01 V, -0.06 V, and -0.20 V, respectively ($ERHE = E_{Ag/AgCl} + 0.197 + 0.059 \text{ pH}$). Hence, according to UV-Vis spectrum and Mott-Schottky curve, the valence band (E_{VB}) of MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF can be calculated as +2.19 V, +2.14 V, and +2.0 V since $E_{VB} = E_{CB} + E_g$, respectively. The test result is that compared with MgCr-LDH/PS, the flat band potential of MgCr-LDH/NF is a negative shifted (-0.01 $\rightarrow$ -0.20 V), indicating the upward movement of energy level of n-type MgCr-LDH/NF. Usually, the Fermi level is implicit at 0.1 eV down the CB of n-type semiconductors as like MgCr-LDH/NF ($E_f = -0.10 \text{ V}$), alternatively the O_v always occupies a space about 0.9 V depth than the CB of any semiconductor, so for MgCr-LDH/NF (+ 1.1 V)³⁸. The XPS and PL spectra also verify the presence of defect site and oxygen vacancies. Moreover, Cr³⁺ cations present electronic arrangement ($t^3_{2g}e^0_g$), which induces charge transfer, separation and electronic capture for facilitating the H₂ production. These features provide strong support that the upward shifting of energy level is related with the successful formation of nanoflowers (verified from TEM and FESEM results) with defect sites as oxygen vacancies and Cr³⁺ as dopant for triggering excitonic separation.

With these valid discussions, the possible CB and VB position of MgCr-LDH/NF and the mechanism of water reduction and oxidation reaction over MgCr-LDH/NF were proposed in Figure 12. With the visible light irradiation, semiconductors could absorbed photon energy equal to or greater than the band gap energy, and get excited to produce electrons and hole pairs. The photogenerated electrons transition from the VB position of MgCr-LDH/NF to the CB, and leaving behind holes in the VB. The electrons

accumulated on the CB of MgCr-LDH/NF are easily trapped by the Ov center together with the Cr^{3+} cations presents unique electronic arrangement ($t^3_{2g}e^0_g$), which facilitate electron capture to reduce the H^+ in the solution to facilitate H_2 production (H^+ / H_2 (0 vs. RHE)), whereas the holes are consumed by the sacrificial agents ³⁸. Alternatively, rich O vacancies produced on MgCr-LDH/NF containing nanosheets assist simplistic adsorption of water oxidation intermediates such as $-\text{OH}$ and $-\text{OOH}$ onto the nearby interface of Cr^{3+} and low-coordinated Mg^{2+} ions, which is formed by (i) $\text{H}_2\text{O} \rightarrow \text{H} + \text{OH}$, $\text{OH} + \text{H}_2\text{O} \rightarrow \text{OOH} + 2\text{H}$, and (ii) $\text{H}_2\text{O} + \text{OH} + \text{H} \rightarrow \text{HOOH} + 2\text{H}$ ⁴⁷. The V_0 percentage of MgCr-LDH/NF was higher than MgCr-LDH/NS as verified from the peak area fitting in the XPS spectra. Moreover, the LSV curve is also in agreement of defect sites for high current density. Furthermore, water oxidation intermediates are more favorably adsorbed on oxygen vacancies with the help of doped Cr^{3+} in pulling up their electrons. The corresponding Tafel slope is 82 mV/decade and these results confirm that the incorporation of Cr^{3+} is the crucial factor in increasing the reaction kinetics of MgCr-LDH/NF. Cr^{3+} as Lewis acid cations can modulate the ligand fields of the hydroxyl groups of LDH layers. In this way the electrons are concentrated in the CB and attracted towards V_0 of Cr^{3+} cations and thereafter in the CB of MgCr-LDH/NF and holes intense at VB of MgCr-LDH/NF (+2.0 V vs. RHE) possess sufficient potential to produce $\cdot\text{OH}$ radicals $E^\ominus (\cdot\text{OH} / \text{OH}^- = +1.99 \text{ eV vs. NHE})$ ¹⁷. Therefore, the holes on the VB of NiFe LDH could react with H_2O to produce the $\cdot\text{OH}$ radicals, which used for water oxidation reactions ($\text{O}_2 / \text{H}_2\text{O}$ (1.23 V vs. RHE)). Moreover, the hole enriched VB of MgCr-LDH (+2.0 V vs. NHE) could directly oxidized H_2O to produce O_2 gas. Consequently, both rich oxygen vacancies and doped Cr^{3+} cations lead to the increased charge carrier density and decreased the resistance arises owing to the presence of $\text{Mg}(\text{OH})_2$ at the interface for charge transfer, thus promoting the kinetics for water splitting reactions. A state of art for comparing the photocatalytic activities of MgCr-LDH/NF and PEC properties with literature reported materials were depicted in Table S2 and Table S3 in supporting information, respectively.

This type of work exemplify the inherent performance of the photocatalysts by designing the appropriate catalyst composition (Cr^{3+} cation) with defect sites and the effect of high active sites in open framework -3D nanostructures for enhanced PEC properties triggering superior water splitting performance. After constructing the open nanoflower structure, the contact position of MgCr-LDH/NF can be considered as a small photoelectrochemical (PEC) cell. From the perspective of a PEC photoanode material, the band structures of MgCr-LDH/NF could be best fitted and compared with MgCr-LDH/NS and MgCr-LDH/PS as depicted earlier by comparing UV-DRS and Mott-Schottky plot. The upward shift of CB edge of the MgCr-LDH/NF system offers adequate cathodic potential for H_2 reduction from H_2O , causing the water oxidation reaction under visible light exposure as shown in Figure 13. Hence, the entire MgCr-LDH/NF can be regarded as a high-efficiency PEC cell assembly connected in three electrode series. This is advantageous to the improvement of hydrogen evolution performance.. In addition, compared with other variant of LDH-based photoelectrode, the MgCr-LDH/NF photoelectrode also reveals comparable PEC properties, as shown in Table S4.

Conclusions

In summary, we have successfully designed defect-rich 3D flower-like MgCr-LDHs composed of 2D nanosheets by using a facile hydrothermal and light irradiation method, and taken advantage of these special 3D flower-like structures that provided added active sites, thereby behave as an effective photocatalysts by reducing the recombination of photo-induced e^- and h^+ pairs, for enhancing the water splitting activities. In addition, XPS and PL analyses shows the dominance of oxygen vacancies and defects site with special electronic configuration of Cr^{3+} dopant ($t^3_{2g}e^0_g$), and synergistically facilitates charge transfer, conductivity, electron capture and adsorption of water oxidation intermediates for facilitating the H_2 and O_2 production. Moreover, the MgCr-LDHs nanoflowers delivered interesting PEC properties with low Tafel slope values of 82 mV/decade for a current density of 6.9 mA/cm^2 , which is significant and these LDH might be used as a potent photoanode material for future PEC water splitting activities. Evidently, MgCr-LDH nanoflowers exhibited superior photocatalytic H_2 evolution activities of $1315 \mu\text{mol/h}$, which was 1.8 and 4.3 times than MgCr-LDH nanosheets ($726 \mu\text{mol/h}$) and pristine MgCr-LDH ($300 \mu\text{mol/h}$) under visible-light exposure. Alternatively, MgCr-LDH nanoflower shows the highest O_2 production activities of $579 \mu\text{mol/h}$, which is 1.6 and 2.2 times superior than MgCr-LDH nanosheets ($356 \mu\text{mol/h}$) and pristine MgCr-LDH ($254 \mu\text{mol/h}$), respectively. Additionally, the MgCr-LDH nanoflower system showed robust recyclability without degradation of their surfaces. Due to the synergistic effects of oxygen vacancies and Cr^{3+} doping, we expect further that nanoflowers derived from LDH nanosheets by hydrothermal and light irradiation could be utilized to attain high activity and robust stability in water splitting even for many other nanostructures. Such eco-friendly binary LDHs can be used as photoanode material in PEC cell for industrial transformation.

Material And Methods

$Mg(NO_3)_2 \cdot 6H_2O$ (98%, Sigma-Aldrich), $Cr(NO_3)_3 \cdot 9H_2O$ (98%, Sigma-Aldrich), 23 vol% formamide (Sigma-Aldrich), anhydrous NaOH (98%, Sigma-Aldrich), were straight in use for the fabrication method. Nafion solutions were obtained from Sigma-Aldrich-India. Deionized (DI) water was used all through the experimental procedure

2.1. Strategic Fabrication Process of Pristine MgCr-LDH (Mg: Cr = 3:1)

A simplistic one-pot co-precipitation method was implemented for the synthesis of pristine MgCr-LDH at room temperature by slowly bubbling N_2 gas throughout the experimental process. At first instance, 10 mL of the DI H_2O was constantly purged with N_2 for a minimum period of 15 min. Then 20 mL solution of mixed metal nitrate containing Mg ($(NO_3)_2 \cdot 6H_2O$ (0.030 M) and Cr ($(NO_3)_3 \cdot 9H_2O$ (0.010 M), were drop wise added to the 20 mL of DI H_2O and 20 mL ethanol under constant N_2 purging and slow aging at room temperature. After then 1M NaOH solution was dropwise added into the aqueous solution slowly until the pH of the solution was maintained at about 7 and the resultant suspension was kept under constant

aging at room temperature for over 18 h. Consequently, the product isolation was settled by speedy centrifugation of 7000 rotation per minutes (RPM), and finally washed with DI water and ethanol for three times, and then vacuum dried at 80 °C overnight. The as-synthesized product was distinct as pristine MgCr-LDH.

Strategic Fabrication Process of Exfoliated 2D MgCr-LDH (Mg: Cr = 3:1) Nanosheets

In a unusual synthetic protocol, 20 mL of mixed metal nitrate solution containing Mg (NO₃)₂·6H₂O (0.030 M) and Cr (NO₃)₃·9H₂O (0.010 M) were drop wise added to 10 mL solution of 23 vol% formamide with 20 mL of ethanol and constantly stirred to obtain a clear homogenous solution under N₂ atmosphere at room temperature. Subsequently, the pH adjustment of the mixed metal nitrate solution was constant at pH = 7 by slow addition of aqueous 1M NaOH solution till the completion of the saturation point of the green precipitate of MgCr-LDH nanosheets. Then the centrifuged MgCr-LDH colloidal gel was washed with deionized water and ethanol 3-4 times and finally dried in vacuum at 40°C for couple of days.

2.3. Strategic Fabrication Process of hierarchal flower like 3D MgCr-LDH (Mg: Cr = 3:1)

In order to synthesized hierarchal flower like 3D MgCr-LDH, the recovered gel of 2D MgCr-LDH nanosheets was again redispersed and diffused in 10 mL of formamide solution and sonicated for 30 mins followed by stirring for 30 mins under N₂ atmosphere at room temperature. The formamide treated colloidal dispersion was transferred to 100 mL Teflon lined autoclave reactor and treated at 80°C for 24 h. After cooling down to room temperature, the as-synthesized MgCr-LDH gel precipitate was slowly aged under the irradiation of visible light for 30 mins. Finally, the as-synthesized hierarchal 3D MgCr-LDH was washed with DI water and ethanol for three times and vacuum dried overnight at 40°C for further use. The most significant feature of this proposed synthetic approach is the tremendous simplification and greener route of the synthesis procedure for the flower like 3D MgCr-LDH composed of 2D nanosheets.

Photocatalytic Water Splitting Measurement Studies

The catalytic competence of the as prepared MgCr-LDH samples were tested towards water splitting reaction under visible light exposure from 125 W Xe lamp (power density = 100 mW cm⁻²) attached to a quartz reactor fitted with Julabo based chiller and 1 M NaNO₂ as UV cut off filter to filter out visible light of $\lambda \geq 400$ nm. The water splitting reaction was begin with the addition of 0.02 g of catalyst to 20 mL of 10 vol% CH₃OH solution and other sacrificial agents then purged with N₂ gas for 15 mins to remove any dissolved O₂ gas to make the environment inert prior to light exposure. Then the reaction suspension was stirred continuously for 1h to avoid any catalyst settlement under the exposure of visible light. The evolved gas was collected using downward displacement of water and further detected by GC-17A and column packed with 5 Å molecular sieves, set with thermal conductivity detector (TCD). Similar

experiment condition was implemented, for O₂ evolution, with 0.03 g of catalyst added to 30 mL of 10 vol% of AgNO₃ and other tested sacrificial agents.

Apparent Conversion Efficiency (ACE) for H₂ evolution =

The apparent conversion efficiency (ACE) of the MgCr-LDH/NF photocatalyst producing H₂ gas of 1315 μmol/h and O₂ gas of 579 μmol/h by using 125 W Hg lamp as the visible light source positioned 9 cm away from the photocatalytic reactor) could be determined by using the below mentioned equation (9) :

$$\text{ACE (\%)} = \frac{\text{Stored chemical energy}}{\text{Incident photon energy}} \times 100 \quad (24)$$

Where ΔH_c = heat of combustion of hydrogen in kJ/mol,

Stored chemical energy = (number of moles of hydrogen produced per second) × ΔH_c kJ/mol =

$$0.3652 \times 10^{-6} \text{ mole/s} \times 285.8 \times 10^3 \text{ J/mol} = 0.1043 \text{ J/s or W}$$

The calculated power density for 250 W Hg lamps as visible light source is approximately 100 mW cm⁻².

Incident photon energy = power density of the incident visible light × (light exposed spherical surface area of the reaction container) = 100 mW cm⁻² × π × r² (r = radius of the spherical surface = 1.5 cm)

$$= 100 \text{ mW cm}^{-2} \times 3.141 \times (1.5 \text{ cm})^2 = 0.7067 \text{ W}$$

Thus, ACE (H₂ evolution) = 0.0521 W/0.7067 W = 0.1475 = 14.75%

Apparent Conversion Efficiency (ACE) for O₂ evolution =

The ACE for O₂ evolution could be calculated by applying same equation (24) as used for H₂ evolution.

Stored chemical energy = Number of moles of O₂ produced/sec after reaction completion × ΔH_c of O₂ in kJ/mole = 0.1608 × 10⁻⁶ × 285.8 × 10³ = 0.0459 W

Incident photon energy = Intensity of 125 W Xe lamp × Area of spherical surface on which light is irradiated (πr²) = 100 mW cm⁻² × 3.141 × (1.5 cm)² = 0.7067 W

ACE (O₂ evolution) = 0.0459 W/ 0.7067 W = 0.0649 = 6.4%

Preparation of photoelectrode and PEC measurements

Electrode preparation

20 mg of each MgCr-LDH samples were suspended in 1 mL ethanol, plus 1 mL methanol and 20 μ L Nafion and sonicated for 20 mins. Then the mixture was coated onto fluorine-doped tin oxide (FTO) by drop-casted method in the dimension of $1 \times 1 \text{ cm}^2$. The LDH coated thin films were vacuumed dried at 80°C for overnight prior to use.

PEC measurements

PEC measurements were carried out by potentiostat–galvanostat (IviumStat) terminal at a scan

rate of 10 mV s^{-1} , with accessories of 300 W Xenon lamps of 100 mW/cm^2 illumination was maintained as the light source, three-electrode system carrying Pt, Ag/AgCl (3.5M KCl), and FTO, as counter, reference, and working electrode, respectively. 0.1 M Na_2SO_4 solution with tested pH 6.5 was used as the electrolyte. The linear sweep voltammetry (LSV) study was deliberate by applied bias within -0.5 to $+1.5 \text{ V}$ at scanning rate of 10 mV s^{-1} under visible light exposure. The MgCr-LDH deposited over FTO containing thin films were used as a working electrode with approximately 0.35 cm^2 geometric area exposed to the electrolyte solution under light irradiation. The experiments were performed in a conventional three-electrode quartz cell using Ag/AgCl (3.5M KCl) as a reference electrode, Pt-foil as counter electrode and the MgCr-LDH coated film as the working electrode. Electrochemical impedance spectroscopic (EIS) measurements were performed using a similar experimental setup, of 0.1 M Na_2SO_4 solution with frequency response of 5000-30 Hz. Mott-Schottky analysis was carried out at a DC potential range -0.9 V to $+1.2 \text{ V}$ vs. RHE with the AC potential frequency 5 kHz and the amplitude of AC potential 0.050 V under dark condition in a 0.1 M Na_2SO_4 solution (pH 6.5). The stability of the material undergoing water splitting reaction was examined through chronoamperometry using the same reaction condition under constant illumination of 100 W/cm^2 at an applied potential of 0.5 V for 6000 s. The chopped illumination was achieved by an electronic shutter with light on and off cycle of 30 s and the transient LSV measurements were conducted at a scan rate of 10 mV/s to match the chopped illumination cycles.

Materials characterization Techniques

The phase purity of the as-prepared materials were characterized by XRD, Rigaku Miniflex powder diffractometer) with Cu K α as radiation source ($\lambda = 1.54 \text{ \AA}$, 30 kV, 50 mA). The functional groups associated with the bending and stretching mode of vibration of the materials were specified by JASCO FT-IR-4600, using KBr reference. The exterior surface morphology and structural features of the materials were obtained by FESEM by using ZEISS Sigma 500 VP microscope. The internal structure and morphology was explored under the TEM and HR-TEM by using JEOL 2100. The XPS measurement was taken at an X-ray photoelectron spectrometer (ESCALAB 250XI) with X-ray source as nonmonochromatized Mg K α and energy of 0.8 eV. The optical absorption measurements were recorded by JASCO-V-750 UV–Vis spectrophotometer. The PL emission spectra were recorded by applying excitation energy of 320 nm using JASCO-FP-8300 spectrophotometer. PEC measurements of samples were carried out by potentiostat–galvanostat (IviumStat) terminal.

Declarations

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Author Contributions

S. Nayak and K.M. Parida visualized and deliberate the experiments. S. Nayak synthesized the materials, performed the experiments and wrote the manuscript. S. Nayak participated in interpreting and analyzing the data. All the authors reviewed and commented on the manuscript.

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Supporting Information

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Figures

Figure 1

Growth mechanism of MgCr-LDH nanoflower.

Figure 2

(a, b) FEEM morphology of MgCr-LDH/NF at different dimension, (c-e) TEM morphological features of MgCr-LDH/NF at different dimension, and (f) lattice spacing of MgCr-LDH/NF as identified from HR-TEM image, and corresponding SAED pattern (in-set image) of the material structure.

Figure 3

(a) PXRD spectra of MgCr-LDH/PS , and exfoliated MgCr-LDH/NS; (b) PXRD spectra of MgCr-LDH/NF under the influence of hydrothermal treatment of 80 °C and visible light exposure of 30 mins.

Figure 4

Analysis of the XPS results of the deconvoluted XPS spectra of MgCr-LDH/NS and MgCr-LDH/NF for Mg2p, Mg2s, Cr2p, O2p, and C1s.

Figure 5

(a, b) Dark and light current density of MgCr-LDH/PS, MgCr-LDH/NS and MgCr-LDH/NF via LSV plot, (c) Tafel slope plot of MgCr-LDH/PS, MgCr-LDH/NS and MgCr-LDH/NF, and (d) Transient photocurrent density of MgCr-LDH/PS, MgCr-LDH/NS and MgCr-LDH/NF measured through light on-off cycle.

Figure 6

Electrochemical impedance spectra of the as-synthesized MgCr-LDH/PS, MgCr-LDH/NS and MgCr-LDH/NF samples.

Figure 7

Mott Schottky plot of MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF sample.

Figure 8

(a, b) Volume of H₂ and O₂ production plot under visible light illumination for 1 h, and (c, d) Recyclability studies of MgCr-LDH/NF towards H₂ and O₂ evolution under visible light exposure.

Figure 9

(a, b) Effect of different sacrificial agent on H₂ and O₂ evolution under visible light exposure, and (c) Hydroxyl radical test plot for all samples.

Figure 10

(a) UV-Vis DRS spectra of MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF. (b-d) Band gap energy plot of MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF as derived from Kubelka-Munk equation through Tauc plot.

Figure 11

PL spectral plot of MgCr-LDH/PS, MgCr-LDH/NS, and MgCr-LDH/NF.

Figure 12

Relative band positions and charge transfer mechanism of the MgCr-LDH/NF for water splitting reaction under visible light exposure.

Figure 13

Schematic illustration of the future proposed expected carrier charge transfer dynamics of deposited MgCr-LDH/NF photocatalyst to current-collector substrates.

Supplementary Files

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- [SupplementaryInformationMgCrLDHNanoflower.docx](#)