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Topotactic Transformation of Solvated MgCr-LDH Nanosheets to Highly Efficient Porous MgO/MgCr₂O₄ Nanocomposite for Photocatalytic H₂ Evolution

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Supporting Information

ABSTRACT: The hybrid structure of nanoparticles (NPs) with nanosheets has the advantage of both anisotropic properties of NPs and large specific surface areas of nanosheets, which is desirable for many technological applications. In this study, MgCr₂O₄ spinel NPs decorated on highly porous MgO nanosheets forming MgO/MgCr₂ $O_4(x)$ nanocomposites were synthesized by a one pot coprecipitation method followed by a heat treatment process of the solvated wet gel of MgCr-LDH with polar solvent N,N-dimethylformamide (DMF) at 400 °C. This novel synthetic methodology generates materials consisting of porous metal oxides nanosheets adhered with spinel phase NPs due to the slow generation of gases such as H2O, CO2, and NH3 under moderate temperature during the heat treatment process. The synergistic effect of much wider band gap MgO nanosheets and narrow band gap MgCr₂O₄ NPs added increased stability due to the stronger bonding coordination of



MgCr₂O₄ NPs with MgO nanosheets. The obtained MgO/MgCr₂O₄(x) nanocomposites possess large specific surface areas, highly porous structure, and excellent interface between MgCr₂O₄ NPs and MgO nanosheets, which proved from N₂ sorption isotherm, TEM, HR-TEM study. With metallic ratio of MgCr3:1, MgO/MgCr₂O₄(MgCr3:1) nanocomposites exhibit highest H₂ evolution rate of 840 μ molg⁻¹2h⁻¹, which was 2 times higher than that of pure MgCr₂O₄(420 μ molg⁻¹2h⁻¹). The LSV measurement study of MgO/MgCr₂O₄ (MgCr₃:1) nanocomposite shows an enhancement of light current density of 0.22 μ A/ cm^2 at potential bias of -1.1 V. The Mott–Schottky analysis suggested the band edge positions of the n-type constituents and formation of n-n type heterojunctions in MgO/MgCr₂O₄ (MgCr3:1) nanocomposite, which facilitates the flow of charge carriers. The EIS and Bode phase plot of MgO/MgCr₂O₄ (MgCr3:1) nanocomposite signifies the lower interfacial charge transfer resistance and higher lifetime of electrons (2.7 ms) for enhanced H₂ production. Lastly, the enhanced photocatalytic H₂ production activity and long-term stability of MgO/MgCr₂O₄(MgCr3:1) could be attributed to maximum specific surface area, porous structure, close intimacy contact angle between two cubic phases of MgCr₂O₄ NPs and MgO nanosheets, abundant oxygen vacancies sites, reduced charge transfer resistance and suitable band edge potential to drive the thermodynamic energy for H₂ production. This work highlighted an effective strategy for the synthesis of cost-effective 2D porous heterojunctions nanocomposite photocatalyst for promising applications in the field of clean H_2 production utilizing abundant solar energy.

INTRODUCTION

Two-dimensional (2D) layered nanostructured materials triggered hot research spot for photocatalytic H₂ production with the primary goal being improved charge carrier separation, transport characteristics, short lateral diffusion length, and morphological aspects to improve apparent conversion efficiency.¹⁻⁵ Among various Cr-based multicomponent spinel-type metal oxides, magnesium chromite, symbolized as MgCr₂O₄, materials have received special attention due to their unique crystalline structure and remarkable properties toward magnetism,⁶⁻⁹ interconnection material for solid fuel cells,¹⁰ high temperature ceramics,¹¹ humidity sensor elements,¹² catalysts support,¹³ strengthening agents,¹⁴ and combustion catalysts.^{15–17} Recent reports have highlighted the potential of MgCr₂O₄ as an efficient photocatalyst.¹⁸ MgCr₂O₄ is a narrow band gap semiconductor with band gap lying within 1.3 to 1.8 eV and crystallizes in normal cubic spinel structure in which the bivalent Mg-ions occupy the tetrahedral sites and the trivalent Cr-ions hold the octahedral sites.^{19,20} The heterogeneous cationic substitution could lead to multiple valence states at these multimetal centers and reduce the activation energy for electron transport between cations and endow desirable electronic conductiv-

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Scheme 1. Growth Mechanism of Porous $MgO/MgCr_2O_4(x)$ Nanocomposite

ity.^{20,21} However, owing to poor photoelectric conversion and competing thermodynamic stability of Cr₂O₃ with MgCr₂O₄ resulting as biphasic MgCr₂O₄-Cr₂O₃, most of the current study about $MgCr_2O_4$ is mainly limited in the field of combustion catalyst²² and ceramic refractories.^{23,24} Nitta et al. reported a binary MgCr₂O₄-TiO₂ system, which is very important in refractories because of maintaining good mechanical and thermal stabilities at high temperatures.²⁵ Furthermore, there is no report on photocatalytic application of MgCr₂O₄ up to now apart from the report about the oxidative degradation of Xylenol Orange and photodegradation of Rhodamine-6G dyes as environmental pollutants by Nagarajan et al. in 2015.¹⁸ Besides the photocatalysis using MgCr₂O₄, systematic study and mechanistic approach toward clean H₂ production with high efficiency under visible light irradiation is still needed. Therefore, there is an urgent demand but still significant challenge to rationally design MgCr₂O₄ NPs with optimized performance by tailoring the structure, morphology, and surface or hybridizing with other nanostructured porous metal oxide to form hybrid nanostructure materials.

In addition, photocatalytic activity is related to morphology and dimensions of photocatalytic material. It is well-known that two-dimensional (2D) porous structure catalyst usually presents higher photocatalytic activity than one dimension (1D) catalyst with advantages including high surface area, abundant pore size distribution, and large number channels, which provides smooth electron transport to contribute toward the light scattering effect for photoreactions.^{26–28} Magnesium oxide (MgO) is an important functional metal oxide that has been widely used as catalyst, adsorbent to remove toxic metal ions from water,^{29,30} adsorbents for $CO_{2,}^{31}$ supports for metals,³² photocatalyst for optical activities,³³ photodegradation of organic pollutants,³⁴ and catalyst for organic transformation reactions.³⁵ Moreover, MgO has a promising role in the field of superconductor³⁶ and ferroelectric applications.³⁶ In the catalysis field, MgO acts as catalyst or catalyst support for many types of organic and inorganic reactions.³⁷ It has been reported that MgO NPs serve as an excellent support based on their lower particle size as compared to other materials. As the particle size decreases, the number of surface atoms increases and it is expected to enhance the catalytic activity.³⁸ MgO supported metal catalysts were reported to be used for a set of catalytic reactions such as Fischer-Tropsch reaction, dry and steam reforming of methane, water gas shift reaction, and many organic transformation reactions.^{31,39} Also, nanosized MgO has been investigated as nontoxic and benign.40,41 More interestingly, the presence of oxygen vacancies in MgO has tremendous influence on their electronic and chemical properties.⁴² Therefore, the combination of wide band gap 2D MgO semiconductor as support for spinel type MgCr₂O₄ by integrating their advantages would be an effective approach to obtain a novel kind of photocatalyst. 2D MgO structures provide higher surface area and improve the porosity for better light scattering effects and enhance the solar light harvestation ability of MgCr₂O₄ NPs. These phenomena would reduce recombination of charge carriers and facilitate the electrolyte diffusion process to regenerate the oxidized species for enhanced conversion efficiency of water reduction reactions.

One effective way to manipulate the shape of metal oxide particles is their synthesis through mild thermal decomposition of an anisotropic precursor compound. Metal oxide particles can be obtained as pseudomorphs of the decomposable precursor. Important examples are layered double hydroxides (LDHs) also known as hydrotalcite-like materials. LDHs typically crystallize in the form of thin hexagonal platelets due to their 2D layered crystal structure and can be easily synthesized with nitrate anions by a coprecipitation method. A special class of 2D metal oxide nanocomposite derived directly from heat treatment of LDHs nanosheets emerged as promising material owing to their utmost utilization of each single-layer with abundant reactive sites providing large surface area for reducing the recombination of photoexcited charge carriers.43-45 Nitrates containing LDH have the general composition $M^{II}_{1-x}M^{III}_{x}(OH)_{2}(NO_{3})_{x} \cdot nH_{2}O$. Upon mild heat treatment of LDH precursor, the anions decompose at moderate temperature and the resulting metal oxide particles often retain the anisotropic platelet morphology irrespective of the usually preferred arrangement in the lattice space group. Generally, the formation of mixed metal oxide (MMO) nanocomposite materials composed of metal oxide phase $(M^{II}O)$ and spinel-type phase $(M^{II}M^{III}_{2}O_{4})$ from a single LDH precursor is hindered by the compositional incompatibility between precursor and target compound. Stable LDHs require a M^{II}/M^{III} ratio between approximately 2:1, 3:1, and 4:1 (0.2 $\leq x \leq 0.3$). There are several examples of mixed metal oxide derived from LDH such as ZnO/ZnAl₂O₄ from ZnAl-LDH,⁴ NiCoFe spinel-type oxide from NiFeCo-LDH,⁴⁷ and aluminasupported CoFe alloy catalysts derived from LDH nanosheets.43

Herein, we report the formation of a special MgO/MgCr₂O₄ (x) (x = molar ratio between Mg^{II}:Cr^{III}, i.e. 2:1, 3:1, and 4:1) nanocomposite developed by heat treatment of precursor MgCr-LDH, precipitated via a coprecipitation method in the presence of N_N-dimethylformamide (DMF). The resultant MgO/MgCr₂O₄ (x) nanocomposites possess a unique form of crystalline, porous nanosheets with NPs and demonstrate its potential in the photocatalytic H₂ production. The design concept and growth mechanism are presented in Scheme 1. First, in the proposed coprecipitation synthetic methodology, the above-mentioned compositional restriction was overcome by using a mixture of Mg^{II} and Cr^{III} for the synthesis of the MgCr-LDH precursor at a constant pH value of 7 under N₂ atmosphere. The target composition of the MgCr-LDH coprecipitate was $Mg^{II}_{0.9}Cr^{III}_{0.3}(OH)_2(NO_3)_{0.3} \cdot nH_2O$ in accordance with the Mg^{II}/Cr^{III} metallic ratio of 3:1 (x = 0.3) by employing DMF as chelating agent. Finally, during heat treatment, a nanosheets-like MgO matrix was generated as the foundation of the porous structure of MgO/MgCr₂ $O_4(x)$ with a large surface area that significantly facilitates the interaction between MgO and MgCr₂O₄. Afterward, the presence of DMF acts as surface-modifying ligand, which not only activates the surface of MgO nanosheets but also facilitates the particle dispersion of the catalyst. With the progress of heat treatment time, thermal decomposition of the organic impurity (DMF) and slow release of a majority amount of gases such as H_{2} , CO₂, and H₂O in a confined space during the sintered process led to the formation of 2D porous MgO/MgCr₂ $O_4(x)$ heterojunctions nanocomposites. Consequently, 2D porous $MgO/MgCr_2O_4(MgCr_3:1)$ nanocomposites achieve 2 times enhanced photocatalytic activity toward clean H₂ energy production as compared with pure MgCr₂O₄. More interestingly, MgO/MgCr₂O₄(MgCr3:1) nanocomposite is very stable under visible light irradiation. Such finding extends the photocatalytic application of MgCr₂O₄ based photocatalyst to the entire solar light spectrum and opens a new avenue for the practical utilization of solar energy.

EXPERIMENTAL DETAILS

Materials. Magnesium nitrate hexahydrate $(Mg(NO_3)_2 \cdot 6H_2O)$, chromium nitrate nonahydrate $(Cr(NO_3)_3 \cdot 9H_2O)$, anhydrous sodium hydroxide (NaOH), and *N*,*N*-dimethylformamide (DMF) were all of analytical grade and purchased from Sigma-Aldrich Chemical Reagents. The mixed metal salt solutions were prepared by using deionized water. All other chemicals and solvents purchased are of

analytically pure grade and directly used without further purification throughout this research work.

Synthesis of MgO/MgCr₂O₄ Nanocomposite. At first, solvated MgCr-LDH gel consisting of exfoliated nanosheets was prepared by a coprecipitation method at room temperature. In a typical synthesis procedure, an aliquot amount of 100 mL of mixed metal nitrate solution containing 0.01 M Mg(NO₃)₂·6H₂O and 0.005 M Cr- $(NO_3)_3$ ·9H₂O (Mg^{II} + Cr^{III} = 2:1), 0.015 M solution of Mg(NO₃)₂· $6H_2O$, and 0.005 M solution of $Cr(NO_3)_3 \cdot 9H_2O$ (Mg^{II} + $Cr^{III} = 3:1$) and 0.02 M solution of Mg(NO₃)₂·6H₂O with 0.005 M solution of $Cr(NO_3)_3 \cdot 9H_2O$ (Mg^{II} + $Cr^{III}=4:1$) were taken in separate funnels. Then each mixed metal nitrate solution and 1 M NaOH solutions were taken in two separate dropping funnels and simultaneously dropwise added to a beaker containing 25 mL of DMF until the pH reaches to 7. After addition, the resulting slurry was aged for 2 h and then the precipitate was filtered and finally the gel product was washed two times with 1:1 vol ratio of ethanol and DMF mixed solvents. Afterward, heat treatment of the wet gel product was carried out in a muffle furnace at 400 °C with a heating rate of 15 °C min⁻ for 3 h. After the heat treatment, the sample cooled naturally to room temperature and was grounded to a powder for further use. The porous MgO/MgCr₂O₄ (x) nanocomposites with variable M^{II} to M^{III} metal ratio of 2:1, 3:1, and 4:1 were synthesized and named as MgO/ $MgCr_2O_4(x)$, where x = (MgCr2:1), (MgCr3:1), and (MgCr4:1). For comparison study, MgO and MgCr₂O₄ were prepared by similar coprecipitation and heat treatment process at 400 °C with heating rate of 15 °C min⁻¹ for 3 h. The molar ratio of Mg to Cr was fixed to 1:0 and 1:2 for the synthesis of MgO and MgCr₂O₄, respectively. The physical mixtures between MgO and MgCr₂O₄ were prepared by grinding the as prepared calcined MgO and MgCr₂O₄ samples using a mortar and pestle.

Photocatalytic H₂ Production Activity. The photocatalytic activity of the synthesized catalyst was evaluated for photocatalytic H₂ evolution in a batch reactor. For H₂ production about 0.02 g of the catalyst was dispersed in 20 mL of 10% aqueous methanol solution (pH = 5) as sacrificial agent. Prior to irradiation, the solution was purged with N₂ gas to evacuate the presence of other gases and then the solution was stirred in the dark to attain equilibrium. A 125 W medium pressure Hg lamp with 1 M NaNO₂ as UV cut off filter ($\lambda \geq$ 400 nm) was used as the visible-light source to irradiate over the solution for 2 h. The average power density incident on the reactor was around 100 mW cm⁻² and the sensor was adjusted in such a way to give maximum intensity to the solution. During the course of reaction, the temperature of the solution was maintained at 283 K by circulating cold water in the jacketed reactor. The evolved H₂ gas was analyzed by GC-17A (Shimadzu) using a 5 Å molecular sieves column and thermal conductivity detector (TCD). Several blank experiments were carried out under the same ambient condition in order to confirm the evolution of H₂ gas without the presence of photocatalyst.

Characterization Techniques. The crystal structure and phase composition of all the as prepared materials were recorded by powder X-ray diffraction measurements at room temperature using a Rigaku D/MAX III VC diffractometer using Cu K α radiation at 40 kV, at a scanning rate of 5°/min and 2 θ angle ranging from 7° to 80°, respectively. The Fourier transform infrared (FTIR) spectra of the samples were measured on a Bruker Alpha FTIR spectrophotometer using KBr as reference compound for the measurement process. The diffuse reflectance UV (DRUV)-Vis spectra of all the samples were measured by JASCO-V750 UV-vis spectrophotometer attached with a diffuse reflectance accessory in the region 200-800 nm. The photoluminescence (PL) spectra of the prepared samples were analyzed with a JASCO-FP-8300 fluorescence spectrometer with excitation energy of 320 nm at room temperature. The X-ray photoelectron spectroscopy (XPS) measurements were performed on a VG Microtech Multi lab ESCA3000 spectrometer with nonmonochromatized Mg K α X-ray source and energy of 0.8 eV. The binding energy correction was performed by the C 1s reference peak of the carbon atom at 284.9 eV. The photoelectrochemical measurements were taken using a three electrode cell system consisting of a platinum wire as counter electrode, Ag/AgCl electrode



Figure 1. XRD patterns of (a) precursor of MgO/MgCr₂O₄(MgCr₃:1) nanocomposite (MgCr-LDH nanosheets, Mg:Cr = 3:1) and pure MgO; (b) MgO/MgCr₂O₄(*x*) nanocomposite consisting of (i) MgO/MgCr₂O₄(MgCr₂:1), (ii) MgO/MgCr₂O₄(MgCr₃:1), (iii) MgO/MgCr₂O₄(MgCr₄:1), and (iv) pure MgCr₂O₄.

as reference electrode, and a prepared electrode as working electrode, respectively. The working electrode of the as-synthesized MgO, MgCr₂O₄, and MgO/MgCr₂O₄(MgCr3:1) catalyst were prepared by the electrophoretic deposition method coated over the surface of fluorine-doped tin oxide (FTO). Thirty milligrams of the assynthesized catalyst were mixed with 20 mg of iodine powder and 30 mL of acetone solution and sonicated for 15 min. After that two FTO electrodes were dipped inside the solution facing parallel to each other and the separation between them is approximately 10-20 mm apart. An applied potential of 60 V bias was fixed for 3 min through a potentiostat. The uniformity of the coated area was fixed at $1 \text{ cm} \times 1$ cm and then dried at 80 °C for 2 h. The electrochemical cell was filled with an aqueous solution of 0.1 M Na₂SO₄. The electrolyte was saturated with nitrogen gas prior to electrochemical measurements. All the photoelectrochemical studies were performed using an Ivum multichannel potentiostat under both dark and light illumination conditions and irradiated using a 300 W Xe lamp ($\lambda \ge 400$ nm) with 400 nm cutoff filters. The Nyquist plot using electrochemical impedance study (EIS) was measured at 105 Hz to 1 Hz at a potential of 0.1 V in 0.1 M Na₂SO₄ solution in the presence of light in an open circuit potential. The Mott-Schottky (M-S) measurement was carried out at a constant frequency of 500 Hz under dark conditions. The linear sweep voltammetry (LSV) plots were evaluated by potential biasing of -1.0 to +1.8 V at a scan rate of 0.05 mV s⁻¹ under both dark and light illuminations, respectively. The field emission scanning electron microscopy (FESEM) images were obtained using a HITACHI 3400N microscope. The high resolution transmission electron microscopy (HRTEM) and scanning transmission electron microscopy (STEM) images were obtained on JEM-2100, ZEOL-Japan in which the samples were prepared by dispersing the powdered samples in ethanol by sonication for 15 min and then drop-drying on a copper grid coated with carbon film. The N2 physisorption measurements for the MgCr-LDH (MgCr3:1) and $MgO/MgCr_2O_4$ (MgCr = 3:1) nanocomposite material were carried out on a NOVA3000 (Quantachrome GmbH, Germany) at liquid nitrogen temperature (77 K). Potentially adsorbed water on the sample was removed in a degassing step at a temperature of 80 °C under vacuum conditions for 2 h prior to the actual measurement. 200 mg of the sample in a sieve fraction of 250-355 were pretreated at 473 K for 2 h under vacuum to remove water. The specific surface areas were determined from the adsorption isotherm using the BET method. Applying the BJH method, the pore volume and the pore size distribution were obtained.

RESULTS AND DISCUSSION

XRD Study. The mesoporous $MgO/MgCr_2O_4(x)$ nanocomposite was prepared by heat treatment of a solvated wet gel of precursor MgCr-LDH exfoliated in DMF at 400 °C. In the first step, i.e. in the liquid-phase growth process, homogeneous alkalinization of Mg/Cr nitrate solutions was processed by using aqueous NaOH solution and DMF as polar solvent. In the second step, heat treatment of solvated wet gel product of MgCr-LDH at a temperature of 400 °C resulted in the formation of MgO/MgCr₂ $O_4(x)$ nanocomposites, consisting of a MgO nanosheets matrix adhered with MgCr₂O₄ NPs forming heterojunctions at the interface of two phases. An insight into the XRD patterns of MgCr-LDH(MgCr3:1) precursor (inset of Figure 1a) displays characteristic diffraction peaks that clearly resemble exfoliated LDH nanosheets.⁴³ The transparent MgCr-LDH aqueous dispersion clearly exhibits the existence of colloidal LDH nanosheets. After centrifugation of the colloidal LDH dispersion, MgCr-LDH gel sample was collected consisting of loosely and randomly stacked LDH nanosheets. The gel of MgCr-LDH with metallic ratio of Mg:Cr = 3:1 exhibits a diffraction peak at $2\theta = 35^{\circ}$ and 60.4° corresponding to the (012) and (110) planes, respectively. The other intense characteristic peaks of the (003) and (006)planes were totally absent in the MgCr-LDH (MgCr 3:1) sample, which indicates the exfoliation of bulk MgCr-LDH into MgCr-LDH nanosheets with almost no stacking. Figure 1(b-ii) represents the XRD patterns of MgO/ MgCr₂O₄(MgCr3:1) nanocomposites resulted from heat treatment of solvated MgCr-LDH gel at 400 °C. During the heat treatment process of MgCr-LDH gel at 400 °C, the exfoliated nanosheets structure of LDH crumples and dehydrates to form a combination of MgO nanosheets with spinel phase MgCr₂O₄ NPs structure.⁴³ The diffraction peak of $MgO/MgCr_2O_4(MgCr_3:1)$ nanocomposite mainly consists of major peaks at $2\theta = 18.1$, 36.1, 57.5, and 63.3, which can be indexed to (110), (311), (511), and (440) crystal planes of cubic spinel MgCr₂O₄ (JCPDS card no. 10-0351) as well as the (200) planes of MgO at $2\theta = 43.5$ with cubic structure (JCPDS card no. 04-0829). This shows that a layered MgCr-LDH nanosheet structure was transformed to a random anisotropic morphology consisting of a porous structure in the metallic ratio of Mg:Cr = 3:1. The broad and less intense diffraction peaks of MgO and MgCr₂O₄ in MgO/MgCr₂O₄ (MgCr 3:1) nanocomposite can be ascribed to the formation of porous MgO nanosheets adhered with MgCr₂O₄ NPs. No other phases like Cr₂O₃ impurity were detected in the XRD spectrum of MgO/MgCr₂O₄(MgCr3:1) nanocomposite, suggesting the formation of phase pure material. In addition, the XRD spectra of both MgO/MgCr₂O₄(MgCr 2:1) and MgO/ $MgCr_2O_4(MgCr 4:1)$ nanocomposite are displayed in Figure

1(b). The XRD spectra of both these nanocomposites consist of phases of MgO and MgCr₂O₄, while Cr₂O₃ impurity phases were detected in the XRD spectrum of MgO/ $MgCr_2O_4(MgCr4:1)$ nanocomposite (Figure 1b-iii). The XRD spectrum of MgO (Figure 1a) displays sharp diffraction peaks indexed to (111), (200), and (220) planes of cubic MgO (JCPDS card no. 04-0829), suggesting the successful preparation of MgO nanosheets. The XRD spectrum of pure MgCr₂O₄ (Figure 1b-iv) shows main characteristic diffraction peaks of (110), (111), (220), (311), (422), (511), and (440) crystal planes, assigned to the cubic spinel MgCr₂O₄ phase (JCPDS Card No. 22-1012). In comparison to diffraction peaks of MgCr₂O₄, there was no shifting of any MgCr₂O₄ diffraction peaks in MgO/MgCr₂ $O_4(x)$ nanocomposites. The structural data of the samples are given in Table S1 of the Supporting Information. Correspondingly, the lattice parameter "a" is the average distance between two metal cations within the layer, and the value of $a (=2d_{110})$ is a function of the average radii of the metal cations. The lattice parameter "c" is three times the distance from the center of one layer to the next layer, and the value of $c \left[=1/2 \left(3d_{003} + 6d_{006}\right)\right]$ is a function of a number of factors, including the average charge of the metal cations, the nature of the interlayer anion, and the extent of hydration by water molecules. Hence, it can be found from Table S1 that the lattice parameter "a" of MgCr-LDH (MgCr = 3:1) nanosheets was 3.064 Å. However, the "c" parameter value in the MgCr-LDH nanosheets sample could not be estimated due to the absence of a (003) and (006)lattice reflection plane due to the formation of nanosheets. The lattice parameters of constituent cubic phases of MgO and $MgCr_2O_4$ in $MgO/MgCr_2O_4(MgCr_3:1)$ nanocomposite were calculated to be 4.224 and 8.337 Å, respectively. These values were noticed to be slightly different from the reported lattice parameter values of MgO (a = 4.211 Å, JCPDS 45-0946) and $MgCr_2O_4$ (a = 8.333 Å, JCPDS 10-0351), respectively.

FTIR Study. The FTIR spectrum of $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposite was shown in Figure 2. The



Figure 2. FTIR spectra of MgO/MgCr₂O₄ (MgCr3:1).

broad band at 3422 cm⁻¹ was assigned to the stretching vibration of the O–H bond of H_2O , caused by water absorption of the catalysts. The two distinct bands observed at 1630 and 1443 cm⁻¹ correspond to MgO and are attributed to the adsorbed water and carbonate species on the MgO surface.^{48,49} The bands located at 745 and 444 cm⁻¹ were

assigned to the characteristic Mg–O stretching and bending vibrations, respectively.^{50,51} The presence of MgCr₂O₄ was verified by the sharp absorption bands at 654 and 535 cm⁻¹, which are attributed to the Cr(III)–O.¹⁷ The weak absorption band at 932 and 897 cm⁻¹ can be ascribed to the characteristic of Mg(II)–O, respectively.¹⁷

N₂ Sorption Isotherm Study. The N₂ sorption isotherms of MgO/MgCr₂O₄(MgCr3:1) nanocomposite in comparison with the precursor MgCr-LDH(MgCr3:1) were shown in Figure 3a. Both the materials were showing type-IV isotherm with H1 hysteresis (Figure 3a). These isotherms represent the mesoporous behavior of these materials.⁵² The adsorption steps of both the materials were centered in the relative pressure (P/P_0) region from 0.1 to 0.5. This phenomenon indicates the presence of framework-confined mesopores or framework mesoporosity.⁵³ The generation of mesoporosity in MgCr-LDH was due to the arrangement of metal hydroxides with nitrates and the swelling nature of hydroxyl groups, but the generation of mesoporosity within MgO/ MgCr₂O₄(MgCr3:1) nanocomposite was due to the removal of nitrates and other ions, which enables us to create mixed metal oxides after heat treatment at 400 °C. The pore size distribution curves of both MgCr-LDH and MgO/ MgCr₂O₄(MgCr 3:1) nanocomposites were 11.8 and 5.5 nm, respectively (Figure 3b), which belong to the mesoporous region. The surface area, pore diameter, and pore volume of the samples were summarized in Table 1. These values are obtained from N₂ sorption isotherms. The large specific surface area of $MgO/MgCr_2O_4(MgCr3:1)$ nanocomposite as compared to MgCr-LDH indicates an efficient removal of nitrate and other ionic impurities after heat treatment leads to form mesoporosity. This phenomenon is helpful to enhance the surface area of the MgO/MgCr₂O₄(MgCr3:1) nanocomposite. Table 1 shows the narrow pore diameter (5.5 nm) of MgO/ MgCr₂O₄ (MgCr3:1) nanocomposite as compared to MgCr-LDH (11.8 nm), which was due to the pore contraction after removal of nitrate and other ionic impurities and formation/ rearrangement of metal oxides. The wide pore volume of MgO/MgCr₂O₄ (MgCr3:1) nanocomposite indicates their larger surface area as compared to MgCr-LDH. Hence, the large surface area of MgO/MgCr₂O₄(MgCr3:1) nanocomposite would act as an efficient catalyst for interaction with reactant molecules.

UV-DRS Study. Figure 4 shows the UV-vis diffuse reflection (UV-vis DR) spectra of MgO, MgCr₂O₄, and $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposite. In the UV region, the absorption spectrum of MgO shows an intrinsic absorption peak at 290 nm with steep absorption edge at 354 nm, which is due to the ligand to metal charge transfer (LMCT) transition of the O-2p \rightarrow Mg-2p orbital and corresponds to a band gap energy (E_{σ}) of 3.51 eV.⁵⁴ In the absorption spectrum of MgCr₂O₄, the sharp absorption peak at 250 nm is attributed to the LMCT of O-2p \rightarrow Cr-3dt_{2g} in an octahedral environment.^{18,55} The two absorption peaks centered at 410 and 580 nm correspond to the ${}^{4}A_{2g}^{1} \rightarrow {}^{4}T_{1g}(F)$ and ${}^{4}A_{2g} \rightarrow {}^{4}T_{2g}(F)$ d-d transitions of Cr^{3+} ions with absorption tail extending to the visible region.⁵⁶ The absorption spectrum of MgO/MgCr₂O₄ (MgCr3:1) nanocomposite displays an intense absorption band at 300 and 370 nm in the UV region, which may be ascribed to the well-defined excitation band of both MgO and MgCr₂O₄.⁵⁷ The absorption intensity of MgO/ $MgCr_2O_4(MgCr_3:1)$ in the visible region increases along with the red-shift of the absorption edges at 450 and 690 nm,



Figure 3. N₂ sorption isotherm (a) and pore size distribution (b) of mesoporous MgCr-LDH and MgO/MgCr₂O₄ (MgCr₃:1).

Table 1. Surface Area, Pore Diameter and Pore Volume of the MgCr-LDH (MgCr3:1) and MgO/MgCr₂O₄ (MgCr3:1) Nanocomposite, Which Were Analyzed by BET Measurement

Samples	Surface area (m²/g)	Pore volume (cm ³ /g)	Pore diameter (nm)
MgCr-LDH (MgCr3:1)	210	0.745	11.8
MgOMgCr ₂ O ₄ (MgCr3:1)	290	0.916	5.5



Figure 4. UV–vis diffuse reflectance spectra (UV–vis DRS) of (a) MgO, (b) $MgCr_2O_4$, and (c) $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposite.

which is due to the synergistic effects of both MgO and $MgCr_2O_4$ and mainly due to the d-d transitions of Cr^{3+} ions. The characteristic optical features of $MgO/MgCr_2O_4$ (MgCr3:1) can be ascribed to the cooperative effects of both MgO and $MgCr_2O_4$. In addition, the deep valley found from 300 to 390 nm in $MgO/MgCr_2O_4$ (MgCr3:1) is due to the loss peaks to electronic transitions of F centers located at differently coordinated sites on the surface of MgO.⁵⁸

The band gap energies (E_g) of the as-synthesized materials were estimated by fitting the absorption data with Kubelka– Munk absorbance and Tauc's plot via the following equation:

$$(\alpha h\nu)^{1/n} = A(h\nu - E_g) \tag{1}$$

where α is the absorption coefficient, *h* is the Planck's constant, ν is the energy of incident lights, *A* is an arbitrary constant, and E_g is the optical band gap energy of a semiconductor material. In Tauc's expression, the value of *n* signifies the kind of optical transition of a semiconductor (n = 1/2 for direct transition and n = 2 for indirect transition).⁵⁵ The E_g value of MgO, MgCr₂O₄, and MgO/MgCr₂O₄(MgCr₃:1) were estimated to be 3.51, 1.71, and 2.17 eV, respectively (Figure S1). This band gap energy (2.17 eV) of MgO/MgCr₂O₄ (3:1) is quite sufficient to drive the thermodynamic requirement for water splitting i.e. 1.23 V vs Ag/AgCl.

Article

PL Study. Understanding the concept of the indirect to direct electronic band gap transition of semiconductor materials is of significant interest for the realization of atomic arrangement for thin, porous, and transparent materials. Photoluminescence (PL) spectral analysis gives an idea about the emission properties of the heterojunctions along with the separation efficiency of the photogenerated charge carriers. In general, the photocatalytic activity is strongly affected by the recombination rate of photoexcited electrons and holes. The lower PL emission intensity of material indicates the higher rate of charge separation. The PL emission ($\lambda_{exc} = 320$ nm) spectra of the as synthesized materials were presented in Figure 5. Figure 5(a) displays the PL spectrum of MgO having three peaks at 407, 454, and 524 nm were referred to violet emission, blue emission, and green emission, respectively. The emission peak at 407 nm is due to the presence of holes trapped on magnesium ion vacancies acting as acceptors (F+ center), and the emission peaks at 454 and 524 nm are due to the surface defect sites and oxygen vacancies, respectively.⁵⁹ In addition, MgO does not show a PL emission peak due to its wide band gap. The occurrence of luminescence in MgO is due to the charge transfer phenomena in the surface state.⁶⁰ The charge transfer phenomena are due to the presence of a defect in the surface and oxygen vacancies. Furthermore, the fact that the oxygen vacancies and defects are created within MgO crystal is due to the incomplete oxidation process during transformation of the $Mg(OH)_2$ into $MgO.^{61}$ It is noted that MgO having polyhedral or hexagonal shapes possess more defect surface.⁶² In the present study, MgO has hexagonal structure which favors surface defects and vacancies sites. Figure 5(b) shows the PL spectra of $MgCr_2O_4$ and $MgO/MgCr_2O_4(MgCr_3:1)$. The three characteristic peaks referred to the F+ center, defect state, and oxygen vacancies are also found in the case of







Figure 6. FESEM images of (a) MgCr-LDH(3:1) and (b) MgO/MgCr₂O₄(3:1) nanocomposite; (c-d) TEM micrograph, (e) SAED pattern, and (f) HR-TEM images of MgO/MgCr₂O₄ (3:1) nanocomposite.

 $MgCr_2O_4$ and $MgO/MgCr_2O_4(MgCr_3:1)$. The defect state and oxygen vacancies created in $MgCr_2O_4$ are due to the charge transfer within the Mg surface and from the Mg surface to Cr, whereas in the case of $MgO/MgCr_2O_4(MgCr_3:1)$ the defect state and oxygen vacancies are created due to the charge transfer within MgO and from Mg to Cr. The blue shifting of oxygen vacancies from MgO (524 nm), $MgCr_2O_4$ (511 nm), and $MgO/MgCr_2O_4(MgCr3:1)$ (472 nm) may be due to the

overlapping of different orbital's which facilitate high charge transfer phenomena, resulting in high photocatalytic activity (Figure 5a and 5b). The PL intensity gradually decreases from MgO to MgO/MgCr₂O₄(MgCr3:1), indicating a decrease of charge (electrons and holes) recombination. The suppression of electrons and holes recombination in MgO/MgCr₂O₄(MgCr3:1) as compared to MgO and MgCr₂O₄ indicates that the nanocomposite can capture the photo-induced charge carriers and inhibit the recombination of electrons and holes, which will enhance the photocatalytic H₂ evolution.

Morphological Aspect Analysis. The FESEM images (Figure 6) are used to identify the morphology of MgO/ MgCr₂O₄ (MgCr₃:1) nanocomposite and its precursor i.e. MgCr-LDH (MgCr3:1). As shown in Figure 6a, MgCr-LDH was synthesized by using alkali an aqueous solution of NaOH in the presence of DMF to precipitate the mixed metal nitrate solution of Mg(NO₃)₂·6H₂O and Cr(NO₃)₃·9H₂O. In these synthetic steps, highly polar solvent DMF was used in order to inhibit the complete growth of the layered structure of LDH.^{63,64} In Figure 6a, the morphology of MgCr-LDH composed with hexagonal nanoplatelets is shown, which are a typical characteristic of delaminated LDH material and well supported with the corresponding XRD results.^{64,65} For further evidence of the formation of hexagonal sheetlike nanoplatelets of MgCr-LDH, the TEM image and SAED pattern of MgCr-LDH was taken into account and the TEM micrograph clearly shows the formation of hexagonal sheetlike nanoplatelets (Figure S2). As shown in Figure 6b, heat treatment of the precursor (wet gel of MgCr-LDH calcined at 400 °C) generates porous microstructure of $MgO/MgCr_2O_4(MgCr_3:1)$ consisting of irregular MgO matrix and MgCr₂O₄ NPs. The inset in Figure 6b also shows that both MgO and MgCr₂O₄ NPs aggregate into large particles with rough surface due to magnetic force of attraction of MgCr₂O₄.⁷ However, the FESEM image of MgO/MgCr₂O₄(MgCr3:1) could not reveal the exact sheetlike morphology of MgO with MgCr₂O₄ NPs and for this TEM, HRTEM, TEM-mapping, and HAADF-STEM image of the as synthesized $MgO/MgCr_2O_4(MgCr_3:1)$ were taken into consideration. As shown in Figure 6c, TEM images of MgO/MgCr₂O₄(MgCr3:1) reveal the formation of $MgCr_2O_4$ spinel NPs strongly adhered to the irregular sheetlike morphology of the MgO matrix structure. Distribution of MgCr₂O₄ spinel NPs over MgO matrix is discontinuous and nonuniform with clear visibility of nanointerfaces. Furthermore, TEM images (Figure 6c) specify that $MgCr_2O_4$ NPs are formed within the range of 50-100 nm dimensions and then aggregate to form large particles due to the magnetic force of attraction of MgCr₂O₄.⁷ After heat treatment of solvated MgCr-LDH gel, the resultant MgO/MgCr₂O₄(MgCr3:1) nanocomposite exerts aggregates of MgCr₂O₄ spinel NPs surrounding the MgO sheet matrix consisting of a large number of pores (5.5 nm), which is due to the slow and uniform release of gaseous species such as NH₃, H₂O, and CO₂ during the heat treatment process (Figure 6d). Such structures possess more reactive sites and broader light harvesting ability for superior photocatalytic activity. The SAED pattern of $MgO/MgCr_2O_4$ (MgCr3:1) indicates solid and smooth concentric rings (Figure 6e), which is due to the polycrystalline nature of the as synthesized materials. The HR-TEM image of $MgO/MgCr_2O_4$ (MgCr3:1) in Figure 6f reveals clear lattice fringes and a visible interface between MgO and MgCr₂O₄ phases, confirming the formation of heterojunctions

between MgO and MgCr₂O₄ phases. The measured lattice spacings of 0.22 and 0.26 nm were very close to the (200) and (311) interplanar spacings of MgO ($d_{200} = 0.21$ nm; reference no: 87–0651) and MgCr₂O₄ ($d_{311} = 0.25$ nm; reference no: 77-0007), respectively. Both MgO and MgCr₂O₄ grow in cubic crystal phases with little difference in lattice fringes as found in HR-TEM images of MgO/MgCr₂O₄(MgCr3:1), which indicates good epitaxial attachment of MgCr₂O₄ NPs over the MgO sheet matrix for the formation of n-n type heterojunctions.⁶⁶ The HAADF and STEM images (Figure S3a) show that $MgO/MgCr_2O_4(MgCr3:1)$ holds a planar area. A layered image of elemental maps of MgO/ $MgCr_2O_4(MgCr_3:1)$ sample demonstrating the uniform presence of Mg-K, Cr-K, and O-K was well-defined with sharp contrast as in Figure S3b-e. In an attempt to carry out more precise chemical composition analyses, EDX area scanning of the $MgO/MgCr_2O_4(MgCr3:1)$ sample was performed and shown in Figure S4. The results clearly indicated uniform distribution of elements, namely Mg, Cr, and O throughout the heterojunctions nanocomposite sample. In comparison with the morphological view of MgO/ MgCr₂O₄(MgCr2:1) and MgO/MgCr₂O₄(MgCr4:1) as shown in Figure S5, the former composed with porous clusters of MgO and MgCr₂O₄ NPs and later formed agglomerated MgO and MgCr₂O₄ NPs. Therefore, the morphological advantage of MgO/MgCr₂O₄(MgCr3:1) provides better efficiency for photocatalytic H₂ production due to the synergistic behavior and heterojunctions compatibility of the MgO sheet matrix with MgCr₂O₄ NPs.

Growth Mechanism. In the growth process of the designed n-n heterojunctions (Scheme 1), an improved synthetic route is used for the structural transformation of delaminated MgCr-LDH to heterogeneous structure of MgO matrix embedded with MgCr₂O₄ NPs at 400 °C as confirmed by HR-TEM images. The control growth of delaminated MgCr-LDH was achieved by using DMF as hydrolyzing agents during the coprecipitation method.^{59,60} During the hydrolysis process, continuous release of solvation energy of DMF together with NaOH solution makes the mixed metal nitrate solution basic and induces nucleation growth of LDH nanoplatelets due to limited availability of nutrients in a confined space.^{59,60} The heat treatment of MgCr-LDH(3:1) material resulted in the topotactic transformation to MgO/ MgCr₂O₄(MgCr3:1) at 400 °C in which MgCr₂O₄ spinel NPs formed at an early stage followed by the oriented attachment of these building blocks into the sheetlike matrix of MgO as confirmed by TEM. The XRD results of both MgCr-LDH and MgO/MgCr₂O₄(MgCr3:1) exhibit identical phase transformation behaviors verified by the TEM image and are due to the inherent properties of the LDH materials. However, the transition of the MgCr-LDH material occurred via a different mechanism, with development of a porous matrix in MgO/ $MgCr_2O_4(MgCr_3:1)$. The porous nanostructure of MgO/ $MgCr_2O_4(MgCr3:1)$ was developed during the heat treatment process of the MgCr-LDH gel, which resulted in the thermal decomposition of the DMF to formate and dimethylamine with slow release of the majority amount of gases such as H_{2} , CO2, NH3, and H2O in a confined space. The chemical equations of the reaction process agreed well with the growth mechanism and TEM images and are as follows:

 $+ NaOH \rightarrow Hydrolysis$

$$12N, N(CH_{3})_{2}-CHO + Mg(NO_{3})_{2} \cdot 6H_{2}O + Cr(NO_{3})_{3} \cdot 9H_{2}O \rightarrow Aging Mg^{2+} \cdot Cr^{3+}[N, N(CH_{3})_{2}HCOO(OH)]_{12} \cdot 13H_{2}O$$
(2)
$$Mg^{2+} \cdot Cr^{3+}[N, N(CH_{3})_{2}HCOO(OH)]_{12} \cdot 13H_{2}O$$

$$Mg(OH)_2 \cdot Cr(OH)_3 \downarrow +HN(CH_3)_2 + HCOO^{-}$$
(3)

$$Mg(OH)_{2} \cdot Cr(OH)_{3} \downarrow +HN(CH_{3})_{2} + HCOO^{-}$$

$$\rightarrow In \ air \ (\Delta, \ 400 \ ^{\circ}C)$$

$$MgO \cdot MgCr_{2}O_{4}(s) + NH_{3} \uparrow + CO_{2} \uparrow + H_{2}O\uparrow$$
(4)

Linear Swift Voltammetry (LSV) Study. The photoelectrochemical behaviors of a photocatalyst reflect the production and separation of electrons and holes under visible light irradiation. The LSV measurements of the as prepared MgO, MgCr₂O₄, and MgO/MgCr₂O₄(MgCr3:1) nanocomposites were analyzed under both dark and light current (Figure 7). The LSV curve shows that photocurrent density increases



Figure 7. LSV plot of MgO, $MgCr_2O_4$, and MgO/ $MgCr_2O_4$ (MgCr3:1) nanocomposite under dark and visible light irradiation.

toward anodic direction with respect to the applied potential and is of typical nature of n-type semiconductors.⁵⁵ The current density of MgO and MgCr₂O₄ under light current was found to be 0.09 μ A/cm² and 0.13 μ A/cm², respectively. The $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposites show an enhancement in current density of 0.22 μ A/cm² toward the anodic direction upon positive biasing under visible light irradiation. These results signify the existence of n-type constituents in MgO/MgCr₂O₄(MgCr3:1) nanocomposites, which would direct to the formation of n-n type heterojunctions and facilitate the flow of charge carriers in the anodic to cathodic direction.⁵⁵ The formation of n-n type heterojunctions with band edge positions of the n-type constituents was further confirmed from the Mott-Schottky analysis of the MgO/MgCr₂O₄(MgCr 3:1) nanocomposite. However, the dark current responses of MgO, MgCr₂O₄, and $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposite were much weaker, which confirmed that electron transfer and electronhole pair separation on MgO/MgCr₂O₄ (MgCr3:1) nanocomposite could only be possible under visible light irradiation. This phenomenon was ascribed to the synergistic effect of both MgO nanosheets and $MgCr_2O_4$ NPs in forming heterojunctions in MgO/MgCr_2O_4 (MgCr3:1) nanocomposite. Table S2 depicts the dark and light current density of MgO, $MgCr_2O_4$, and $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposite, respectively.

Mott-Schottky Analysis. Mott-Schottky (M-S) analysis was performed in order to identify the type of semiconductor and band edge potential (Figure 8). The straight line with positive slope drawn to the potential axis in MgO, MgCr₂O₄, and MgO/MgCr₂O₄(MgCr3:1) nanocomposites suggests intrinsic n-type character. The conduction band edge potential (CB) values of n-type MgO, n-type MgCr₂O₄, and n-n type heterojunctions in MgO/MgCr₂O₄(MgCr3:1) were calculated by extrapolation of the straight line toward the x-axis with positive slope. According to the intercept of the M-S plots, the calculated CB edge potentials of MgO, MgCr₂O₄, and MgO/ MgCr₂O₄(MgCr_{3:1}) were estimated to be -0.6, -0.9, and -1.1 V vs Ag/AgCl, respectively. Furthermore, by analyzing these data combined with the band gap energy (E_{α}) achieved from the Kubelka-Munk absorbance (Figure 4), the VB edge potentials of the MgO, MgCr₂O₄, and MgO/ $MgCr_2O_4(MgCr_3:1)$ were estimated to be +2.91, +0.81, and +1.61 V, respectively. Generally, the Fermi level is assumed to be present at 0.1 eV below the CB of n-type semiconductor and 0.1 eV above the VB of p-type semiconductor.⁶ Therefore, the respective Fermi level positions of MgO, MgCr₂O₄, and MgO/MgCr₂O₄(MgCr3:1) were estimated to be -0.5, -0.8, and -1.0 V vs Ag/AgCl, respectively.

Impedance Study. Electrochemical impedance study (EIS) or Nyquist diagram has been proven to be a significant tool for the investigation of the charge carrier separation and transfer process across the electrode and electrolyte interface in a three electrochemical workstation.^{65,68} Nyquist plots of the MgO, MgCr₂O₄, and MgO/MgCr₂O₄(MgCr₃:1) as prepared electrodes are shown in Figure 9a. The radii of the semicircles in Nyquist plot are used for the analysis of charge transfer resistance across the electrode/electrolyte interface. The equivalence fitted model circuit for the MgO/ $MgCr_2O_4(MgCr_3:1)$ electrode is shown in the inset of Figure 9a. The arc in the EIS spectra is ascribed to the contribution of charge transfer resistance (R_{ct}) and the constant phase element.⁶⁵ The inclined line corresponds to the ion diffusion process in the electrolyte in accordance with the Warburg impedance (Z_w) .⁶⁵ The reduced diameter of the arc radius represents the faster transportation and separation efficiency of the charge carrier, while the enlarged diameter of the arc radius represents the highest resistivity with faster recombination of electron-hole pairs. These Nyquist plots clearly indicate the reduced diameter of the arc radius of MgO/ $MgCr_2O_4(MgCr_3:1)$ than other as prepared electrodes, which reveals the faster interfacial charge transportation and separation efficiency of MgO/MgCr₂O₄(MgCr3:1). In accordance with the fitted model value (Figure 9a), markedly reduced arc diameter (R_{ct} = 44.6 Ω) was found for MgO/MgCr₂O₄ (MgCr3:1) than MgO ($R_{ct} = 60.0 \Omega$) and MgCr₂O₄ (52.3 Ω) materials. The largest arc diameter of MgO followed by MgCr₂O₄ reveals the faradic process of the charge transfer electrode that relates to interfacial charge transfer resistance with poor electrical conductivity. However, the reduced arc diameter of MgO/MgCr₂O₄ (MgCr3:1) discloses the formation of n-n type heterojunctions, which stimulates charge



Figure 8. Mott-Schottky plot of (a) MgO, (b) MgCr₂O₄, and (c) MgO/MgCr₂O₄(MgCr 3:1) nanocomposites.



Figure 9. (a) EIS and (b) Bode phase plot of MgO, MgCr₂O₄, and MgO/MgCr₂O₄ (MgCr3:1) nanocomposites.

transfer kinetics across the interfacial contact area of heterojunctions. The results of EIS spectra demonstrate that the creation of novel n–n type heterojunctions in MgO/MgCr₂O₄(MgCr3:1) is advantageous for enhancing the charge separation and transfer efficiency of carriers with decreasing charge transfer resistance and simultaneously improving the photocatalytic H₂ production activity through the water splitting process.⁶⁸

Bode phase plots in Figure 9b show a much larger peak intensity value for $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposites than those of MgO and $MgCr_2O_4$. The photoinduced

electron lifetimes at the CB of an electrode can be calculated using the equation mentioned below:⁶⁹

$$\tau_n = 1/(2\pi f_{\max}) \tag{5}$$

The shift of the peak from the higher frequency region to lower frequency indicated more a rapid electron transfer process because frequency f_{max} is closely related to the lifetime (τ_n) of the injected electrons. The f_{max} of the MgO/MgCr₂O₄ (MgCr₃:1) electrode $(\tau_n = 2.7 \text{ ms})$ was shorter than that of MgCr₂O₄ $(\tau_n = 2.5 \text{ ms})$ and MgO $(\tau_n = 2.4 \text{ ms})$, suggesting greater lifetime of injected electron and considerably inhibited charge recombination in the MgO/MgCr₂O₄ (MgCr₃:1)



Figure 10. XPS spectra of MgO/MgCr₂O₄ (MgCr3:1) nanocomposite (a) Mg 1s spectrum, (b) Cr 2p spectrum, and (c) O 1s spectrum.

electrode. These processes resulted in enhanced charge separation efficiency and improved photocatalytic and photoelectrochemical properties of $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposites.

XPS Analysis. The surface chemical states of MgO/ MgCr₂O₄(MgCr3:1) nanocomposites were studied by XPS as shown in Figure 10. The XPS result signifies that Mg, Cr, and O elements were present in the MgO/MgCr₂O₄(MgCr₃:1) nanocomposites. Figure 10a shows the relevant binding energy of the Mg 1s peak located at 1303.6 eV.⁷⁰ No metallic Mg 1s peak at 1301.1 eV was found in nanocomposites, which indicates the complete oxidation of the Mg layer to MgO. The Cr 2p XPS spectrum and the corresponding fitting lines of Cr $2p_{3/2}$ and Cr $2p_{1/2}$ regions were displayed in Figure 10b. After refined fitting, the Cr 2p_{3/2} region of the Cr 2p spectrum has been deconvoluted into two distinct peaks located at 579.6 and 576.6 eV, corresponding to Cr^{6+} and Cr^{3+} states, respectively.⁷ Similarly, the Cr $2p_{1/2}$ region of the Cr 2p spectrum has been deconvoluted into two peaks centered at 586.3 and 589.0 eV, respectively.⁷² Interestingly, Cr³⁺ and a modest percentage of $Cr^{\delta+}$ coexisted in MgO/MgCr₂O₄(MgCr3:1) owing to MgCr₂O₄ spinel NPs. The O 1s XPS spectrum of MgO/ MgCr₂O₄(MgCr3:1) shows doublet peaks at 530.6 and 530.6 eV, respectively. The peak located at 530.6 eV is attributed to lattice oxygen associated with metal oxide (M-O).⁷³ and the peak located at 530.6 can be assigned to undercoordinated lattice oxygen (M-O-M), related to the oxygen vacancies in MgO/MgCr₂O₄(MgCr3:1).⁷⁴ The presence of oxygen vacancies in MgO/MgCr₂O₄(MgCr3:1) can be further verified by comparing the Cr 2p XPS spectrum of MgCr₂O₄ in Figure S6. In comparison to the Cr^{6+} peaks of pure MgCr₂O₄ (Figure S6), MgO/MgCr₂O₄(MgCr3:1) samples exhibit positively shifted

binding energy of Cr^{6+} peaks (~0.5 eV), indicating that the electron density around Cr decreases in the hybrid and electrons are transferred to the MgO surface. Alternatively, the binding energy related to Cr^{3+} peaks in MgO/MgCr₂O₄(MgCr3:1) negatively shifted to lower electronvolt (~0.5 to 0.8 eV) in comparison to MgCr₂O₄, implying the formation of oxygen vacancy in MgO/MgCr₂O₄(MgCr3:1) samples.^{73,74} The XPS measurement study reveals that there is an effective nanointerface formation among the constituent MgO nanosheets, and MgCr₂O₄ NPS as electron density around each element significantly changed and formation of surface oxygen defects was the prior factor in the separation of electrons/holes pairs and enhancement of photocatalytic activities.

Photocatalytic H₂ Evolution Study. The photocatalytic activities of MgO, MgCr₂O₄, and MgO/MgCr₂O₄(x) nanocomposites were evaluated for H₂ production under visiblelight irradiation ($\lambda \ge 400$ nm). For H₂ production study, 30 mL of 10 vol % aqueous CH₃OH solutions was added to 0.03 g of powdered photocatalyst and the experiment was continued for 2 h. From the blank experiments, no appreciable evolution of H₂ gas was detected in the absence of either photocatalyst or light, which suggests that H₂ is produced by photocatalytic reduction reaction over the as prepared catalyst. As plotted in Figure 11, the photocatalytic activity of pure MgCr₂O₄ was very low as compared to those of the as prepared MgO/ $MgCr_2O_4(x)$ nanocomposites under visible-light irradiation. However, pure MgCr₂O₄ exhibits a H₂ production rate of 420 μ mol/g/2 h. Interestingly, MgO alone was largely inactive for the reaction and no H₂ was detected, confirming that MgO has no activity for photocatalytic reaction. The pursuance of different molar ratios of both Mg and Cr in MgO/MgCr₂ $O_4(x)$

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Figure 11. Temporal changes of the amount of H_2 evolved (μ mol) with MgO/MgCr₂O₄ (MgCr₃:1) nanocomposite material during the course of irradiation.

nanocomposite was also investigated to optimize the reduction reaction conditions. When the metallic ratio between Mg:Cr = 4:1 i.e. in MgO/MgCr₂O₄(MgCr4:1) nanocomposite, the photocatalytic H₂ production is quite improved (590 μ mol/g/ 2 h) as compared to pure $MgCr_2O_4$ materials. The highest photocatalytic H₂ evolution activity of 840 μ mol/g/2 h was found in MgO/MgCr₂O₄(MgCr3:1) nanocomposite and then decreases to 674 μ mol/g/2 h in MgO/MgCr₂O₄(MgCr2:1) nanocomposite. The trend of photocatalytic H₂ evolution in $MgO/MgCr_2O_4(x)$ nanocomposites obeys the following sequence: MgO/MgCr₂O₄ (MgCr3:1) (840 μ mol g⁻¹ 2 h⁻¹) > $MgO/MgCr_2O_4(MgCr2:1)$ (674 μ mol g⁻¹ 2 h⁻¹) > $MgO/MgCr_2O_4(MgCr4:1)$ (590 μ mol g⁻¹ 2 h⁻¹) > $MgCr_2O_4$ (420 μ mol g⁻¹ 2 h⁻¹). These results indicate that Cr³⁺ in MgCr₂O₄ plays a major role in the H₂ evolution rate due to its large work function for trapping electrons.⁷⁵ Simultaneously, an excessive presence of MgCr₂O₄ NPs in MgO/MgCr₂O₄(MgCr2:1) leads to a decrease in H₂ production. This phenomenon may be owing to the shielding effect induced by excessive MgCr₂O₄ NPs aggregation and reduction in the available metal-support sites where both photoactive metal cation (Cr^{3+} in Mg Cr_2O_4) and support metal cation (Mg²⁺ in MgO) are required for the progress of reaction. As found from TEM results (Figure 6cd), MgO/MgCr₂O₄(MgCr 3:1) nanocomposites consist of MgCr₂O₄ NPs adhered with the sheetlike morphology of MgO matrix. Therefore, an appropriate metallic ratio of Mg:Cr = 3:1 is a key factor for optimum H₂ evolution rate, which can generate a strong interaction between two components, i.e. MgO and MgCr₂O₄, therefore enhancing photocatalytic activities. Table S3 summarizes the state of art for comparison of H₂ production activities over MgO/MgCr₂O₄(MgCr3:1) nanocomposite with the relevant literature reports.

Recyclability Study of MgO/MgCr₂O₄(MgCr3:1) Nanocomposites. The long-term stabilities of MgO/ MgCr₂O₄(MgCr3:1) sample were investigated by performing five successive rounds of photocatalytic H₂ evolution reaction, and the results are shown in Figure S7. After three recycle experiments, the H₂ evolution was not decreased, which indicates the sufficient stability of these materials for H₂ evolution without deactivation. Almost 90% of the original activity was preserved after the end of five repeating cycles over MgO/MgCr₂O₄ (MgCr3:1), and the meager decrease in H₂ evolution was due to the powder loss during the collection process, which shows high stability of MgO/MgCr₂O₄ (MgCr3:1) nanocomposite. XRD patterns (Figure S8) and the TEM image with EDX spectrum (Figure S9) of MgO/ $MgCr_2O_4(MgCr_3:1)$ nanocomposite taken after five successive rounds of catalytic reaction reveals that the phases and morphology remain unaltered even after five repeated cycles of reduction reaction process. In order to further ideal the photocatalytic H₂ evolution experiments of MgO/ MgCr₂O₄(MgCr3:1), physical mixture between MgO and $MgCr_2O_4$ (MgCr3:1) was used to study the rate of H₂ production, and consequently the stability study was executed for two runs (Figure S10). Moreover, Figure S10 depicts that very little change in H₂ evolution rate was detected within the first 2 cycles in the physical mixture sample. These results indicate that an efficient interaction between MgO and MgCr₂O₄ (MgCr3:1) was not formed in the physical mixture by simply grinding using a mortar and pestle. In contrast, efficient interaction can be produced by direct heat treatment of a solvated wet gel of MgCr-LDH in DMF. This illustrates the high chemical stability of $MgO/MgCr_2O_4(MgCr_3:1)$ nanocomposite for clean reusability during photocatalytic H₂ evolution.

Photocatalytic Mechanistic Pathway in the MgO/ $MgCr_2O_4$ (MgCr3:1) System. The photocatalytic H_2 evolution reaction is mainly influenced by the charge transfer process. Generally, photocurrent measurement study reveals the dynamics of interfacial charge transfer and separation in heterojunction materials. To demonstrate the superiority of the architecture in the interfacial charge transfer and separation process, transient photocurrent responses of MgO, MgCr₂O₄, and $MgO/MgCr_2O_4(MgCr_3:1)$ nanocomposite were analyzed by using a linear swift voltammetry (LSV) study as shown in Figure 7. The photocurrent response of n-type MgO and ntype MgCr₂O₄ were performed in a uniform and reproducible manner, whereas n-n type MgO/MgCr₂O₄(MgCr3:1) nanocomposite possesses produced dramatic enhancement in photocurrent response due to the synergistic coupling effect of MgO and MgCr₂O₄, respectively. These results indicated that efficient charge separation and transfer was achieved in MgO/MgCr₂O₄(MgCr3:1), where MgCr₂O₄ NPs act as electron transfer channel to MgO sheets, restraining the reverse transportation of the accumulated electrons on the surface of MgO. Alternatively, the crystalline nature of MgO sheets provides a unidirectional electronic pathway for further electron transport. In addition, the mesoporosity of MgO/ $MgCr_2O_4$ (MgCr3:1) provides a buffer effect to avoid structure collapse of the MgO sheets for high photocatalytic stability and endows a large surface area for diffusion and adsorption of molecules onto the surface of the photocatalyst. The PL emission spectroscopy study is an important probe to reveal the dynamics of photoinduced charge separation and transfer in a heterojunction photocatalyst. As shown in Figure 5, the PL intensity of MgO/MgCr₂O₄(MgCr3:1) was significantly diminished compared to that of MgO and MgCr₂O₄, which demonstrates the much higher charge transfer efficiency of MgO/MgCr₂O₄ (MgCr3:1) nanocomposites. The Nyquist plots of EIS spectra (Figure 9a) clearly indicate the reduced diameter of the arc radius of MgO/MgCr₂O₄ (MgCr3:1) compared to those of the other as prepared electrodes, which reveals the faster interfacial charge transfer and separation efficiency of the MgO/MgCr₂O₄ (MgCr3:1) system. In addition, the lifetime of the photoinduced electron in MgO/ $MgCr_2O_4$ (MgCr3:1) was examined by using Bode phase spectra (Figure 9b). Interestingly, $MgO/MgCr_2O_4$ (MgCr3:1) yields the longest decay time (2.7 ms) as compared to MgO

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(2.4 ms) and MgCr₂O₄ (2.5 ms). This result signifies that charge transfer in MgO/MgCr₂O₄ (MgCr₃:1) can be accelerated by the influence of both MgCr₂O₄ and MgO, respectively.

According to the above discussion, recombination of photoinduced charge carriers has been remarkably reduced by the formation of $MgCr_2O_4$ NPs adhered to porous MgO sheets in $MgO/MgCr_2O_4(MgCr3:1)$ nanocomposite with n-n type heterojunctions interaction. Based on this view, a plausible mechanism of effective H₂ production under visible light irradiation using CH₃OH as electron scavenger and $MgCr_2O_4/MgO(MgCr3:1)$ as photocatalyst was depicted in Scheme 2. Generally, the charge carrier generation and

Scheme 2. Mechanistic Approach toward Photocatalytic H_2 Evolution over MgO/MgCr₂O₄ (MgCr3:1) Nanocomposite



migrations pathways depend on the CB and VB potentials of semiconductor photocatalyst. To derive the exact energy levels of CB and VB potentials of MgO and MgCr₂O₄, we have analyzed both the M-S measurements study (Figure 8) and Kubelka-Monk function (Figure 4) of the as synthesized materials to determine the possibilities for H^+ reduction to H_2 . From the M-S measurements study at 500 Hz frequency, the CB potentials of the MgO and MgCr₂O₄ materials were estimated to be -0.6 and -0.9 V vs Ag/AgCl. From the Kubelka-Munk function, the corresponding band gap energies of MgO and MgCr₂O₄ were estimated to be 3.51 and 1.71 eV, respectively. Furthermore, by analyzing the M-S plot combined with the band gap energy (E_{g}) achieved from the Kubelka-Munk function, the VB edge potential of the MgO and $MgCr_2O_4$ were estimated to be +2.91 and +0.81 V, respectively. As discussed in the M-S plot analysis section, the respective Fermi level positions of MgO and MgCr₂O₄ were estimated to be -0.5 and -0.8 V vs Ag/AgCl, respectively. The M-S plot results also show that the CB potential of MgO/MgCr₂O₄ (MgCr3:1) shifted to more

negative potential of -1.10 V than that of the H⁺/H₂ reduction potential (-0.58 V vs Ag/AgCl),⁵⁴ which leads to higher photocatalytic H₂ evolution efficiency.

Under visible light irradiation, MgCr₂O₄ was excited and produces oscillation of electrons, which decays into an electron-hole pair. MgO as d⁰ oxides tends to be a wideband gap semiconductor material, which was inactive under visible light irradiation with VB maxima composed primarily of O 2p states and CB minima composed of mainly metal dstates.⁷⁶ These d⁰ metal oxides contain fully oxidized transition metal cations, whose d-band is considered to be completely empty. These d⁰ metal oxides have a tendency to form oxygen vacancy (O_v) as defect sites that result in filling of the empty dband and give rise to occupied gap states(Os).⁷⁷ These occupied states push the Fermi level of d⁰ metal oxides very close to the CB and their low-lying CB make them capable of accepting electrons from the CB level of many narrow band gap semiconductors.⁷⁸ After coupling of MgO with MgCr₂O₄, the photoexcited electrons at the CB edge of MgCr₂O₄ can be further transferred to the CB of MgO by the n-n junction induced electric fields, promoting the separation of photogenerated electrons and holes in MgCr₂O₄. Meanwhile, the formation of the n-n junction causes the up-bending of MgO's energy bands due to filling of occupied gap states (O_s) until the equilibrium Fermi level was formed between MgO and MgCr₂O₄.⁷⁸ The accumulated electrons at the CB of MgO can directly reduce H^+ to H_2 and the holes at VB of MgCr₂O₄ were trapped by sacrificial agent CH₃OH. The MgCr₂O₄ NPs behave as visible light harvester narrow band gap semiconductor, which injects electrons to the CB of MgO and the hybrid MgO/MgCr₂O₄ (MgCr3:1) nanocomposite behaves as visible light active photocatalyst. Therefore, the role of MgO as an electron acceptor can extract electrons from MgCr₂O₄, retarding recombination of the electron-hole pair. This strategy promotes separation of electron-hole pair, and higher H_2 evolution rate was achieved in MgO/MgCr₂O₄ (MgCr3:1) nanocomposites.

In brief, the synergistic effect of both MgO and MgCr₂O₄ in enhancing the photocatalytic ability of MgO/MgCr₂O₄ (MgCr3:1) nanocomposites can be ascribed in the following points: (1) The photoinduced electrons migrated from $MgCr_2O_4$ NPs to MgO sheets, which act as an electron conductive platform that can effectively improve the separation efficiency of the electron-hole pair. (2) As MgO and MgCr₂O₄ both grow in the cubic crystal phase with closely matching lattice, n-n type heterojunctions and the formation of Schottky junction would be preferred in MgO/MgCr₂O₄ (MgCr3:1), which enables tunable band offset engineering for further migration of electrons from $MgCr_2O_4$ to MgO. (3) The surface defects formed in MgO/MgCr₂O₄ (MgCr3:1) due to interstitial oxygen vacancies (O_v) of porous MgO sheets, which behave as an electron trapping site to retard the electron-hole recombination process. $(\bar{4})$ The presence of Cr³⁺ ions plays an important role in MgCr₂O₄ toward visible light absorption behavior and photocatalytic H₂ evolution. On visible light irradiation, electrons get excited from O-2p to Cr-3d orbital due to LMCT and the d–d transition from $3d{-}t_{2g}\rightarrow 3d{-}e_g$ due to higher energy level of empty Cr-3d-eg orbital. The potential of the $Cr-3d-t_{2g}$ band lies just below the H^+/H_2 reduction potential, making $MgCr_2O_4$ as H_2 evolution catalyst with effective visible light harvestation ability. (5) The surface area of MgO/MgCr₂O₄ (MgCr3:1) nanocomposite was found to be maximum under low temperature heat treatment.

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Generally, high specific surface area favors the generation of electron-hole pairs to carry out a photochemical reaction with proper distribution of pores, which facilitate the movement and diffusion of photoinduced charge carriers. Finally in accordance to Scheme 2 the results and discussion part have demonstrated that $MgCr_2O_4$ NPs can efficiently store the photoinduced electrons and drive toward MgO sheets, which become easily available to drive the photocatalytic H_2 evolution process. Therefore, the synergistic catalytic effect of both MgO sheets with $MgCr_2O_4$ NPs and establishment of n-n heterojunctions charge transfer channels play a key role in enhancement of practically photocatalytic H_2 evolution activity of $MgO/MgCr_2O_4$ (MgCr3:1) nanocomposite under visible light irradiation.

CONCLUSIONS

In summary, the synthetic approach highlighted herein provides an access to porous MgO/MgCr₂O₄ (x) nanocomposite composed of crystalline spinel MgCr₂O₄ NPs and 2D MgO sheets. The obtained MgO/MgCr₂ $O_4(x)$ nanocomposite exhibit remarkably enhanced photocatalytic H₂ evolution activity as benefited from its high surface area, wide light-harvesting ability, and higher carrier separation ability. Among these as synthesized materials, MgO/MgCr₂O₄ (MgCr3:1) nanocomposite exhibits the highest H₂ production rate of 840 μ mol/g/2 h, which was 2 times higher than MgCr₂O₄ (420 μ mol/g/2 h). The enhanced photocatalytic activity and effective charge separation of MgO/ MgCr₂O₄(MgCr3:1) nanocomposite can be explained by the following points: (1) The photoinduced electrons migrated from MgCr₂O₄ NPs to MgO sheets, which act as an electron conductive platform that can effectively improve the separation efficiency of the electron-hole pair. (2) The formation of Schottky junction and interstitial oxygen vacancies of porous MgO sheets as surface defects in MgO/MgCr₂O₄(MgCr3:1) behaves as an electron trapping site to retard the electron-hole recombination process. (3) As MgO and MgCr₂O₄ both grow in the cubic crystal phase with closely matching lattice, n-n type heterojunctions growth would be preferred, which enables tunable band offset engineering in MgO/MgCr₂O₄ (MgCr3:1) heterojunctions nanocomposite. (4) The maximum surface area of MgO/MgCr₂O₄(MgCr3:1) nanocomposite (290 m^2/g) under low temperature heat treatment and the presence of Cr^{3+} ions in MgCr₂O₄ play an important role toward visible light absorption behavior and photocatalytic H₂ evolution. Furthermore, MgO/MgCr₂O₄ (MgCr3:1) nanocomposite catalyst possesses high stability and reusability for photocatalytic H₂ evolution without any decay and can be reused at least five consecutive runs without appreciable loss. This work is of great importance and provides a promising strategy to construct highly efficient heterojunctions nanocomposite with intimate contact for solar energy conversion as well as technological transfer in many other fields of materials chemistry related to metal oxide and spinel type chromites being used for studying the role of particle anisotropy.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b01517.

Band gap of MgO, MgCr₂O₄, and MgO/MgCr₂O₄ (MgCr3:1) (Figure S1), TEM and SAED pattern of MgCr-LDH (Figure S2), HAADF-STEM image and elemental mapping of MgO/MgCr₂O₄ (MgCr3:1) (Figure S3), EDX of $MgO/MgCr_2O_4$ (MgCr3:1) (Figure S4), TEM and SAED pattern of MgO/ MgCr₂O₄ (MgCr2:1) and MgO/MgCr₂O₄ (MgCr4:1) nanocomposite (Figure S5), XPS spectra of Cr 2p in $MgCr_2O_4$ (Figure S6), reusability study of H₂ evolution over MgO/MgCr₂O₄ (MgCr3:1) (Figure S7), XRD patterns of MgO/MgCr₂O₄ (MgCr 3:1) before and after H₂ evolution (Figure S8), TEM and EDX spectrum of MgO/MgCr₂O₄(MgCr3:1) after H₂ evolution (Figure S9), H₂ evolution rate and stability test by physical mixtures of MgO and MgCr₂O₄ in MgO/MgCr₂O₄ (MgCr 3:1) (Figure S10), Tables describe the crystal structures (Table S1), LSV measurement (Table S2), and comparison of H₂ evolution with other materials (Table S3) (PDF)

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Notes

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