ABSTRACT: Cr-doped SnO₂ nanostructures with a dopant concentration ranging from 1 to 5% have been successfully prepared using low-temperature modified solvothermal synthesis. The as-prepared nanoparticles showed a rutile tetragonal structure with a rough undefined morphology having no other elemental impurities. The particle shape and size, band gap, and specific surface area of the samples were investigated by scanning electron microscopy, transmission electron microscopy (TEM), high-resolution TEM, UV–visible diffused reflectance spectroscopy, and Brunauer–Emmett–Teller surface area studies. The optical band gap was found in the range of 3.23–3.67 eV and the specific surface area was in the range of 108–225 m²/g, which contributes to the significantly enhanced photocatalytic and electrochemical performance. Photocatalytic H₂ generation of as-prepared Cr-doped SnO₂ nanostructures showed improved effect of the increasing dopant concentration with narrowing of the band gap. Electrochemical water-splitting studies also stressed upon the superiority of Cr-doped SnO₂ nanostructures over pristine SnO₂ toward hydrogen evolution reaction and oxygen evolution reaction responses.

1. INTRODUCTION

Ever since the rise of industrial revolution, the planet has been subjected to extremities of environmental deterioration that have been caused by human activities. One of the most recent off-shoot of the environmental deterioration is global warming¹–⁶ which has compelled researchers to come up with sustainable sources of energy such as hydrogen generation by sustainable routes such as photocatalytic and electrocatalytic water splitting.⁷–¹⁴ In order to produce hydrogen by means of photo- and electrocatalyses, a catalytic system is required which should possess remarkable optoelectronic properties along with advanced thermal and chemical stabilities since such processes involve transfer of charged carriers (e⁻–h⁺ pairs).¹⁵–²⁰ Owing to the extraordinary optoelectronic and chemical properties of metal-oxide nanostructures such as TiO₂, In₂O₃, RuO₂, and SnO₂,²¹,²² their usage in photocatalytic applications is increased and these materials have become active thrust areas to pursue photocatalytic water splitting for hydrogen evolution. However, the band energy of metal-oxide nanostructures usually lies in the range of 3–3.5 eV which inhibits their photocatalytic response in the visible light region. Incorporation of a metal ion in the metal-oxide semiconductor enhances its photocatalytic activity as the desired defects are introduced in the interstitial sites of metal-oxide nanostructures which lead to band gap tunability, and therefore, the metal ion-doped metal-oxide nanostructures also show photocatalytic activity in the visible region.²³–²⁶

Since the last decade, tin dioxide (SnO₂) has sought the curiosity of researchers due to its marvelous optoelectronic properties, inherent p-type conductivity, high charge carrier density, and optical transmittance, and band gap tailoring of its wide band gap on the introduction of a metallic dopant shows its capability toward gas sensing and photocatalytic water splitting.²⁷,²⁸ In addition to that, the electrochemical and structural stabilities of SnO₂ and its enhanced electrical conductivity make it suitable for electrocatalytic water splitting.²⁹–³⁴ Wide band gap semiconductors are promising materials in terms of photocatalytic and electrocatalytic activities in water splitting hydrogen generation owing to their excep-
The charge-transfer mechanism in transition-metal ion-doped SnO₂ is predominantly governed by the chemical and electronic nature of the dopant and its concentration. Even a very small fraction of the dopant (~1%) can efficiently lead to the reduction of the recombination rate of SnO₂. Cr-doped SnO₂ is the unique catalytic system as the ionic radii of Cr³⁺ and Sn⁴⁺ are close to each other, and therefore Cr³⁺ ion can comfortably replace the Sn⁴⁺ and occupy the lattice sites in SnO₂. The interfacial charge transfer between Cr³⁺ and SnO₂ can efficiently enhance both its photo- and electrocatalytic responses. The conductivity of Cr-doped SnO₂ can be matchable to that of indium-doped tin dioxide (ITO) owing to which the latter has extensive applications. However, the usage of ITO is not so visionary due to scarcity of indium. Therefore, Cr-doped SnO₂ has the potential to replace ITO, and its photo- or electrocatalytic activity, owing to which SnO₂ is predominantly governed by the shape and size of the as-synthesized pure SnO₂ and Cr-doped SnO₂ nanoparticles studied. Fabricating semiconductor metal oxides for their band gap tuning is of great significance in the photocatalytic H₂ generation to transform UV-light active catalysts into visible light-driven catalysts. Hence, the thought process behind this study is to exploit the Cr-doped SnO₂ nanoparticles in the production of hydrogen via photocatalytic and electrocatalytic water splitting. In the current study, we have fabricated pristine SnO₂ and different compositions of Cr-doped SnO₂ by the economical and environmentally viable low-temperature solvothermal route. Structural, morphological, and optical studies were conducted by means of X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy-dispersive X-ray spectroscopy (EDAX), transmission electron microscopy (TEM), high-resolution TEM (HRTEM), selected area electron diffraction (SAED), UV-visible diffuse reflectance spectroscopy (DRS), and Brunauer–Emmett–Teller (BET) surface area. The photocatalytic and electrocatalytic water-splitting experiments were performed to determine the quantitative and qualitative rates of hydrogen evolution.

2. EXPERIMENTAL SECTION

2.1. Materials Required. All chemicals used, including tin chloride (SnCl₂, Merck, 97%), sodium hydroxide (NaOH, Merck, 97%), chromium acetate (C₆H₁₀O₆CrO₄, Sigma-Aldrich, 99.99%), ethanol (C₂H₅OH, Merck, 99.9%), and double distilled water, were of analytical grade and were used without any further purification.

2.2. Synthesis of Pure SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂ Nanoparticles. Pure SnO₂ nanoparticles were synthesized through a modified solvothermal route using the solvent refluxing assembly. In this method, 0.1 M NaOH solution was prepared in a 50 mL volumetric flask. 25 mL of 0.1 M SnCl₂ solution in ethanol as a solvent was prepared, and it was taken in a round-bottom (RB) flask which was placed in the silicon oil bath. The modified solvothermal refluxing setup was placed on a magnetic stirrer, and the entire solution was stirred for 15 min to obtain a homogeneous solution. To this solution, 50 mL of NaOH solution was slowly added dropwise which acts as a precipitating agent. The mixtures were allowed to reflux for 4 h at 150 °C. To maintain a uniform temperature, a thermometer was placed in the silicon oil bath. Then, the solution was allowed to cool down naturally to room temperature. The as-obtained product was then centrifuged with double distilled water followed by ethanol. The precipitate was then dried in a vacuum oven overnight at 60 °C. The as-obtained final product was then ground for further characterization.

For the preparation of three different compositions, three solutions of SnCl₂ (0.1 M), NaOH (0.1 M), and Cr(OAc)₂(X), where X = 0.001, 0.0025, and 0.005 M are the molar concentrations of Cr³⁺ salt for 1, 2.5, and 5% Cr-doped SnO₂ nanoparticles, respectively, were used. To get 1, 2.5, and 5% Cr-doped SnO₂ nanoparticles, 25 mL of SnCl₂, 25 mL of Cr(OAc)₂ of respective concentration, and 50 mL of NaOH solutions were mixed in the RB flask, and the same process discussed above was followed. The resulting solutions were then centrifuged and washed with distilled water and ethanol several times to remove all dissolved impurities. The precipitate was then dried in a vacuum oven at 60 °C for overnight. The powders were then finally ground for structural characterization.

2.3. Characterizations. To analyze the crystal structure, phase composition, crystallinity, and purity, powder XRD technique on a D/Max 2500 diffractometer with a scan rate of 5°/min having Cu Kα radiation (1.5406 Å) in the 2θ range of 20–80° was carried out for as-prepared samples. FESEM studies were performed with the help of a Nova Nano SEM-450 microscope operating at an accelerating voltage of 20 kV. To carry out the FESEM studies, a dry sample was mounted on a carbon tape coated with an ultrathin layer of gold to prevent the surface charging effect. The shape and size of the as-synthesized pure SnO₂ and Cr-doped SnO₂ nanoparticles investigated by TEM and HRTEM on a TELOS HRTEM operating at an accelerating voltage of 200 kV. UV-visible DR spectrophotometer was carried out by using a PerkinElmer Lambda 365 spectrophotometer in the wavelength range of 200–800 nm. The band gap and absorption maximum spectrum of the samples were calculated from the measured DR spectra. A Nova 2000e BET surface area analyzer supplied by Quantachrome Instruments Limited, USA was employed to determine the surface area and pore size distribution of the as-synthesized nanoparticles by using the nitrogen adsorption–desorption measurements through the multipoint BET equation.

2.4. Photocatalytic Hydrogen Evolution Measurements. The photocatalytic response of pristine SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂ nanostructures was evaluated by investigating their functioning toward photocatalytic water splitting to evolve H₂ efficiently. The photocatalytic studies were examined in ambient conditions in a typical photoreactor that consisted of a specialized sample cell with a cylindrical neck dedicated for the air-tight rubber septum. 20 mg of photocatalyst along with the equimolar Na₂SO₃ and Na₂S were dispersed in 50 mL of water and stirred for 25–30 min in the nitrogen atmosphere in order to provide inertial condition and to eliminate the dissolved oxygen. Na₂SO₃ and Na₂S were employed as the sacrificial agents as electron donor sites during the photocatalytic hydrogen production. After N₂ purging, the photoreactor was exposed to the light source (200 W, Hg–Xe arc lamp, Newport) whose irradiance intensity was 252.7 mW/cm², situated 7 cm away from the dedicated magnetic stirrer on
which the sample cell was placed. The quantitative hydrogen production was evaluated by sampling the gas out of the photoreactor via a specialized air-tight syringe in 1 h time interval. The evolved hydrogen gas was examined in a gas chromatography setup (PerkinElmer, Clarus 590 GC) endowed with a thermal conductivity detector using N₂ as the carrier gas. The duration of photocatalytic reaction was extended as far as 8 h to analyze the stability of photogenerated electron–hole pairs in terms of their photocatalytic response. Furthermore, the recyclability experiments were carried out up to three cycles to verify the stability and reusability of the photocatalyst in the water-splitting studies. The catalyst was recovered from the reaction mixture through centrifugation and then washed with ethanol, centrifuged, dried, and reused for further studies.

2.5. Electrode Preparation and Electrocatalytic Measurements. Prior to the electrocatalytic analysis of pristine SnO₂ and 1, 2.5 and 5% Cr-doped SnO₂ nanostructures, individual working electrodes were prepared by depositing the as-prepared electrocatalyst on pretreated ITO, which provided the conductive support to the fabricated working electrodes. The ITO substrates (dimensions 1 × 1 cm²) were pretreated to clean it from the oxide layer by sonicatoring with acetone, ethanol, and isopropanol. The electrocatalyst was prepared by mixing 2–2.5 mg of the nanostructures with 10 µL of Nafion and 200–300 µL of isopropanol after which it was deposited on an ITO surface and dried at 60 °C to achieve the working electrodes of pristine SnO₂ and 1, 2.5 and 5% Cr-doped SnO₂. Electrocatalytic response was investigated on the Autolab PGSTAT204 instrument at room temperature with a three-electrode cell assembly in 0.1 N KOH solution toward oxygen evolution reaction (OER) activity and in 0.5 N H₂SO₄ solution toward hydrogen evolution reaction (HER) activity. Calomel electrode to analyze the stability of photogenerated electron–hole pairs

3. RESULTS AND DISCUSSION

3.1. XRD Analysis. The as-synthesized nanoparticles were analyzed for the XRD studies to reveal the information regarding phase purity, phase composition, and crystallinity. Figure 1 shows the XRD patterns of pure SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂. The major and intense XRD peaks of the pure SnO₂ could be matched with the JCPDS card no. 78-1063 with a rutile tetragonal phase structure. From the XRD patterns, as shown in Figure 1, the broadening and slight shifting of the diffraction peaks were observed which demonstrates the successful doping, and associated with that, Sn ions were successfully substituted by the Cr ions into the host lattice of SnO₂. Furthermore, the peak intensity decreases with the increase in the concentration of Cr, reflecting the incorporation of Cr in the SnO₂ host matrix. This phenomenon is also associated with the crystallinity growth of the SnO₂ nanostructures which is purely dependent on the dopant concentration. Due to the small ionic size radius of Cr³⁺ (0.063 nm) ions than Sn⁴⁺ (0.069 nm) ions, there is a decrease in the lattice parameters of the host matrix. The phenomenon of lattice distortion takes place in the host lattice as a result of the difference in the ionic radii of the dopant and the host lattice which consequently leads to the formation of a dopant compressional strain in the host matrix that is also referred to as the lattice contraction in the crystalline structure. The average crystal size of all samples was also determined from XRD studies by using the Scherrer’s equation, and it was found to be 5.64, 1.94, 1.35, and 1.19 nm for pure SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂, respectively.

3.2. FESEM/EDAX Analysis. SEM studies were carried out to study the morphological characteristics of the as-synthesized pure SnO₂ and its 5% Cr-doped SnO₂ nanoparticle aggregates. SEM and EDAX spectra of pure SnO₂ and 5% Cr-doped SnO₂ nanoparticle aggregates are shown in Figure 2. From the SEM analysis, it is revealed that rough and irregular pure SnO₂ nanoparticle aggregates with an undefined morphology are formed (Figure 2a). Furthermore, as the dopant concentration is increased to 5% of the Cr-doped SnO₂, the surface morphology of as-prepared sample changes a bit in texture with more dense constitution of the nanoparticle aggregates as compared to pure SnO₂ as shown in Figure 2c. EDAX spectral studies were also carried out in addition to the SEM studies to determine the elemental composition of the as-synthesized pure SnO₂ and 5% Cr-doped SnO₂ nanoparticle aggregates as shown in Table 1 and 2. The loaded theoretical compositions were found to have a very close agreement with the experimental compositions as estimated using EDAX studies.

3.3. TEM/HRTEM/SAED Analysis. The TEM/HRTEM studies were carried out to study the effect of Cr doping on the particle size and shape of the Cr-doped SnO₂ nanoparticle aggregates. TEM micrographs of pure SnO₂, 1, 2.5, and 5% Cr-doped SnO₂ nanoparticles are shown in Figure 3a–d respectively. The appearance of rough and undefined geometries of agglomerated nanoparticles could be seen clearly, while 5% Cr-doped SnO₂ shows segregated and well-dispersed nanoparticles with comparatively less agglomeration. The TEM images of pure SnO₂, 1, 2.5, and 5% Cr-doped SnO₂ nanoparticle aggregates show that the particle sizes were found to be in the range of 5–30 nm as shown in Figure 3a–d. The smaller nanoparticle aggregates of Cr-doped SnO₂ might be advantageous in the catalytic applications. The SAED images as shown in the inset of Figure 3a–d reveal that all concentric

Figure 1. XRD patterns of pure SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂ nanoparticles.
rings were satisfactorily indexed with the lattice planes of as-synthesized nanoparticle aggregates.

Further, the HRTEM images of pure SnO₂ shows the well-defined lattice fringes separated by an interplanar spacing of 0.335 nm which corresponds to the (112) crystallographic planes of the rutile SnO₂. To further investigate the interior and crystalline structure, the HRTEM studies were also carried out for the doped samples. The apparent lattice fringes of the HRTEM images reveal that the lattice spacings of the adjacent planes for 1, 2.5, and 5% Cr-doped SnO₂ nanoparticles were estimated to be 0.347, 0.333, and 0.344 nm which correspond to the (112) crystallographic plane of the rutile structure of SnO₂ as shown in Figure 4a-d.

3.4. UV–Visible DRS Studies. UV–visible absorption spectroscopy was employed to study the optical properties of pure SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂ nanoparticles as shown in Figure 5a. Kubelka–Munk equation was employed on

Table 1. Elemental Composition of Pure SnO₂

| element | atomic number | series | unn. C [wt %] | norm. C [at. %] | atom. C [at. %] | error (1σ [wt %]) |
|---------|---------------|--------|---------------|----------------|----------------|------------------|
| O       | 8             | K-series | 27.17         | 41.52          | 84.04          | 5.87             |
| Sn      | 50            | L-series | 38.27         | 58.48          | 15.96          | 1.27             |
| total   |               |         | 65.44         | 100            | 100            |                  |

Table 2. Elemental Composition of 5% Cr-Doped SnO₂

| element | atomic number | series | unn. C [wt %] | norm. C [at. %] | atom. C [at. %] | error (1σ [wt %]) |
|---------|---------------|--------|---------------|----------------|----------------|------------------|
| O       | 8             | K-series | 19.10         | 33.59          | 78.69          | 3.68             |
| Sn      | 50            | L-series | 37.27         | 65.56          | 20.70          | 1.17             |
| Cr      | 24            | K-series | 0.48          | 0.84           | 0.61           | 0.07             |
| total   |               |         | 56.84         | 100            | 100            |                  |

Figure 2. (a) SEM image and (b) EDAX spectrum of pure SnO₂ nanoparticles. (c) SEM image and (d) EDAX spectrum of 5% Cr-doped SnO₂ nanoparticle aggregates.

Figure 3. TEM micrographs of as-prepared (a) pure SnO₂ and (b) 1, (c) 2.5, and (d) 5% Cr-doped SnO₂ nanoparticle aggregates. Inset shows the corresponding SAED pattern.
the transmission spectra to calculate the band gap as: $F(R) = \frac{\alpha}{s} = \left(1 - R\right)^2/2R$.

The terms in the above equation like $F(R)$, $\alpha$, $s$, and $R$ denote the Kubelka–Munk function, absorption coefficient, scattering factor, and reflectance of as-synthesized SnO$_2$ and Cr-doped SnO$_2$ nanostructures, respectively. The reflectance spectra depict a shift with an increase in the concentration of Cr which can also be attributed to the interaction between the Cr and SnO$_2$ as also evidenced by the EDAX analysis. The band gap values were calculated using the Kubelka–Munk plot and found to be 3.67, 3.47, 3.27, and 3.23 eV for pure SnO$_2$ and 1, 2.5, and 5% Cr-doped SnO$_2$ nanoparticles, respectively, as shown in Figure 5b, which shows the possibility of their applications in photo- and electrocatalyses.

3.5. BET Analysis. The surface area of a material plays an important role in determining the properties and its potential applications. Therefore, the materials with a large surface area possess a large number of surface-active sites and hence greater catalytic sites which in turn consequently improves the property dependent on the catalytic activity. N$_2$ adsorption–desorption isotherms were considered to determine the BET surface area and porosity of as-synthesized pure SnO$_2$ and 1, 2.5, and 5% Cr-doped SnO$_2$ nanoparticles as shown in Figure 6a. The surface area was found to be 108, 176, 206, and 225 m$^2$/g for pure SnO$_2$ and 1, 2.5 and 5% Cr-doped SnO$_2$ nanoparticles, respectively, by applying the BET equation on the isotherms. The particle size decreased as we increase the doping concentration of Cr in the SnO$_2$ nanoparticles, and hence consequently, the surface area increases. By using the BJH (Barrett–Joyner–Halenda) analysis, the pore size distribution was also determined for pure SnO$_2$ and 1, 2.5 and 5% Cr-doped SnO$_2$ and was found to be 58.93, 18.34, 19.54, and 18.34 Å as shown in Figure 6b, respectively, which reveals the mesoporous nature of the as-synthesized samples. By using Dubinin and Astakov (DA) method, the pore radius of the as-synthesized samples was calculated and found to be 13.4, 12.6, 12.86, and 12.26 Å as shown in Figure 6c for pure SnO$_2$ and 1, 2.5 and 5% Cr-doped SnO$_2$ nanoparticles, respectively.

3.6. Photocatalytic Water-Splitting Studies. The photocatalytic hydrogen evolution response of pristine SnO$_2$ and 1, 2.5 and 5% Cr-doped SnO$_2$ nanostructures is illustrated in Figure 7a. 5% Cr-doped SnO$_2$ photocatalyst shows optimum photocatalytic activity by producing 11.74 mmol/gcat H$_2$ in a time span of 8 h followed by 2.5, 1% Cr-doped SnO$_2$, and pristine SnO$_2$ photocatalysts which exhibited 9.02, 8.37, and 8.22 mmol/gcat H$_2$. The photocatalytic activity of 5% Cr$^{3+}$-doped SnO$_2$ photocatalyst was found to be almost 1.43-fold higher than that of pristine SnO$_2$ photocatalyst. Enhancement in the photocatalytic activity of Cr$^{3+}$-doped SnO$_2$ photocatalysts is attributed to the lowering of pristine SnO$_2$ band energy on incorporating the Cr$^{3+}$ which expanded the photocatalytic scope of SnO$_2$ as its range of illumination extended from the UV to visible light region. On increasing the Cr$^{3+}$ dopant concentration in the SnO$_2$ lattice, more number of Cr$^{3+}$ replaced Sn$^{4+}$ ions due to their near analogous ionic radii which resulted in augmented interfacial charge transfer. The tailoring of band gap and the improvement in interfacial charge transfer lead to advancement in the photocatalytic activity of Cr$^{3+}$-doped SnO$_2$ photocatalysts. BET studies also manifested the increase in the surface area of SnO$_2$ on increasing the Cr$^{3+}$ concentration. This explains the superior photocatalytic response of 5% Cr$^{3+}$-doped SnO$_2$ photocatalyst as owing to its highest surface area, there were more active sites available for photocatalytic reaction. As depicted in Figure 7c, 5% Cr-doped SnO$_2$ photocatalyst generated H$_2$ at a marvelous rate of 1.47 mmol/gcat/h, which is much superior to the previous report on a similar Ag-doped SnO$_2$ system. The as-synthesized photocatalyst was then employed for the reproducibility experiments to determine the stability and reusability determination with 8 h reaction time of each cycle. The gas chromatography analyzer was used to check the H$_2$ gas evolved. The stability and reusability for the rate of hydrogen production and the performance of the catalyst were...
checked for three consecutive cycles as shown in Figure 7d. It was deduced from the results that the amount of hydrogen evolution in the first cycle was 11.74 which then subsequently showed a decrease up to the third cycle with a value of 11.42 mmol/gcat.

3.7. Electrocatalytic Water Splitting Studies. The electrocatalytic activity of pristine SnO₂, 1, 2.5, and 5% Cr-doped SnO₂ nanostructures was evaluated toward electrocatalytic water splitting in order to determine their respective HER and OER electrodic parameters and responses.50,51 HER response of pure SnO₂ and 1, 2.5 and 5% Cr-doped SnO₂ was examined in 0.5 N H₂SO₄ electrolytic solution as demonstrated in Figure 8a which revealed the LSV plots of the pristine SnO₂ and 1, 2.5 and 5% Cr³⁺-doped SnO₂ toward HER activity. On increasing the concentration of Cr³⁺ in the SnO₂ lattice, the polarization curve revealed the decreasing trend of overpotential needed to escalate the cathode current density of 10 mA/cm². Thus, the incorporation of Cr ³⁺ in SnO₂ enhanced its electrocatalytic response. The overpotential values of SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂ were estimated to be 1.38, 1.31, 1.29, and 1.24 V, respectively. It implies that 5% Cr-doped SnO₂ exhibited optimum electrocatalytic response toward HER.

The CV plot of 5% Cr-doped SnO₂ electrocatalyst for HER activity was examined till 150 cycles in order to monitor its durability and stability as depicted in Figure 8b. The CV plots of pristine SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂ for HER activity are shown in the inset of Figure 8b. The OER activity of as-synthesized nanostructures was evaluated in 0.1 N KOH electrolytic solution. The LSV plots toward OER are shown in Figure 8c which indicate the generation of anodic current density at the applied potential window. 5% Cr-doped SnO₂ nanostructures have shown the most superior electrocatalytic activity toward OER with an onset potential of around 1.01 V; there onward, increment in its anodic current density was detected and yielded 1.08 mA/cm² at 1.5 V overpotential. The obtained onset potential of 5% Cr-doped SnO₂ nanostructures was found to be in vicinity to the onset potential of IrO₂ electrocatalyst which is the flag-bearer of electrocatalytic water splitting for oxygen production. The long-term stability of 5% Cr-doped SnO₂ nanostructures was examined by analyzing its CV plot until 150 cycles as shown in Figure 8d. The CV plots of pristine SnO₂ and 1, 2.5, and 5% Cr³⁺-doped SnO₂ toward OER activity are depicted in the inset of Figure 8d. The reaction kinetics and mechanism for electrocatalytic HER and OER responses were studied by utilizing the Tafel equation.52–55 Figure 8e,f illustrates the Tafel plots of pristine SnO₂ and 1, 2.5, and 5% Cr-doped SnO₂ toward HER and OER, respectively. The estimated HER and OER electrocortic parameters are depicted in Table 3. The CV plots of the optimum HER and OER electrocatalyst (5% Cr-doped SnO₂) were investigated at different scan rates varying from 20 to 100 mV/s to monitor their cyclic stability and diminution in resistance on increasing the applied potential window as shown in Figure 8g,h.

3.8. Mechanistic Pathway for Hydrogen Evolution. Plausible mechanistic pathway is propounded to comprehend the photocatalytic hydrogen evolution by the utilization of Cr-doped SnO₂ photocatalytic system as revealed in Figure 9. The tailoring of Cr-doped SnO₂ band gap expanded its spectral response region where the e⁻−h⁺ pairs originated in the UV-visible region and escalated the electron transfer rate which facilitated the reduction of H⁺ ions to generate H₂ effectively. Due to the analogy in the ionic radii of Cr³⁺ and Sn⁴⁺ ions, the increase in the Cr³⁺ ion concentration resulted in more substitution of Sn⁴⁺ interstitial sites which implies the advancement in the interfacial charge transfer of the Cr-doped SnO₂ photocatalytic system. The charge transfer depends majorly on the contact area between Cr³⁺ ions and SnO₂, and since the surface area of 5% Cr-doped SnO₂ photocatalyst was maximum, it exhibited remarkable charge transfer which ultimately resulted in its exceptional photocatalytic response during water splitting. The contact between metal—metal oxide system having different work functions results in the formation of Schottky barriers which gushes the electrons to create new Fermi energy levels until equilibrium establishes between the metal and metal oxide, because of which a built-in electric field is generated near the contact area of the metal and the metal-oxide interface.49,52–54 This phenomenon is reciprocated in the Cr-doped SnO₂.
photocatalytic system due to which it has shown excellent photocatalytic activity.

4. CONCLUSIONS

Monophasic, rutile tetragonal structure of pure and Cr-doped SnO$_2$ nanostructures have been successfully synthesized through the simple and modified solvothermal route. The particle size, shape, and structural characteristics were investigated through FESEM, EDAX, TEM, HRTEM, and SAED studies. The band gap values obtained through UV-visible DRS analysis were 3.67, 3.47, 3.27, and 3.23 eV for pure SnO$_2$ and 1, 2.5, and 5% Cr-doped SnO$_2$ nanoparticles, respectively. BET surface area studies revealed high specific surface areas of 108, 176, 206, and 225 m$^2$/g for pure and Cr-doped SnO$_2$ nanostructures, respectively. The enhancement in the hydrogen evolution during photocatalytic water splitting studies was obtained due to the synergistic effect of doping. Among all as-prepared nanomaterials, 5% Cr-doped SnO$_2$ nanoparticles exhibited the highest photocatalytic H$_2$ production rate (11.74 mmol/gcat), which is almost 1.43-fold higher than that of pure SnO$_2$ nanostructures. The electrocatalytic water-splitting studies of as-synthesized nanostructures revealed that 5% Cr-doped SnO$_2$ exhibited optimum electrocatalytic response toward HER and OER by yielding 1.24 V overpotential.

Figure 7. (a) Photocatalytic H$_2$ evolution as a function of the irradiation time, (b) comparison of photocatalytic activity, (c) average H$_2$ evolution per hour of the pure SnO$_2$ and 1, 2.5, and 5% Cr-doped SnO$_2$ nanoparticles, and (d) stability and reusability tests of the 5% Cr-doped SnO$_2$ for up to three cycles.
at 10 mA/cm² cathodic current density and by generating 1.08 mA/cm² anodic current density at 1.5 V overpotential, respectively. The synergistic photo- and electrocatalytic water splitting makes Cr-doped SnO₂ nanoparticles the potential

**Figure 8.** (a,b) shows the LSV and CV plots toward HER, (c) and (d) shows the LSV and CV plots toward OER, (e,f) shows HER and OER Tafel plots of pure and Cr-doped SnO₂, and (g,h) shows the CV plots of 5% Cr-doped SnO₂ toward HER and OER at different scan rates.

**Table 3.** HER and OER Electrodic Parameters of Pure and Cr-Doped SnO₂ Nanostructures

| s. no. | electrocatalyst | HER | OER |
|-------|----------------|-----|-----|
|       | overpotential (V) to attain 10 mA/cm² | Tafel plot (mV/dec) | onset potential at 1.5 V (mA/cm²) | Tafel plot (mV/dec) |
| 1     | SnO₂           | 1.38 | 223.92 | 0.32 | 76.77 |
| 2     | 1% Cr-SnO₂     | 1.31 | 145.49 | 0.10 | 81.80 |
| 3     | 2.5% Cr-SnO₂   | 1.29 | 129.56 | 0.50 | 94.91 |
| 4     | 5% Cr-SnO₂     | 1.24 | 54.82  | 1.08 | 66.31 |

Figure 9. Schematic mechanism of the photocatalytic water splitting for H₂ generation.
candidate for renewable energy resource in industrial applications.

**AUTHOR INFORMATION**

Corresponding Author

Tokeer Ahmad – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India; orcid.org/0000-0002-7807-315X; Phone: 91-11-26981717 extn 3261; Email: tahmad3@jmi.ac.in

**Authors**

Sapan K. Jain – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Mohd Fazil – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Nayeem Ahmad Pandit – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Syed Asim Ali – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Farha Naaz – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Huma Khan – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India

Amir Mehtab – Nanochemistry Laboratory, Department of Chemistry, Jamia Millia Islamia, New Delhi 110025, India; Department of Chemistry, Texas A&M University, College Station, Texas 77843-3255, United States

Jahangeer Ahmed – Department of Chemistry, College of Science, King Saud University, Riyadh 11451, Saudi Arabia; orcid.org/0000-0003-2331-6406

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c00707

**NOTES**

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