Synthesis and Characterization of Various Doped TiO₂ Nanocrystals for Dye-Sensitized Solar Cells

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ABSTRACT: Few works are reported on solvothermal preparation of nanoparticles by utilizing acetone alone without a surfactant. This synthesis approach is found to be prominent for producing the mesoporous structure, which is crucial in improving the dye loading of the photoanode. In addition, doping of metal ions is advantageous in order to bring down the excitation energy, which is promising for boosting the performance of the doped oxides. This research aims to synthesize various kinds of doped-TiO₂ nanocrystals to serve as photoanode materials in dye-sensitized solar cells (DSSCs). An X-ray diffraction study evidenced the existence of the crystalline phase in pure and doped-TiO₂ nanocrystals. Rietveld refinement study showed the mixed phases of crystalline TiO₂ in the CrT, CuNT, and ST as compared to a single anatase phase in the samples PT, AgT, BT, CoT, FeT, SnT, ZT, VT, and ZMT. The absorption spectroscopy analysis demonstrated the reduced optical band gap from 3.10 to 2.79 eV. Scanning electron microscopy investigation endorsed the formation of TiO₂ mesoporous microspheres with a mean diameter ranging from 200 to 331 nm along with a nanocrystal diameter ranging from 10 to 20 nm. Doping with the different dopants enhanced the conversion efficiency of DSSCs from 1.31 to ∼6%. Furthermore, we have performed the electrochemical impedance spectroscopy of DSSCs, and the findings are presented.

1. INTRODUCTION

The titanium dioxide (TiO₂) material is the most demanded one by the scientific community for several applications due to its excellent properties. TiO₂ is the backbone of cost-effective dye-sensitized solar cells (DSSCs) as the photoanode material. In spite of exciting properties of TiO₂, its solar spectrum response is limited (<10%). In addition, the photocatalytic response of TiO₂ is weak, owing to its wide band gap, and also possesses a high charge carrier recombination issue. Therefore, doping of non-metal and metal ions has been intensively investigated to modify the band structure, which enhances the optical properties of TiO₂ for the DSSCs and photocatalytic applications.¹⁻⁴

The main purpose of the doping is to moderate or reduce the optical band gap by introducing the intermediate energy levels in the host TiO₂ so that electron transition could be possible with the low excitation energy. Seo et al. demonstrated the performance of DSSCs based on the photoanode made up of sulfur-doped TiO₂ (S-TiO₂) nanoparticles synthesized by the sol–gel route. As a result, the absorption band edge was found to be shifted toward the visible wavelength, indicating the enhanced light absorption. An S-TiO₂ nanoparticle-based solar cell showed improved efficiency, which has been assigned with the increased electron lifetime, as evidenced by the electrochemical impedance spectroscopy (EIS).⁵ In another report, Sun et al. presented the study of DSSCs based on S-TiO₂ nanoparticles prepared by the ball milling of titania nanoparticles. The sulfur doping was confirmed by the photoelectron spectroscopy study, whereas the reduced band gap was attributed to the shifting of the conduction band. The solar cell based on the S-TiO₂ photoanode showed about 24% enhanced efficiency as compared to the un-doped TiO₂-based photoanode.⁶ Arunmetha et al. prepared the S-TiO₂ nanoparticles by varying the sulfur concentration and presented the experimental studies. Upon doping, the crystallite size was found to be decreased. DSSC’s photoanode was fabricated using doped...
titania particles and endorsed the enhancement in the cell efficiency as compared to pure TiO₂ nanoparticle-based solar cells. This improvement was associated with the increased ultraviolet–visible (UV–vis) absorbance and the reduced band gap of 2.8 from 3.25 eV. Pillai et al. synthesized the mesoporous–macroporous S-TiO₂ nanoparticles and studied the various properties. The prepared nanoparticles exhibited different surface morphologies by preparing the mesoporous walls, and with the increased doping concentration, the S-TiO₂ nanoparticles evidenced the extraordinary photocatalytic activity. Avansi et al. presented the synthesis of vanadium-doped TiO₂ (V:TiO₂) nanocrystals by a hydrothermal approach and performed various characterizations. The crystallinity was maintained irrespective of the variation of doping concentration; however, the morphological study revealed the formation of isotropic structures from anisotropic ones. An X-ray absorption spectroscopy evidenced the V doping in the Ti⁴⁺ site, and accordingly, the optical properties were also found influenced by the doping mechanism. Sutrisno et al. reported the preparation of mesoporous V-TiO₂ nanoparticles and investigated the physicochemical characteristics. They performed the Rietveld refinement analysis and fit the X-ray diffraction results in the crystal system with the space group of anatase-TiO₂. The surface area of the nanoparticles was found to be decreased with the rise in doping concentration. In addition, Sacco et al. discussed the importance of catalysts during the sol–gel synthesis of nanoparticles and evaluated the photocatalytic activity. They varied the doping concentration of V and investigated the photocatalytic activity for the elimination of caffeine mixed in water. In the degradation of caffeine, approximately 96% was noticed under UV light beyond the exposure time 360 min. Ahmadi et al. employed the V-TiO₂ nanoparticles for preparing the electron transport layer of the organic photovoltaic cells. The solar cell based on the photoanode film having a thickness of 30 nm endorsed the enhanced conversion efficiency. This enhanced performance can be attributed to the increased light absorption with the rise in external quantum efficiency in the longer wavelength region. Zinc-doped TiO₂ (Zn-TiO₂) nanoparticles are known to be a promising photocatalytic material and possess high electron mobility. Nguyen et al. studied the Zn-TiO₂ nanoparticles by the sol–gel and ammonia evaporation processes and reported the noticeable photoodegradation of methylene blue dye. Pang et al. presented the experimental study of Zn-TiO₂ nanoparticles prepared via the sol–gel route. After treating the nanoparticles with H₂O₂, they reported an improvement in the photocatalytic activity. As compared to a pure TiO₂ sample, the Zn-TiO₂ sample evidenced the phase transformation from anatase to a rutile phase. Further, Zn-TiO₂ treated with H₂O₂ exhibited the better photoodegradation as compared to the untreated sample, which has been attributed to the decreased band gap to a greater extent and the enhanced light absorption in the visible spectrum. Alternatively, Sabbaj et al. utilized the thin film of Zn-TiO₂ to fabricate the room-temperature liquefied petroleum gas sensor. The prepared film endorsed the presence of rutile-TiO₂, while the optical band gap was estimated to be 3.26 eV. The sensor-based on the Zn-TiO₂ film demonstrated a reasonable sensitivity to liquefied petroleum gas. Yu et al. synthesized the Zn-TiO₂ nanoparticles based on different Zn-doping concentrations and sintering temperatures. The role of sintering temperature and the dopant concentration demonstrated the phase transformation of TiO₂ from anatase to rutile. Further, this study explored the doping mechanism of Zn⁵⁺ ions in Zn-TiO₂ nanoparticles. Yuan et al. reported the doping in TiO₂ with various metal ions such as Ag⁺, Al³⁺, Cu²⁺, Fe³⁺, Mn⁷⁺, Ni²⁺, V⁴⁺, and Zn²⁺ and investigated the photocatalytic activity. The strong impact of doping was noticed depending upon the ionic radii, valence state, and the configuration of the dopants. Among the various doped samples, Fe³⁺ doping with a 1% concentration showed the extraordinary photocatalytic activity and enhanced the tolune removal efficiency as much as 71%. Werapun and Pechwang studied the structural, optical, and morphological properties of iron-doped (Fe-TiO₂) nanoparticles prepared by the sol–gel method. The choice of calcination temperatures of 500 and 800 °C yielded the phase transformation from anatase to rutile-TiO₂. The appearance of a brookite phase was noticed from the sample prepared by further increasing the doping concentration. As compared to anatase- and rutile-TiO₂ nanoparticles, the rutile-TiO₂ evidenced an enhancement in the antibacterial activities using Escherichia coli, Bacillus subtilis, and Staphylococcus aureus. Ochoa Rodríguez et al. reported the sol–gel preparation of mesoporous Fe-TiO₂ nanoparticles by varying the concentration of iron. As compared to Fe-TiO₂ samples prepared by using 0.0125, 0.025, 0.1, and 1.0 wt % concentrations, the sample based on the 0.1 wt % concentration showed an improvement in the photocatalytic activity, which was assigned to the reduced optical band gap. Similarly, Moradi et al. prepared the Fe-doped TiO₂ nanoparticles by changing the doping concentration of Fe. Among the various Fe-TiO₂ samples, the sample prepared with the 1 wt % doping concentration demonstrated the extraordinary photodegradation/decolorization of reactive red 198. Alvaro et al. presented the study of copper-doped TiO₂ (Cu-TiO₂) nanoparticles and explored the band gap variation by varying the dopant concentration. The doped TiO₂ nanoparticles size was 27 nm, while the absorption band showed a redshift. The optical band gap was decreased to 1.6 eV with the doping of a 7.5% Cu concentration. Dubey and Singh studied the chromium-doped TiO₂ (Cr-TiO₂) nanoparticles via the solvothermal process and reported the preparation of anatase nanoparticles with their size from 11 to 13 nm. The crystal size varied by changing the Cr concentration, and the redshift of the absorption edge was noticed. Asemi et al. presented the performance of dye-sensitized solar cells by using Cr-TiO₂ nanoparticles prepared by the simple sol–gel route. The optical band gap was found to be reduced to its lowest value for the sample prepared by using a 0.5% doping concentration of Cr. In addition, they prepared the compact layer of the Cr-TiO₂ film before preparing the photoanode. The photovoltaic performance evidenced as much as 110% enhanced efficiency as compared to a device fabricated without a compact layer. In a similar way, Mittal et al. prepared the Cr-TiO₂ nanoparticles via an aqueous route. They performed the photodegradation study of methylene blue by using as-prepared nanoparticles. Reduced photocatalytic activity of Cr-TiO₂ nanoparticles was noticed as compared to pure TiO₂. The unusual result was assigned to the reduced adsorption of dye molecules arisen due to the increased doping concentration of Cr. Park et al. investigated the co-doped TiO₂ nanoparticles with copper (Cu) and nitrogen (N) prepared by the simple sol–gel route for the DSSC application. Cr/N-TiO₂ nanoparticles endorsed the improved light absorption in the visible spectrum. The prepared nanoparticles used as the photoanode material, and the solar cell demonstrated the enhanced conversion efficiency. Liu et al. reported the solvothermal preparation of mesoporous Cu/NT-TiO₂ microspheres. The prepared nanoparticles exhibited an...
increased surface area-to-volume ratio with better light absorption in the visible spectrum and thus demonstrated the improved photocatalytic activity. Likewise, Mathis et al. investigated the photocatalytic activity of Cu/N-TiO2 nanoparticles. To improve the photocatalytic activity, they suggested the preparation of monodisperse microsphere of nanoparticles. The various samples of Cu/N-TiO2, Mn/N-TiO2, and Co/N-TiO2 were prepared and showed enhanced photocatalytic activity. Duane et al. explored the various properties of tin-doped TiO2 (Sn-TiO2) nanocrystals synthesized by the hydrothermal approach and studied the performance of the dye-sensitized solar cell using a photoanode based on Sn-TiO2 nanocrystals. Upon doping with the different Sn concentrations in TiO2, it did not affect the crystallinity. However, the shifting of the XRD peak was noticed, indicating the Sn-ion doping, and finally, the solar cell showed improved conversion efficiency.

In the same way, Bayan et al. investigated the various properties of Sn-TiO2 nanoparticles prepared by the sol-gel process. With the variation of the dopant concentration, they noticed the corresponding change in the phase compositions and phase transitions; however, anatase-TiO2 was found thermally stable and showed the better photocatalytic activity with the nanoparticles obtained with the 5 mol % concentration of Sn. In another study, Mehraz et al. reported the preparation and characterization of tin-doped TiO2 aggregates. They observed the influence of the process temperature and Sn doping concentration over the morphology and the phase transformation of the nanoparticles. Further, Lübbe et al. synthesized the Sn-TiO2 nanoparticles and performed the electrochemical study. By using these as the electrode material, they reported the promising charging and discharging cycles without applying the thermal treatment and conductive coating. Senthil Kumar et al. synthesized and presented the study of Ag-TiO2 nanoparticles for the photo-treatment application. The Ag-TiO2 nanoparticles showed the redshift of the absorption edge, whereas the estimated band gap of 2.74 eV was reported. The prepared sample was employed to study the photocatalytic activity, and the boosted photodegradation was remarked. Zhang et al. reported the preparation of Ag-TiO2 nanoparticles by the hydrothermal approach. They used a polyamide network polymer to overcome the issue of nanoparticle aggregation and obtained the uniform size of the particles. The prepared Ag-TiO2 nanoparticles demonstrated an enhancement in the photocatalytic activity under UV and vis light. As a result, the better stability and repeatability of the photodegradation mechanism were noticed. Similarly, Gaidau et al. reported the electrochemical preparation of Ag- and N-TiO2 nanoparticles by using an electrochemical process. They studied the self-cleaning capability of these nanoparticles; however, co-doped Ag-N-TiO2 nanoparticles strengthened the self-cleaning capability. Vijayalakshmi and Sivaraj employed the barium-doped TiO2 (Ba-TiO2) nanoparticles to study the antibacterial activity. Though the prepared sample was of mixed anatase and rutile phases, it showed an improvement in the antibacterial activity as compared to undoped TiO2. Scarsella et al. presented the investigation of Sr- and Ba-TiO2 nanoparticles prepared by the sol-gel route and studied the photocatalytic activity. The prepared nanoparticles revealed the improved photodegradation of methylene blue under visible light irradiation in comparison to pure TiO2 nanoparticles. Gu et al. preferred the hydrothermal route to prepare the BaTiO3 nanoparticles with the controlled diameter of the nanoparticles. They explored the promising application of the prepared nanoparticles for energy storage device application.

Liu et al. studied the synthesis of zinc–magnesium co-doped TiO2 (Zn-Mg-TiO2) nanoparticles by the hydrothermal process and evaluated the performance of the dye-sensitized solar cell. The conversion efficiency was found to be improved to 27% as compared to the solar cell based on undoped TiO2 nanoparticles. This outcome was attributed to the co-doping, which could yield the positive flat-band shifting and, therefore, the fast carriers transport. Wattanawikram and Pecharapa prepared the Zn-Mn-TiO2 nanoparticles by the sonochemical route. The prepared sample exhibited the single-phase anatase-TiO2 with the formation of spherical and uniform nanoparticles. The use of the co-doped sample evidenced the extraordinary photodegradation of rhodamine B dye with the 10 times faster degradation rate as compared to pure TiO2 nanoparticles. Husain et al. explored the structural and optical analyses of cobalt-doped titanium dioxide (Co-TiO2) nanoparticles synthesized by the sol-gel route. The prepared nanoparticles exhibited the anatase phase and were found to be spherical with their size from 35 to 50 nm. The corresponding shifting of the absorption edge was noticed after decreasing the Co concentration. In addition, the photoluminescence study was performed, which endorsed the emissions at wavelengths 380 and 680 nm. Mugundan et al. investigated the properties of sol-gel-derived Co-TiO2 nanoparticles by varying the dopant concentration. By adopting the annealing temperatures of 500 and 800 °C, they observed the formation of anatase- and rutile-TiO2 nanoparticles, respectively. The prepared nanoparticles demonstrated the new emission sites as noticed by the photoluminescence investigation. Chanda et al. presented the studies of structural and magnetic properties of Co-TiO2 nanoparticles synthesized by the wet-chemical route. They found the preparation of anatase phase of TiO2 nanoparticles with their diameter about 6–10 nm. The doping mechanism of Co was explored by the Raman and XPS spectroscopy investigations. Further, the ferromagnetic and paramagnetic phases were also observed with an increased magnetization induced by the doping mechanism.

The solvothermal method is suitable for preparing the nanomaterials because the precipitates produced by the sol-gel process are amorphous and need calcination at an appropriate temperature. Further, the solvothermal preparation of nanoparticles using acetone as a solvent with no aid of surfactant is less studied. With the solvothermal synthesis, the use of acetone promotes the aldol condensation, which produces water in the presence of metal compounds. The use of acetone yields mesoporous morphology that intends to boost light absorption and thus suitable for photocatalytic and DSSC applications. The critical factors of this improvement are attributed to the increased surface area and many inter-particle scattering impacts.

Significantly less work has been reported on the solvothermal synthesis of titania nanoparticles using acetone as the solvent. The choice of acetone is promising for the growth of mesoporous microsphere of TiO2 nanoparticles. The mesoporous morphology of TiO2 nanoparticles exhibits a better dye loading and thus suitable for DSSCs. In addition, doped TiO2 nanoparticles demonstrate the reduced optical band gap and enables a low-excitation energy for functionalizing the nanomaterials. Taking these points into account, our aim is to prepare the doped TiO2 nanoparticles using different dopants such as tin, iron, chromium, vanadium, zinc, silver, sulfur, barium, cobalt, copper–nitrogen, and zinc–magnesium as the photo-
anode materials of DSSCs. Such a comprehensive study on the synthesis of various doped TiO₂ nanoparticles has not been documented elsewhere together to the best of our knowledge. This paper reports the structural, optical, and morphological properties of various doped TiO₂ nanoparticles and DSSC fabrications. Section 2 presents the materials, synthesis, method and fabrication of DSSCs, while Section 3 explores the experimental results. Finally, Section 4 summarizes the paper.

2. MATERIALS & METHODS
Titanium isopropoxide (TTIP) procured from Sigma-Aldrich was used as the titanium precursor. The acetic acid glacial supplied by SDFine was used as the catalyst, while acetone supplied by CDH, ethanol supplied by CH Fine Chemicals, and de-ionized water were preferred as the solvents. As the source of dopants of tin (Sn), iron (Fe), chromium (Cr), vanadium (V), zinc (Zn), silver (Ag), copper—nitrogen (CuN), magnesium (Mg), sulfur (S), barium (Ba), and cobalt (Co), the precursors stannous chloride, ferrous chloride, chromium acetate, vanadium pentoxide, zinc acetate, silver nitrate, copper nitrate, magnesium acetate, thiourea, barium acetate, and cobalt chloride, respectively, were preferred as procured.

Pure TiO₂ and the various kinds of doped TiO₂ nanoparticles were synthesized by the solvothermal approach. Figure 1 summarizes the synthesis processes. For the sol–gel step, the process starts from the dissolving of the precursor in the solvent under constant stirring for 1 h (i.e., sol–gel process) and then transferring the prepared solution in the Teflon-lined autoclave. For the solvothermal process, the autoclave was kept in the hot-air oven for 5 h at temperature 180 °C.

Hereafter, the samples are named as PT for pure TiO₂, AgT for Ag-TiO₂, BT for Ba-TiO₂, CoT for Co-TiO₂, CrT for Cr-TiO₂, CuNT for CuN-TiO₂, FeT for Fe-TiO₂, SnT for Sn-TiO₂, ZT for Zn-TiO₂, VT for V-TiO₂, ZMT for Zn + Mg-TiO₂, and ST for S-TiO₂.

To prepare PT nanoparticles, 2 mL of TTIP was dissolved in 40 mL of acetone and kept for 1 h stirring. For the solvothermal process, the above solution was transferred in the autoclave and kept for 5 h while maintaining the temperature at 180 °C. For the preparation of the doped samples AgT, BT, CoT, CrT, FeT, SnT, ZT, VT, and ST, 0.5 mol % of silver nitrate, barium acetate, cobalt chloride, chromium acetate, ferrous chloride, stannous chloride, zinc acetate, vanadium pentoxide, and thiourea were respectively mixed in 40 mL of acetone separately and stirred for 30 min. Later, 2 mL of TTIP was added in the above-prepared solutions dropwise and stirred for 1 h. The preferred chemical compositions for the various synthesis processes are listed in Table 1. Similarly, for the preparation of co-doped samples of ZMT, 1 mol % of zinc acetate and 1 mol % of magnesium acetate were dissolved in 40 mL of acetone sequentially, while for the CuNT sample, 10 mL of copper nitrate was directly dissolved in 40 mL of acetone. After mixing 2 mL of the TTIP precursor, each solution was stirred for 1 h. Finally, the prepared solutions were simultaneously transferred in the autoclave for the solvothermal process by maintaining the temperature to 180 °C for 5 h. After this process, each sample was washed in acetone, sonicated, and dried at 80 °C. The prepared samples were examined for the phase and crystallinity using X-ray diffraction (XRD; D8 Advance Bruker AXS, Germany), the surface morphology study using scanning electron microscopy (SEM: Leica Cambridge 440 Microscope, UK), and the optical absorption using UV—visible spectroscopy (UV 1800, Shimadzu, Japan).

The as-prepared pure TiO₂ sample (PT) and doped ones were used to fabricate the DSSC’s photoanodes. According to the standard protocol, pastes of the respective samples were prepared by using a calculated quantity of nanoparticles with the acetic acid, ethyl cellulose, ethanol, and terpineol followed by incubating at 80 °C to get slurries. The fluorine-doped SnO₂ (FTO) glasses of 1 cm² were cleaned before the use. After this, a compact layer of TiO₂ was also prepared by chemical bath deposition, and then respective pastes were rolled on the FTOs by the doctor blade process. After preparing the film, each sample was dried in a hot-air oven for 15 min at the temperature 60 °C and then sintered at 500 °C for 30 min. After soaking photoanodes in ruthenium dye for 18 h, these were rinsed in

| Table 1. Chemical Compositions Used for the Various Synthesis Processes |
|--------------------|-----------------|-----------------|-----------------|-----------------|
| sample            | titanium precursor | dopant concentration | acetone | temperature & time |
| PT                | none             | 40 mL            | 180 °C/5 h     |
| AgT               | 0.5 mol % silver nitrate | 40 mL | 180 °C/5 h     |
| BT                | 0.5 mol % barium acetate | 40 mL | 180 °C/5 h     |
| CoT               | 0.5 mol % cobalt chloride | 40 mL | 180 °C/5 h     |
| CrT               | 0.5 mol % chromium acetate | 40 mL | 180 °C/5 h     |
| CuNT              | 10 mL copper nitrate | 40 mL | 180 °C/5 h     |
| FeT               | 0.5 mol % ferrous chloride | 40 mL | 180 °C/5 h     |
| SnT               | 0.5 mol % stannous chloride | 40 mL | 180 °C/5 h     |
| ZT                | 0.5 mol % zinc acetate | 40 mL | 180 °C/5 h     |
| VT                | 0.5 mol % vanadium pentoxide | 40 mL | 180 °C/5 h     |
| ZMT               | 1 mol % zinc acetate and 1 mol % magnesium acetate | 40 mL | 180 °C/5 h     |
| ST                | 0.5 mol % thiourea | 40 mL | 180 °C/5 h     |
ethanol and used for the assembly of DSSCs. The dye-sensitized solar cells were tested for their performance by using a Sun Simulator having a Keithley 2420 power source and LED of illumination 80 mW/cm². The electrochemical investigation was performed using an impedance analyzer (NOVA FRA2 μ Autolab type III (μ3Au771301)).

3. RESULTS & DISCUSSION

3.1. Structural Analysis. To identify the phase and crystallinity of the prepared samples, the XRD patterns were recorded in a 2θ range of 20°–80°. Figure 2 depicts the XRD patterns of PT, AgT, BT, CoT, CrT, CuNT, FeT, SnT, ZT, VT, ZMT, and ST nanoparticles. The diffraction peaks that originated at Bragg’s angle 2θ = 25, 38, 48, 53, 62, 68, and 75° were assigned to the planes (101), (112), (200), (105), (204), (116), and (215), respectively, which represent the anatase phase in all the samples as shown in Figure 2a–l.

The presence of these diffraction peaks endorses the tetragonal crystal structure of TiO₂. In addition to the anatase phase, one can also notice the appearance of rutile peaks in the samples CrT, CuNT, and ST as depicted in Figure 2e,f,l, respectively. Our XRD results coincide with the JCPDS file nos.21-1272 and 21-1276, corresponding to the anatase and rutile phases examined in the prepared samples. As shown in Figure 2b, the silver-doped titania (AgT) nanoparticles endorse the anatase phase of the TiO₂ without any other characteristic peak, implying the incorporation of Ag⁺ ions. As compared to pure TiO₂, the AgT sample shows a slight shifting of the Bragg peak (101) to lower angles. The shifting of Bragg peak (101) could be associated with the lattice deformation after doping in the TiO₂ lattice. Such a similar shifting of the Bragg peak has also been reported after doping with various metal ions such as Ag⁺⁺, Al³⁺, Cu²⁺, Fe³⁺, Mn²⁺, Ni²⁺, V⁵⁺, and Zn²⁺.17 BT sample’s XRD pattern depicted in Figure 2c endorses the dominant Bragg reflection peak of the plane (101) after the doping. However, one can also notice the narrow peak as compared to the AgT sample, which led to the improved crystalline nature as a consequence of doping of the higher ionic radius Ba²⁺ ion as compared to Ti⁴⁺.35 This also suggests an intercalated dopant ion, which results in the deformation of the Ti lattice.47 No deviation in the diffraction peaks were observed for BT and CuNT samples as depicted in Figure 2c,f. However, Figure 2d,e and 2g,k depict the same trend of slight left shifting of the dominant diffraction peak of the plane (101) for the samples CoT, CrT, FeT, SnT, ZT, VT, and ZMT.

Among these, all the samples evidence the presence of a pure anatase phase of TiO₂ except in the sample CrT without other impurities.9,38 Figure 2l shows the distinct XRD pattern of the sulfur-doped sample ST as compared to PT. The ST nanoparticles endorse the right shifting of the dominant diffraction peak of the plane (101) after the doping. However, one can also notice the narrow peak as compared to the AgT sample, which led to the improved crystalline nature as a consequence of doping of the higher ionic radius Ba²⁺ ion as compared to Ti⁴⁺.35 This also suggests an intercalated dopant ion, which results in the deformation of the Ti lattice.47 No deviation in the diffraction peaks were observed for BT and CuNT samples as depicted in Figure 2c,f. However, Figure 2d,e and 2g,k depict the same trend of slight left shifting of the dominant diffraction peak of the plane (101) for the samples CoT, CrT, FeT, SnT, ZT, VT, and ZMT.

Figure 2. X-ray diffraction patterns of (a) pure TiO₂, (b) Ag-TiO₂, (c) Ba-TiO₂, (d) Co-TiO₂, (e) Cr-TiO₂, (f) CuN-TiO₂, (g) Fe-TiO₂, (h) Sn-TiO₂, (i) Zn-TiO₂, (j) V-TiO₂, (k) Zn + Mg-TiO₂, and (l) S-TiO₂ nanocrystals.
radius of the dopant ion is the main factor for the doping to take place by the mechanism of either interstitial or substitutional. In simple words, if the ionic radius of the dopant ion is nearer to the Ti$^{4+}$ ion, then the substitutional doping can be expected. Similarly, a smaller ionic radius-based dopant ion leads to interstitial doping, whereas a larger ionic radius-based dopant ion yields no doping. Considering the dominant peak of the plane (101) at angle $2\theta = 25^\circ$ as noticed for all the prepared samples and using Scherrer’s formula, we have estimated the crystallite sizes 7.9, 7.5, 7.7, 7.5, 7.4, 7.6, 6.5, 6.8, 7.3, 7.5, and 6.2 nm corresponding to the samples PT, AgT, BT, CoT, CrT, 

![Image of Rietveld refinement results](https://pubs.acs.org/doi/10.1021/acsomega.0c01614)

Table 2. Rietveld Refinement Parameters of Various Samples

| Sample | Structure | Phase     | $a = b (\text{Å}\text{ cm})$ | $c (\text{Å}\text{ cm})$ | Space Group | Volume ($\text{Å}^3$) | $\alpha = \beta = \gamma$ (degree) | $R_p$ | $R_w$ | $\chi^2$ | GoF |
|--------|-----------|-----------|-----------------------------|--------------------------|-------------|-----------------------|---------------------------------|-------|-------|----------|-----|
| PT     | tetragonal| anatase   | 3.7894                      | 9.5125                   | $I 4_1/amd$ | 136.5958              | 90.000                          | 11.3  | 11.3  | 1.1      | 1.89 |
| AgT    | tetragonal| anatase   | 3.7901                      | 9.4879                   | $I 4_1/amd$ | 136.2943              | 90.000                          | 14.1  | 14.1  | 0.89     | 1.89 |
| BT     | tetragonal| anatase   | 3.7891                      | 9.5105                   | $I 4_1/amd$ | 136.5437              | 90.000                          | 18.4  | 19.7  | 3.21     | 1.8  |
| CoT    | tetragonal| anatase   | 3.7887                      | 9.4971                   | $I 4_1/amd$ | 136.1082              | 90.000                          | 12.1  | 15.0  | 2.1      | 1.4  |
| CrT    | tetragonal| anatase   | 3.7866, 4.5932              | 9.4921, 2.9588           | $I 4_1/amd, P 4_2/mnm$ | 136.1042, 62.4228          | 90.000                          | 22.9  | 20.0  | 1.354    | 1.2  |
| CuNT   | tetragonal| anatase   | 3.7881, 4.667               | 9.5158, 2.4813           | $I 4_1/amd, P 4_2/mnm$ | 136.5472, 54.0467          | 90.000                          | 10.2  | 15.1  | 3.296    | 1.8  |
| FeT    | tetragonal| anatase   | 3.7872                      | 9.4789                   | $I 4_1/amd$ | 135.9437              | 90.000                          | 12.1  | 13.4  | 1.405    | 1.2  |
| SnT    | tetragonal| anatase   | 3.783                       | 9.4887                   | $I 4_1/amd$ | 135.7965              | 90.000                          | 12.1  | 12.8  | 1.329    | 1.1  |
| ZT     | tetragonal| anatase   | 3.7869                      | 9.4825                   | $I 4_1/amd$ | 135.9851              | 90.000                          | 22.2  | 20.0  | 1.412    | 1.2  |
| VT     | tetragonal| anatase   | 3.7861                      | 9.4924                   | $I 4_1/amd$ | 136.0728              | 90.000                          | 10.3  | 10.7  | 0.6348   | 0.8  |
| ZMT    | tetragonal| anatase   | 3.7879                      | 9.5005                   | $I 4_1/amd$ | 136.3126              | 90.000                          | 11.3  | 11.7  | 0.9565   | 0.97 |
| ST     | tetragonal| anatase   | 3.7865, 4.5932              | 9.4804, 2.9567           | $I 4_1/amd, P 4_2/mnm$ | 135.9251, 62.3536           | 90.000                          | 15.2  | 15.5  | 0.7725   | 0.87 |
CuNT, FeT, SnT, ZT, VT, ZMT, and ST, respectively. These results reveal the decreased crystallite sizes upon doping.

The Rietveld process is a well-known methodology for the retrieval of structural information from the XRD data. The approach utilizes a least-square mechanism to match the Bragg intensities with those centered on a theoretical structural model. The first step in refining is to refinish the background and scale variables. The subsequent stage consists of refining in series structural variables such as lattice parameters, shape profile and width parameters, preferred orientation, isothermal, atomic coordinates, and the site occupancy. The fitness quality of XRD data is determined by measuring the variables such as goodness of fit and $R$ factors (which includes the profile factor, Bragg factor, and crystallographic factor). Once these parameters exceed their minimum value, they are ideally suited to analyze the XRD data, and the crystal structure is assumed to be adequate. Figure 3 depicts the Rietveld-refined XRD pattern of the as-prepared and doped TiO$_2$ nanocrystals. Figure 4. UV−vis absorption of (a) pure TiO$_2$, (b) Ag-TiO$_2$, (c) Ba-TiO$_2$, (d) Co-TiO$_2$, (e) Cr-TiO$_2$, (f) CuN-TiO$_2$, (g) Fe-TiO$_2$, (h) Sn-TiO$_2$, (i) Zn-TiO$_2$, (j) V-TiO$_2$, (k) Zn + Mg-TiO$_2$, and (l) S-TiO$_2$ nanocrystals.
AgT, BT, CoT, FeT, SnT, ZT, VT, and ZMT were refined using the space group $I4_1/amd$ of the anatase-TiO$_2$. Meanwhile, the samples CrT, CuNT, and ST were refined with both the space groups $I4_1/amd$ and $P4_2/mnm$ corresponding to the anatase and rutile phases of TiO$_2$, respectively. The obtained R factors values are shown in Table 2, we have noticed the slightly high value of $R_p$ in a few cases, and a similar result is reported in the literature. Further, we can notice the low value of the goodness of fit values, which resembles the quality of the refinement.

3.2. Optical Analysis. We have performed the UV–vis spectroscopy analysis of various doped samples. Using Tauc relation, the estimated optical band gap values are depicted in Figure 4. The band gap of the semiconductor materials is estimated by performing the UV–vis absorbance using a spectroscopy technique. For this, the Tauc equation, $ahv = A(hv - Eg)^m$ was used, where $A$, $a$, and $E_g$ are the optical constant, absorption coefficient, and optical band gap value, respectively. The power factor ($m$) is associated with the band gap of allowed direct, allowed indirect, forbidden direct, and forbidden indirect transitions corresponding to their values 0.5, 2, 1.5, and 3, respectively. By extrapolating the straight line portion of the curves to a zero absorption coefficient value, we have obtained the energy band gap value. We can notice the reduced band gap after doping with various dopants in the order $3.10 > 2.98 > 2.97 > 2.96 > 2.95 > 2.94 > 2.91 > 2.88 > 2.84 > 2.83 > 2.79$ eV corresponding to the samples PT > BT > CrT > CuNT > SnT > VT > AgT > ST > CoT > FeT > ZT. The usual effect of band gap reduction can be noticed. The alternation of the band gap by shifting down the conduction band or shifting up the valance band is promising for the enhancement of light absorption. Here, we can notice the red shift of the absorption peaks after doping, which indicates that the decreased band gap value, which is beneficial for DSSCs or photocatalyst applications. The band gap values of the samples AgT and ZMT were found to be identical.

3.3. Morphology Analysis. Figures 5 and 6 depict the SEM morphology of the various doped samples. One can clearly observe the preparation of microspheres of nanoparticles in all the samples. Referring to Figure 5, the mean diameter of the samples PT, AgT, BT, CoT, CrT, and CuNT were 216, 287, 272, 206, 201, and 187 nm, respectively.

Similarly, Figure 6 depicts the SEM images with somewhat well-distributed and uniform morphology as compared to SEM images shown in Figure 5. The obtained mean diameters were 197, 229, 214, 331, 213, and 225 nm corresponding to the samples FeT, SnT, ZT, VT, ZMT, and ST.

If we compare the morphology of other samples with the SnT and VT, we can also notice the formation of a few bigger size microspheres along with a large quantity of smaller microspheres. For the estimation of the microsphere’s size, we have considered the smaller microspheres in all the samples due to their large quantity. Using ImageJ software, the estimated mean...
diameter of the prepared nanocrystals was found in the range from 10 to 20 nm. The SEM micrographs are shown in Figure 5, and Figure 6 endorses the mesoporous microspheres of undoped and doped titania nanocrystals.

3.4. DSSC Performance. We have evaluated the performance of the DSSCs based on the various doped samples. Figure 7 displays the current density versus voltage characteristics along with the various obtained solar cells parameters. The conversion efficiencies were found to be increased in the order 1.31 < 2.21 < 2.27 < 2.73 < 2.87 < 3.20 < 3.29 < 3.33 < 3.62 < 3.70 < 4.85 < 5.75% corresponding to PT < CuNT < BT < SnT < AgT < CrT < CoT < VT < ST < ZMT < FeT < ZT as observed in Figure 7a. This enhancement in photoconversion could be due to the formation of mesoporous microspheres of nanocrystals, which yielded the increased contact area for the dye loading. The highest achieved efficiency was ~6% using the photoanode based on the ZT. The corresponding change in the solar cell parameters can be compared as depicted in Figure 7b. For example, here, the best-performing dye-sensitized solar cells are ZT and FeT, and accordingly, one can observe the decreased series resistance ($R_s$) and enhanced short-circuit current ($J_{sc}$). Here, $FF$ and $V_{oc}$ are the fill factor and open-circuit voltage, respectively. By comparing the two best-performing DSSCs along with the device based on PT, we have noticed 27 and 33.8% enhancement in cell efficiency obtained by the DSSCs based on FeT and ZT samples, respectively. Similarly, DSSCs based on various doped TiO$_2$ nanoparticles exhibited enhanced photoconversion efficiency. One-dimensional structures of TiO$_2$/ZnO were also reported suitable materials for the DSSC photoanode, which showed the synergetic effect of both the materials in improving the performance of the solar cell efficiency.

To know the durability of three selected DSSCs based on PT, FeT, and ZT samples, we have evaluated the photovoltaic performance several times even after 2−3 days, which evidenced the same efficiency. Later on, cross-sectional surface morphology measurements were carried out to confirm the photoanode layer’s thickness prepared over the FTO plates. Figure 8 shows the SEM cross section images of photoanodes based on PT, FeT, and ZT samples. In SEM images, we can observe the photoanode layer’s peeling-off issue with all the samples as these samples were used several times for the performance evaluation of DSSCs, and the samples have been damaged. Moreover, the fibrous structure shown in Figure 8a endorses the cellulose peeling-off issue. The cellulose was used to prepare the paste for the coating. One can also observe the prepared TiO$_2$ compact layer onto the FTO substrates with their thicknesses 1.0, 1.6, and 1.14 μm as shown in Figure 8a−c, respectively. Most importantly, the coated layers of the TiO$_2$, Fe-TiO$_2$, and Zn-TiO$_2$ can be seen on the TiO$_2$ compact layer. The estimated thickness of the photoanodes was found in the range from 10 to 12 μm.
3.5. EIS Analysis. For the analyses of the electron transport and recombination process, DSSCs based on PT, FeT, and ZT photoanodes were studied by electrochemical impedance spectroscopy (EIS). Generally, the EIS result comprises three semicircles. A semicircle in the high-frequency zone corresponds to the Pt counter electrode | electrolyte interface, which relates the charge-transport resistance ($R_{ct1}$). In the low-frequency range, a semicircle represents the Warburg diffusions ($Z_w$) of $\Gamma^- / \Gamma^+$, while a middle semicircle corresponds to the electron transfer resistance at the photoanode | dye | electrolyte interface ($R_{ct2}$). Figure 9a depicts the Nyquist plot of the DSSCs, which shows the overlapping of first and second semicircles of high and middle frequencies. This kind of overlapping could be associated with the low resistance of the counter electrode.

A big middle semicircle represents the resistance associated with the photoanode | electrolyte interface, whereas the low-frequency range semicircle represents the Warburg impedance. Table 3 shows the obtained values of electrochemical parameters for the DSSCs. The series resistance ($R_s$) value was observed to be increased for the photoanode DSSC-PT. However, a small difference in $R_s$ values was noticed for the photoanodes DSSC-FeT and DSSC-ZT, which corresponds to the contact resistance.

The charge transfer resistance at the counter electrode | electrolyte interface ($R_{ct1}$) was varied, which could be associated with the different counter electrodes used to assemble the DSSCs. The value of charge transfer resistance at the photoanode | electrolyte interface ($R_{ct2}$) was found to be smaller for the DSSC-FeT and DSSC-ZT as compared to DSSC-PT. The reduced $R_{ct2}$ values indicate the improved electron transport on the surface of photoanodes. This resulted in the enhancement of the short-circuit current ($J_{sc}$) and hence improved conversion efficiency as mentioned in Table 3. Our investigation was further explored to a Bode plot as shown in Figure 9b. In general, the Bode plot represents the maximum frequency values corresponding to the charge transport process at the photoanode | electrolyte interface. The maximum frequency values obtained from the DSSC-PT, DSSC-FeT, and DSSC-ZT were 2559, 1456, and 1930 Hz, respectively. Table 3 shows the calculated recombination lifetime of electrons ($\tau_n$) by using the relation $\tau_n = \frac{1}{2\pi f_{max}}$ where $f_{max}$ is the maximum frequency observed in the Bode plot. The higher the value of $\tau_n$ indicates the slow recombination rate of electrons, which implies...
prolonged transport delay of the electrons in the photoanode. Ultimately, this led to increased open-circuit voltages and conversion efficiency, as noticed. Though the electron lifetime is longer for the photoanode DSSC-PT, the increased $R_{ct2}$ value has affected the charge transfer process due to which the conversion efficiency was reduced as noticed in the current−voltage characteristic plot shown in Figure 7. In a similar way, metal-doped samples showed the improved electrochemical properties and therefore demonstrated the enhanced efficiency of the DSSCs.5,53,54

4. CONCLUSIONS
Various doped samples of TiO$_2$ were prepared by the solvothermal approach and examined. The XRD pattern endorsed the presence of a pure anatase phase in the samples PT, BT, CoT, FeT, SnT, ZT, VT, and ZMT, while an additional rutile peaks are noticed in the CrT, CuNT, and ST samples. We have also performed the Rietveld refinement of XRD data and found to be in good agreement. The crystallite size and the optical band gap were found to be reduced from 8 to 6 nm and 3.10 to 2.79 eV, respectively, after doping with the various dopants. The SEM measurements evidenced the preparation of mesoporous microspheres made up of nanocrystals having their diameter from 10 to 20 nm. The DSSCs based on the photoanodes fabricated using various doped TiO$_2$ nanoparticles showed the enhanced short-circuit current density and efficiency. However, the DSSCs based on FeT and ZT samples demonstrated better performance with their conversion efficiencies of about 27 and 34%, respectively, as compared to PT-based DSSCs. Furthermore, EIS investigation of these samples endorsed the decreased electron transfer resistance value at the photoanodelyselectrolyte interface, which led to enhanced cell efficiency.

Table 3. Photovoltaic and Electrochemical Parameters of Various DSSCs

| photoanode | $J_{SC}$ (mA/cm$^2$) | $V_{OC}$ (V) | FF | $\eta$ (%) | $R_s$ (Ω) | $R_{ct1}$ (Ω) | $R_{ct2}$ (Ω) | $C_2$ (mF) | $C_3$ ($\mu$F) | $\tau_n$ (ms) |
|------------|---------------------|-------------|----|------------|-----------|-------------|-------------|-------------|-------------|------------|
| DSSC-PT    | 5.10                | 0.64        | 0.40| 1.30       | 30.64     | 19.82       | 37.13       | 15          | 4.7         | 0.10       |
| DSSC-FeT   | 12.79               | 0.71        | 0.53| 4.83       | 41.08     | 10.48       | 27.03       | 46          | 3.3         | 0.06       |
| DSSC-ZT    | 15.89               | 0.67        | 0.54| 5.74       | 28.35     | 13.33       | 22.67       | 38          | 5.1         | 0.08       |

Figure 9. (a) Nyquist plot and (b) Bode phase plot of DSSCs based on PT, FeT, and ZT photoanodes.

The authors declare no competing financial interest.

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