

Lattice Distortion Creates Enhancements in Photocatalytic and Electrocapacitive Performance of Sol–Gel-Derived Cu-Doped NiTiO_3

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A remarkable 35% enhancement in the photocatalytic and electrocatalytic abilities of an ilmenite nickel titanate (NiTiO_3) material is reported. This boost in catalytic performance is achieved by simply creating a static distortion in the rhombohedral unit cell by replacing a small proportion of a small-size nondegenerate Ni (69 pm) with a large-size degenerate Cu (73 pm). The materials are synthesized by using a simple sol–gel method. The appropriate doping amount of Cu facilitates the better separation of intrinsic charge carrier pairs by inhibiting their recombination. The photocatalytic and electrochemical activities of durable materials in aqueous MB dye (10 ppm) and KOH (1 molar) electrolyte solutions are found to be directly associated with this improvement in inherent charge carrier transfer characteristics. The enhanced photodissociation of MB dye (42–56%) and specific capacitance (381–450 F g^{-1}) in a KOH (1 molar) electrolyte are in full accord with the investigations carried out using crystallographic and optoelectronic analysis, charging–discharging measurements, and electrochemical impedance (EIS) spectroscopy investigations. Same material with high textural surface areas or controllable particle morphologies might show a far better photo/electrocatalytic performance in a variety of practical applications.

focusing on environmental care by exploiting solar radiation-mediated catalytic reactions.^[1,2] To solve these desirable frontier concerns relating to energy conversion and storage, and the removal or decomposition of hazardous and toxic compounds in water and the atmosphere, a variety of nanosize inorganic and organic-type semiconducting materials and core/hollow nanostructures have been utilized and studied for energy and environmental technologies.^[4–6] Perovskite titanate materials with the unit cell formula XTiO_3 , where X is a transition metal (e.g., Fe, Mn, Zn, Co, Cu, and Ni) have been suggested as effective materials for a wide range of promising applications.^[7] Among them, a yellow color ilmenite nickel titanate (NiTiO_3) material is ubiquitously considered low cost, abundant, safe for the environment, and chemically durable pigment material.^[8,9] Due to its unique electronic and catalytic properties, it is potentially utilized in a variety of practical

1. Introduction

The scientific community is consistently working to find ways to meet the future energy demands of humankind while also

applications, such as high-temperature superconductors,^[9,10] gas sensors,^[11] gas detectors,^[12,13] ion batteries,^[13–16] corrosion inhibitors,^[17,18] and most importantly as a visible light-driven catalytic material.^[19–24]

But even with these figures of merits, yet NiTiO_3 has a poor photo- (electro-) conductivity stemming from a fast charge carrier recombination, which therefore limits its performance as an active material in electrochemical energy devices or as a single-phase photocatalytic material.^[25] To address this problem, many tactical methods have been applied to improve the bulk and surface charge transfer characteristics properties of NiTiO_3 . These methods include establishing heterojunctions with other appropriate materials, making composites with conducting carbon-based materials, modifying the size-shape morphology of the particles, and adding extra donor (acceptor) impurities into the unit cell structure.^[26,27] These strategies effectively improve the photo- (electro-) catalytic capability of NiTiO_3 for the specific redox species present in a liquid (or gas) medium.^[26] The valency and radius of an impregnated impurity (donor or acceptor) are two different critical factors that need to be considered separately. Here in this paper, we show how a simple straightforward static crystal lattice distortion in NiTiO_3 by

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doping an appropriate percentage of a large radius size Cu of the same valance and octahedral coordination state to that of a small radius size Ni effectively can offer an improved separation of the inherent charge carrier pair.^[28] The permanent distortion of unit cell (replacing a nondegenerate Ni site with a 2% degenerate Cu ions) doesn't provide additional free charge carriers but rather facilitated the separation of intrinsic charge carrier pairs.

The impact of this efficient charge separation is easily observed in terms of a remarkable $\approx 35\%$ improvement in the photocatalytic and electrocapacitive performance of NiTiO_3 . The bare and Cu-doped NiTiO_3 materials are prepared in powder form by using a simple and easy sol-gel calcination process and characterized using techniques like X-Ray diffraction (XRD), UV-vis spectroscopy, photoluminescence (PL) spectroscopy, and scanning electron microscopy (SEM) and energy-dispersive X-Ray spectroscopy (SEM-EDX). The photo-assisted dissociation performance of powder material is measured for a water pollutant (MB dye molecule) under light irradiation. Cyclic voltammetry (CV) and galvanic charging-discharging (GCD) techniques are utilized to measure electrochemical (capacitive) capability and charge transfer performance at the electrode and electrolyte interface in a standard 1 molar aqueous KOH electrolyte solution.

2. Results and Discussions

Figure 1 displays the XRD patterns of bare NiTiO_3 (S0) and various Cu-doped NiTiO_3 (doping: 1%, S1; 2%, S2 and 3%, S3) powder samples that are synthesized under similar conditions. Without impurity, the diffraction peaks of all binary powder samples are well matched with the unit cell type of ilmenite (IL) NiTiO_3 material (JCPDS no. 33-0960; rhombohedral type, space group: R-3c). Upon increasing the Cu doping up to 2% into Ni lattice sites, initially, crystallinity enhanced as well as all the XRD peaks slightly shifting toward a higher diffraction angle, which therefore indicated a size expansion of a primitive unit cell structure (alternating stacked layers of corner and edge-sharing TiO_6 and NiO_6 octahedra) with a slight shape (non-symmetry) distortion as well (inset in **Figure 1**, **Table 1**). However, by increasing the Cu doping level further, for example, to 3% and above,

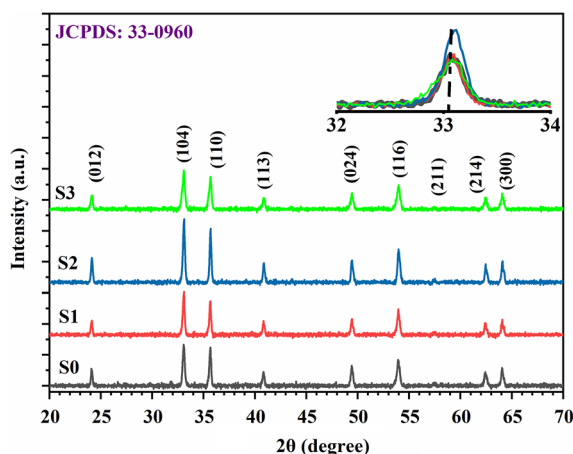


Figure 1. XRD patterns of as-synthesized powder samples.

crystallinity decreased, and all the XRD peaks started shifting towards a lower diffraction angle, which indicated a very strong shape distortion of the unit cell.

The calculated size parameters (a and c , and assuming conventional trigonal crystal with $\alpha = 90^\circ$, $\gamma = 120^\circ$) of rhombohedral lattice and the estimated crystallite sizes of powder samples are listed in **Table 1**. The average crystallite size (D) was estimated by applying the well-known Scherrer equation ($D = k\lambda/\beta\cos(\theta)$), where $k = 0.9$, $\lambda = 0.15406$ nm, θ = diffraction angle, and β = full-width half maximum) to the highest intensity (104) diffraction peak of the powder sample. Compared to bare NiTiO_3 , lattice size expansion is expected in Cu-doped NiTiO_3 samples, which could be understood by a relative difference in the ionic radii of host Ni^{2+} (69 pm) and the foreign dopant Cu^{2+} (73 pm).^[29]

Beyond a certain Cu doping level, the distinct shape distortion (noncentral symmetry) in the unit cell becomes more pronounced (S3 sample in **Table 1**). It is known to be caused by the strongly electronically degenerate nature of Cu^{2+} ($3d^9$ electronic configuration) when it existed in its favorite octahedral coordination (CuO_6) as compared to the nondegenerate nature of Ni^{2+} ($3d^8$ electronic configuration, NiO_6 octahedra).^[30,31] These degenerate d -electrons induced deformation of lattice (z -in or z -out direction) which is expected to cause structural defects both in apical and basal directions during the growth of the crystallite and the particles and thus lead to a reduction in crystallite size with further increasing the Cu doping concentration, for example, above 2% and more.

The bright yellowish hue of all powder is visible to the unaided eye (optical picture, **Figure 2**). The yellow color of powder samples is also known to originate from the selective absorption of visible light (VL) in their valance band (VB; Ni d - d charge-transfer).^[8,32] The microscopic SEM pictures (**Figure 2**) showed the highly irregular size/shape of particles and the high polydispersity of all powder (S0, S1, S2, and S3) samples, with particle sizes ranging from several μm to a few hundred μm . Additionally, elemental SEM-EDX surface mapping shows that chemical composition (insets in EDX images of **Figure 2**) of the powder samples is relatively very near to the atomic proportion of reagents used during their synthesis procedures. The atomic percentage of elements in powder samples is also determined by the XPS analysis techniques (see **Table 1**).

The permanent static distortions of rhombohedral unit cell are also expected to modify the optical and electronic characteristics of the NiTiO_3 (S0, **Figure 2**) sample.^[31] The light absorption of a well crystalline NiTiO_3 is attributed to charge transfer occurring between the uppermost part of its valance band (VB) edge (t_{2g} orbitals), formed by a strong hybridization of Ni ($3d$) with O ($2p$) states, and the lowest part of its conduction band (CB) edge (e.g., orbitals), mainly formed by Ti ($3d$) states. The horizontal position of absorption spectra in UV-vis ($\text{O} \rightarrow \text{Ni}$; $\text{Ni} \rightarrow \text{Ti}$; $\text{O} \rightarrow \text{Ti}$) and near-infrared (Ni, $d \rightarrow d$) regimes of various Cu-doped NiTiO_3 samples resembled the absorption characteristics of bare NiTiO_3 (S0) sample as shown in **Figure 3**. Thus, based on XRD examination (**Table 1**), it can be inferred that the quantity of Cu doping clearly influences the absorption intensities of CB and VB states of S0 sample, that is of Cu doping enhanced the nonsymmetric distortion of cation-oxygen octahedra.

Table 1. Crystallographic (average crystallite size $\approx D$, unit cell volume $\approx V$), optoelectronic (bandgap energy $\approx E_g$), elemental composition (a%), oxygen species (lattice- O_L ; surface hydroxyl- O_H and surface adsorbed- O_2), photocatalytic (MB dye), and electrocatalytic (SC-specific capacity and R_{ct} -charge transfer resistance) properties of bare and various Cu-doped $NiTiO_3$ powder and/or electrode samples. Bare: S0; doped: 1%-S1; 2%-S2, 3%-S3.

Sample	D [nm]	(104) Peak [2 θ , deg.]	Unit cell parameters		E _g [eV]	Composition ^{a)} [%]	O _L ^{b)}	MB degradation [%] ^{c)}	Rate constant [10 ⁻⁵ s ⁻¹]	SC ^{d)} [F g ⁻¹]	R _{ct} ^{e)} [Ohm]
–	–	–	Lattice Size [Å]	V [Å ³]	–	Ti Ni Cu	O ₂ O ₃	–	–	–	–
S0	35.6	33.0788	$a = 5.0302$	302.1647	2.37	30.4 (26.7): 25.7 (23.2) 0	1.00 1.00 1.00	42.38	1.73	381.2	32.9
			$c = 13.79$			41.1 (46.3)					
S1	38.8	33.0789	$a = 5.0412$	305.6893	2.36	28.4 (25.9) 23.7 (21.82) 0.8 (0.94) 43.3 (44.2)	1.31 0.76 0.94	36.12	–	–	–
			$c = 13.89$								
S2	37.6	33.117	$a = 5.0433$	307.4906	2.35	27.4 (23.4) 20.5 (21.9) $c = 13.96$ 47.4 (46.9)	1.24 1.05 1.08	55.96	2.63	450.4	21.2
S3	27.6	33.0788	$a = 5.0293$ $c = 13.74$	300.9609	2.38	30.3 (26.2) 27 (23.3) 2.8 (2.9) 45.1 (46.9)	–	46.82	–	–	–

^{a)}SEM-EDX and XPS analysis technique (parentheses); ^{b)}Oxygen species from peak area of XPS O1s signal; ^{c)}Hg-lamp (250 W, $\lambda > 355$ nm). Powder (10 mg), solution (50 mL of 10 ppm MB), continuous 4 h illumination; ^{d)}One molar KOH solution; GCD measurements (applied current density—0.625 Ag⁻¹); ^{e)}Nyquist EIS plot (voltage = 0.5 V, frequency range = 1–100 MHz).

The first principle theoretical structural calculations showed that in a pure $NiTiO_3$, the interaction or hybridization of $Ti(3d)-O(2p)$ is stronger than $Ni(3d)-O(2p)$, the VB ($Ni-O$) bonds are more ionic, and CB ($Ti-O$) bonds are more covalent; an almost complete charge transfer takes place in the VB regime (between O and Ni) and the Ni and Ti states are very localized in the top of the VB and bottom of the CB, respectively.^[33] Thus, lattice-distorting (z-in or z-out; nonsymmetric) nature of degenerate Cu^{2+} in an octahedral environment effectively will lead to a delocalization of electronic charge through the changes of polar (covalent or ionic) characteristics of the apical and basal bonds formed between specific ions and the effective Born charges on such ions.^[30] The UV-vis absorption spectra (Figure 3) indicated that if 1% Ni of $NiTiO_3$ (S0) is replaced by 1% Cu, then it significantly alters the VB-states ($Ni-O-Ni$, $Ni-Ni$; near IR region) only and leaves the CB-states unaffected. Also, a 2% Cu doping slightly impacted the VB states, and the delocalization of charge (electron-electron interaction) associated with the CB states ($Ti-O-Ti$) was largely affected. Interestingly, a 3% Cu doping strongly and simultaneously impacted both VB and CB states of $NiTiO_3$. These results are fully supported by the Kubelka–Munk analysis of UV-vis diffuse reflectance (DR)

spectra (optical bandgap energy) that confirmed the acceptable photo response consistently increases with doping up to 2% concentration of Cu and then decreases with larger doping amount (Table 1).

Although light absorption analysis implied that the Cu doping did serve as a mediator for better absorption of visible light by delocalizing the orbitals of VB state, CB state, or both states, that is, increasing concentration of intrinsic charge (electron–hole) pairs, however, the excessive Cu doping (CuO_6) also increases the nonsymmetric lattice distortion of TiO_6 and NiO_6 octahedra which therefore might reduce the semiconductive properties.^[34] The structural defects especially oxygen vacancies and the separation of electrons and holes in a material (particle) are important electronic processes that play a crucial role in all types of catalytic redox reactions that must take place at the same time. During such complex reaction processes, the catalyst must maintain the stability of its main physical features, such as crystalline structure, surface states, and electronic and optical behaviors.

Thus, the separation efficiency of charge pairs is further revealed through PL emission spectroscopy.^[35] Figure 4a displays the recorded PL spectra of all powder samples. The introduction of Cu hardly changed the shape of PL spectra, therefore primarily

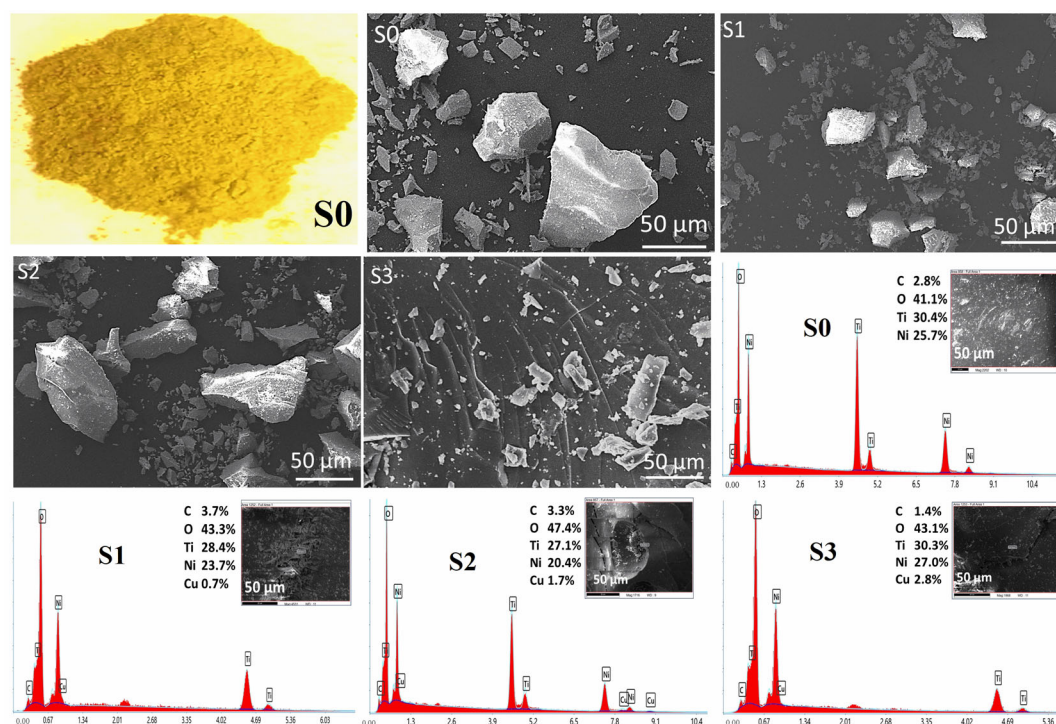


Figure 2. Ordinary optical (by Sakshi Chaudhary) and microscopic SEM pictures with mapped SEM-EDX elemental composition of powder samples. C is carbon present at the surface of the particle.

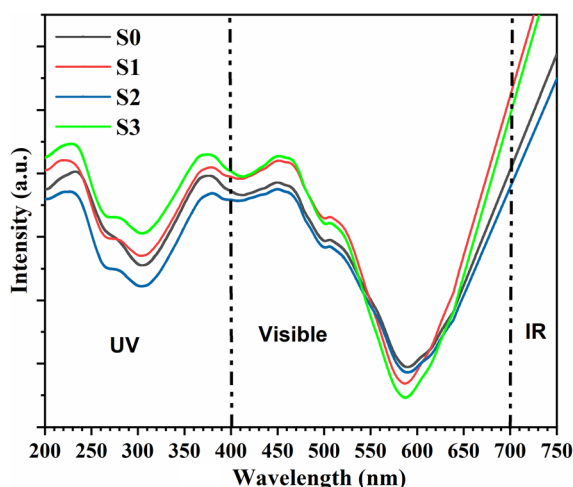


Figure 3. Measured UV-vis absorption spectra of powder samples.

pointing out the existence of quite similar types of bulk and surface defect levels/sites, ionic valences, and the oxygen vacancy in all powder samples (Figure 2, chemical composition, Table 1). However, the noticeable PL intensity increases or decreases depending on the Cu doping concentration. The nearly unchanged higher shoulder of all PL spectra is associated with the crystal field splitting of NiTiO_3 , giving rise to metal-to-metal transitions between the VB edges.^[36] Among all these doped powder samples, S2 sample possessed the lowest PL intensity

and thus showed a maximum separation efficiency for the charge carrier pairs, that is, delayed recombination of light-generated electron-hole pairs.^[37] This confirmed that the lifetime of photo-generated electrons is improved by a suitable Cu-doping concentration only that is, there is an optimum permanent lattice distortion leading to the optimum delocalization of ligand charge onto ions forming VB states and CB states in a Cu-doped NiTiO_3 (S2) sample than in a bare NiTiO_3 sample (S0). Note that the lattice distortion becomes more pronounced if the degeneracy directly occurs in CB states (e.g., orbitals of TiO_6 octahedra). We speculate that the shifting of metal cations from the center of the oxygen octahedron leads to a noncoincidence of the gravity centers of positive and negative charges (see Figure 1 and Table 1). This rattling of metal cations inside the octahedron gives rise to intrinsic dipoles, which help in the separation of charge carrier pairs. Based on the XRD, UV-vis, and PL measurements presented above, it can be confirmed that among all Cu-doped NiTiO_3 powder samples, S2 has the two most advantageous properties: 1) a maximum absorbance for visible light due to its smallest optical band gap energy and 2) an efficient separation of intrinsic charge carrier (electron-hole) pairs.

The formation of PL emission peaks in metal oxides in the visible range is mostly associated with oxygen vacancies ($\text{F} \rightarrow$ two trapped electrons and $\text{F}^{2+} \rightarrow$ no trapped electrons) at either deep or shallow bandgap levels.^[38] Therefore, the self-trap (localized) CB ($\text{Ti}3d$ orbitals) electron caught by the VB (hybridized $\text{Ni}2p$ and $\text{O}2p$ orbitals) holes can be attributed to the emission peak near 423 nm (2.93 eV), which represents charge-pair recombination. Here, the oxygen vacancy centers are the pathway through which recombination happens. Thus, the XPS technique

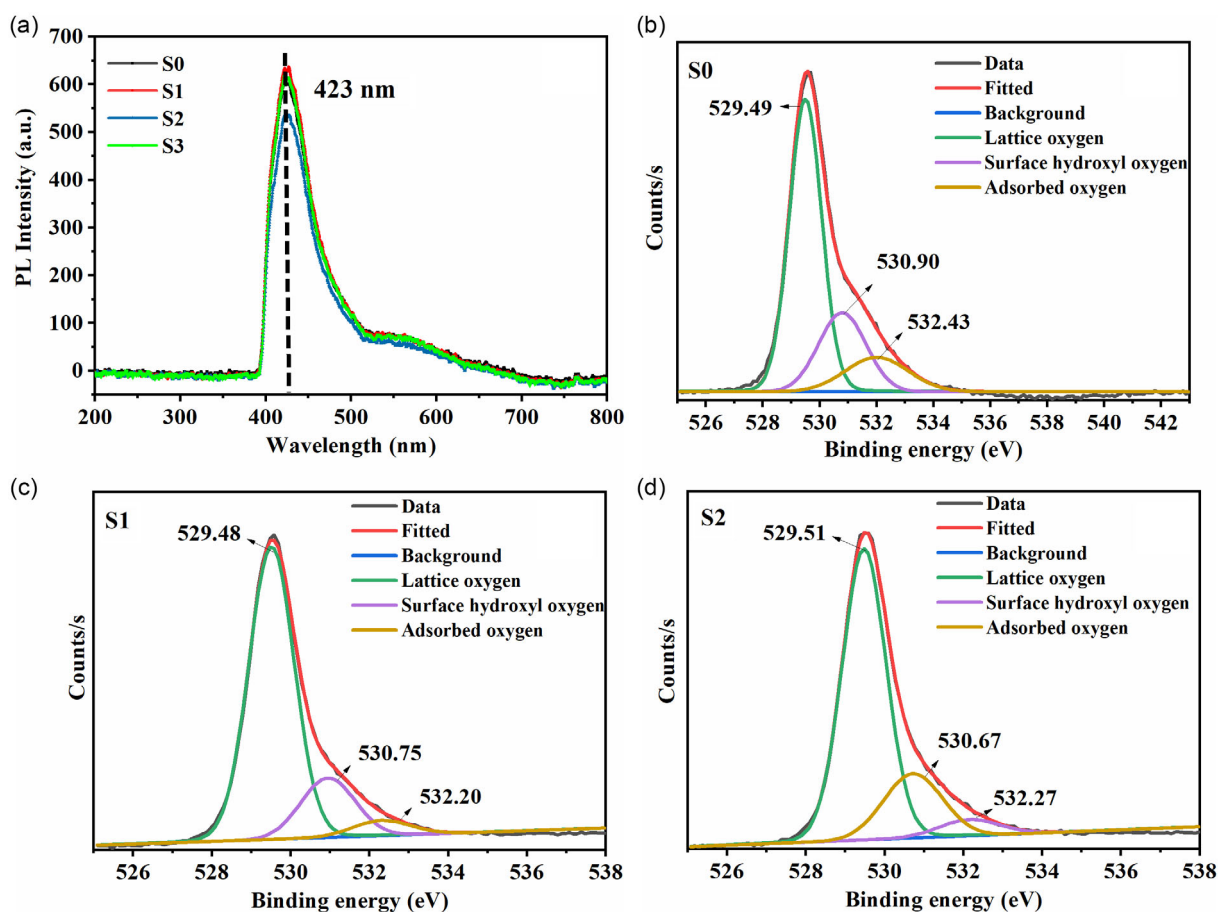


Figure 4. a) PL spectra of powder samples (excitation source is LED laser ≈ 385 nm) and b–d) high-resolution O1s XPS spectra of powders (calibrating reference, C1s peak, 284.6 eV).

is utilized to detect the changes in lattice oxygen, if any, resulting from Cu-doping in respective power samples.

Figure 4b–d displays the high-resolution XPS O1s signals obtained from the surface of bare (S0) and Cu-doped (S1 and S2) NiTiO_3 powder samples, which were synthesized under similar environmental conditions (600 °C, air, 6 h). The development of a shoulder at the high binding energy (BE) side of the lattice oxygen (O_L) is due to the surface oxygen passivated with hydrogen (chemisorbed H_2O molecules) as well as irreversibly adsorbed oxygen (H_2O molecules).^[39–41] Therefore, slightly differing BE values (insets, Figure 4) for three types of oxygen peaks (fitting function: pseudo-Voigt function, Lorentzian to Gaussian distribution, set ratio ≈ 0.1) corresponded to the amount of lattice oxygen (O_L), surface hydroxyl oxygen (O_H), and surface adsorbed oxygen (O_A) species presented in the respective powder samples (see Table 1).^[40,41]

The photocatalytic or electrocatalytic activity of the material for the functional groups may be affected by these oxygen species. Thus, the solid-state addition approach is used to determine the effect of Cu doping on the surface adsorption capacity of an ilmenite NiTiO_3 (S0) sample.^[42] The measured surface isoelectric points (IEP) of all powders lie between 5.7 and 5.9 (pH); hence, the IEP of bare NiTiO_3 is mostly unaltered via Cu doping

(up to 3%).^[43] The surface-adsorbed oxygen species (O_A) is expected to be fully saturated under an equal equilibrium environmental (aqueous media) situation. In such a case, the photo- and electrocatalytic activity related to the efficiency of charge-pair recombination should be primarily determined by the particle's lattice oxygen (bulk) vacancies.^[39]

In Table 1, the powder samples S1 (and S2) have roughly 31% (and 24%) higher lattice oxygen (O_L) amounts than sample S0, which should be indicative of fewer oxygen vacancies (bulk defects). Therefore, the charge trapping rate must follow an ascending order, that is, $\text{S0} > \text{S2} > \text{S1}$, according to this XPS O1s signal analysis. This is contrary to the results of PL spectroscopy (Figure 4a; $\text{S0} > \text{S1} > \text{S2}$) and UV-vis analysis (optical bandgaps, see Table 1). This outcome is expected since the $\text{Ni}2\text{p}$ state, not the $\text{O}2\text{p}$ state, dominates the uppermost region of the VB of bare or Cu-doped NiTiO_3 . Accordingly, the XRD, UV-vis, PL, and XPS (O1s) and IEP analyses indicate that although lattice distortion resulting from Cu doping contributes very little to bandgap narrowing of an ilmenite NiTiO_3 (refer to Table 1), it does inhibit the recombination rate of intrinsic electron–hole pairs. In addition to producing lattice distortion, we conjecture that the electrically degenerate character of Cu also alters the oxidation states of both Ti and Ni.^[44–47]

Consequently, the distorted TiO_6 (CB states) and NiO_6 (VB-states) octahedra exhibit a synergistic effect among themselves, and hence, the rate of electron-hole pair separation is boosted by the most effective quantity of Cu doping.^[46,47]

From herein, we will solely focus on and access the photo-(electro-) catalytic ability of powder (or electrode) samples directly associated with the density and the separation of their intrinsic charge carrier (electron-hole) pairs. **Figure 5** shows the time-dependent photocatalytic dissociation of the cationic MB dye solution (absorbance maximum at 668 nm) using powder (≈ 10 mg) suspension observed under identical light irradiation (Hg lamp, 250 W, $\lambda > 355$ nm). The photo-dissociated amount of MB dye listed in Table 1 is determined by the standard equation (% degradation = $\{(C_0 - C)/C_0\} \times 100$; where C_0 and C refer to the instantaneous concentrations of MB dye kept in dark condition and under light illumination at a particular time.^[48,49] Among all powder samples, S2 showed a much higher photodecomposition ability than any other sample. Following a 4 h continuous light irradiation, the samples S0 and S2 though have very large particle sizes (Figure 2), yet they demonstrate $\approx 42.38\%$ and

55.9% photodegradation of MB concentrations, respectively. It is noteworthy that sample S1 exhibits lower photodegradation (36.1%) than sample S0 despite having a smaller optical bandgap energy (Table 1). As previously inferred by the findings of the optoelectronic analysis, that is, UV-vis and PL studies (Figure 3 and 4), the $\approx 35\%$ higher photocatalytic performance of the S2 powder over the S0 powder is attributed to a slightly lower (≈ 0.02 eV) optical bandgap energy, that is, higher concentration of intrinsic charge pairs and mainly to their efficient separation (see Figure 3). The peculiar charge carriers react with oxygen and water molecules presented in the dye solution and produced higher number of hydroxyl radicals and super-radical oxygen species.^[44] These species thus lead to the overall photo-dissociation MB dye molecules.^[36,50] The linear fit of a plot between $\log(C/C_0)$ and elapsed photocatalytic reaction time yielded the first-order reaction rates listed in Table 1.

The electrocapacitive ability of S0 and S2 electrode with similar physical measures (mass and area) in an aqueous of KOH electrolyte solution (1 molar, pH = 14) are shown in **Figure 6**. The recorded voltage-current curves of polarized electrodes

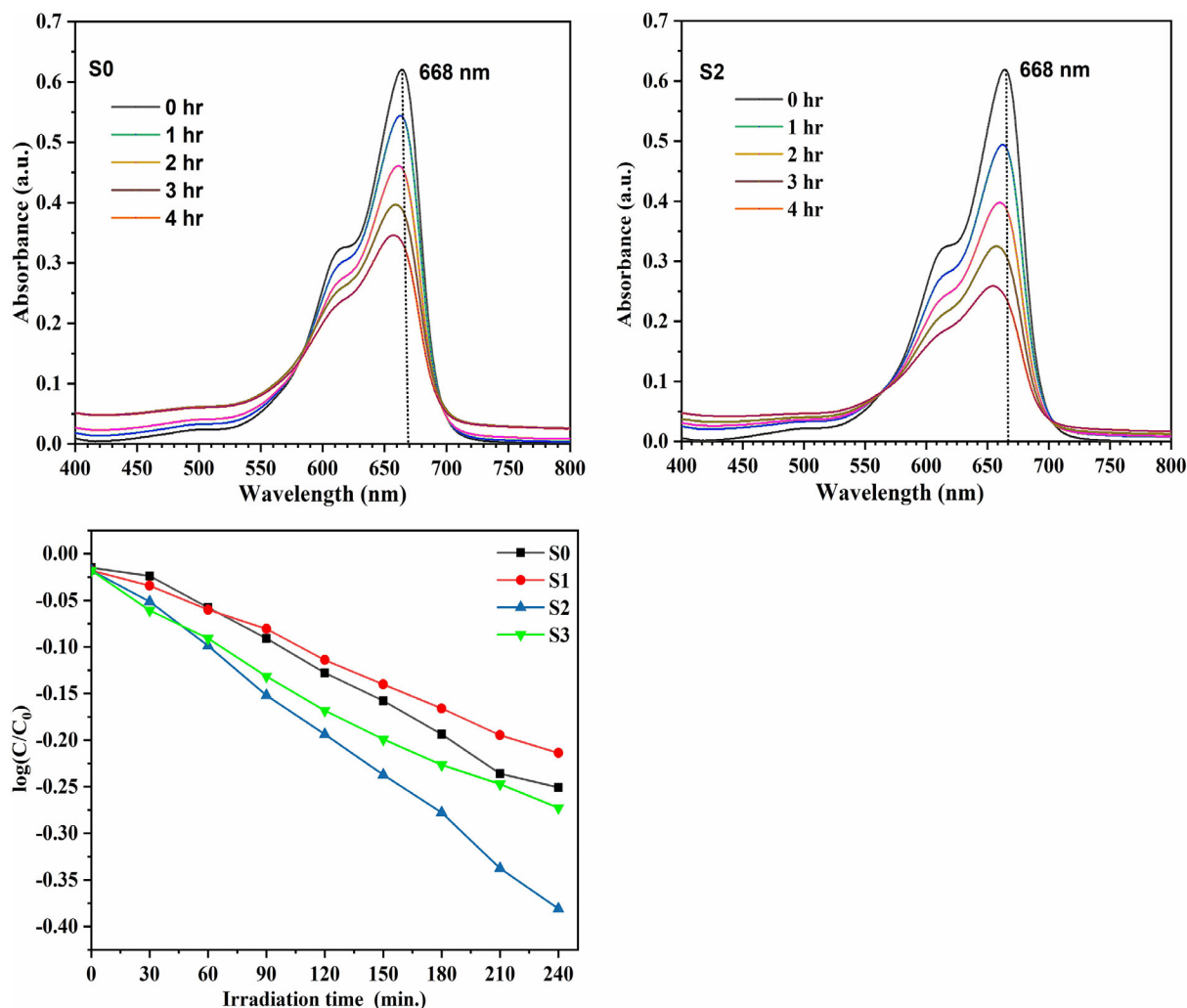


Figure 5. Time-dependent absorption spectra and the 1st order photodissociation kinetics of MB dye using powder suspension under light illumination (Hg-lamp, 250 W, $\lambda > 355$ nm).

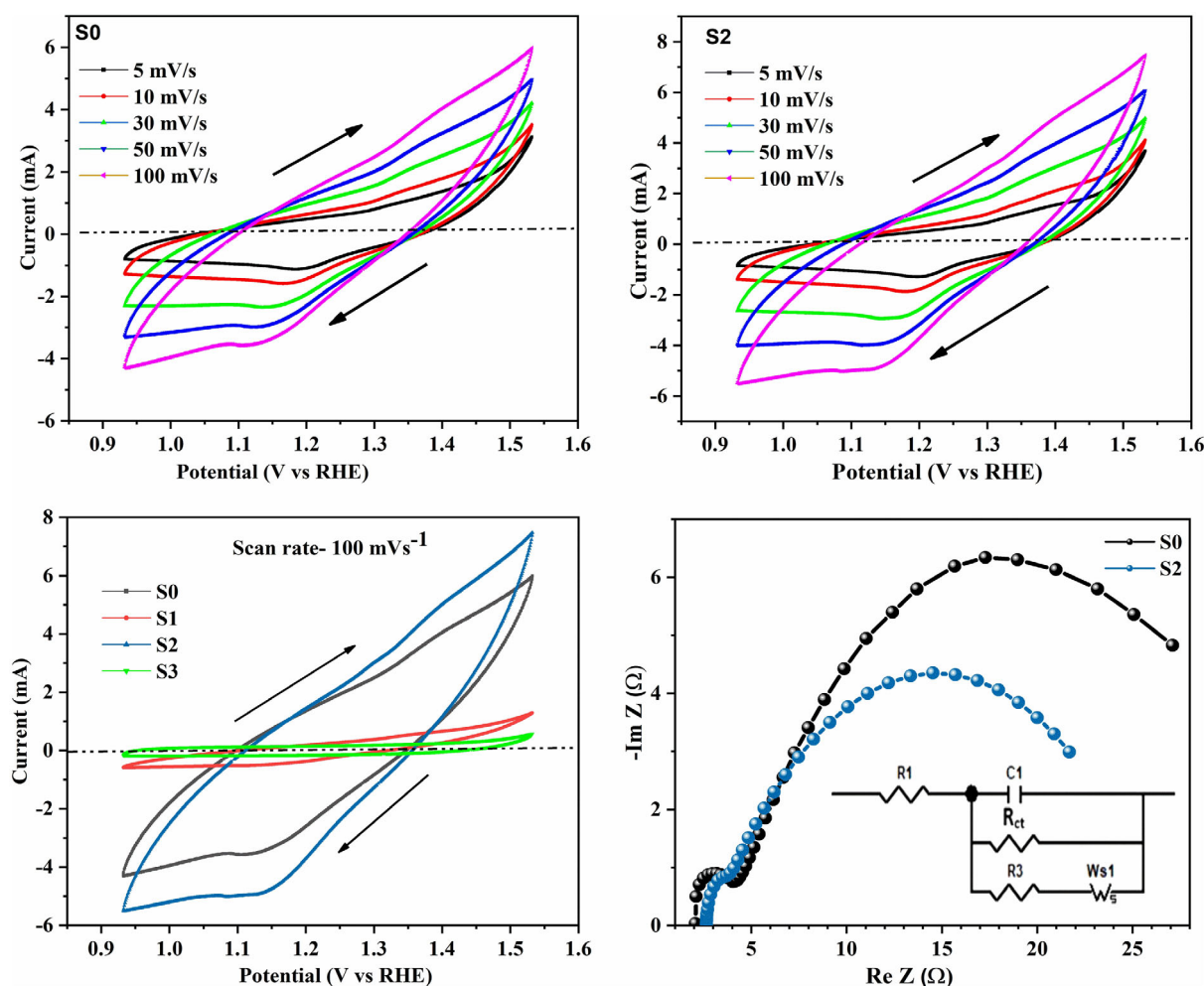


Figure 6. CV curves and Nyquist EIS plot of electrodes fabricated with similar conditions. (Mass of active material ≈ 8 mg, active area ≈ 0.5 cm², supporting electrolyte ≈ 1 molar aqueous KOH solution.).

representing the oxidation (holes) and reduction (electrons) reactions of adsorbed species at the surface of electrode are intrinsically pseudocapacitive in nature.^[51] The electrocatalytic activity (loop area) increased with increasing the applied scan rate which indicates the faster redox reactions at the interfacing contact of material/electrolyte. The mass transport of species during oxidation/reduction can be treated same way as both solid electrodes are fabricated and tested under the same conditions. Therefore, like the distinct photocatalytic behavior for MB dye molecules (Figure 4), the noticeably smaller optical bandgap energy, and more importantly a better electron-hole pairs separation ability of Cu-doped NiTiO₃ sample (S2) over a bare NiTiO₃ sample (S0) resulted in much higher electrocatalytic activities for the heterogeneous catalytic redox reactions. The charge transfer resistance (R_{ct}) of redox reactions occurring at solid/liquid interface is determined from Nyquist plots of EIS measurements (applied voltage = 0.5 V, frequency regimes 1–100 MHz). The internal resistance (electrode/electrolyte) and the equilibrium capacitance are determined by fitting a standard EIS model to Nyquist plots.^[52] The R_{ct} value of the S2 electrode (21.2 ohm) is $\approx 35\%$ lower than that of the S0 electrode (32.9 ohm), which is again

consistent with the previous results obtained for the photocatalytic degradation of MB dye molecules.

Figure 7 shows the GCD curves of S0 and S2 electrodes measured in an aqueous KOH electrolyte solution. The two electrocapacitive parameters of electrode material such as specific capacitance (C ; see Table 1) and energy density (D) are estimated from the GCD curve using the following equations.^[53]

$$C = (I \times t) / (\Delta V \times m) \quad D = (1/2 \times C \times \Delta V^2) \times 0.138 \quad (1)$$

where $I = 0.625$ mA (applied current), t = discharge time (s), $\Delta V = 0.5$ V (potential window), and $m = 8$ mg (mass of active material), respectively. The C and D values of S0 electrode were 381.2 F g⁻¹ and 6.61 Wh kg⁻¹ whereas for S2 they are 450.4 F g⁻¹ and 7.81 Wh kg⁻¹ in 1 molar KOH electrolyte solution, respectively.

The long-term stability of the working material involved in the photo- (electro-) catalytic process is essential. Consequently, cyclic (oxidation/reduction) stability of S2 electrode is calculated (Figure 7) by monitoring the GCD curves. The electrochemical durability of S2 electrode (material) is confirmed as it preserved

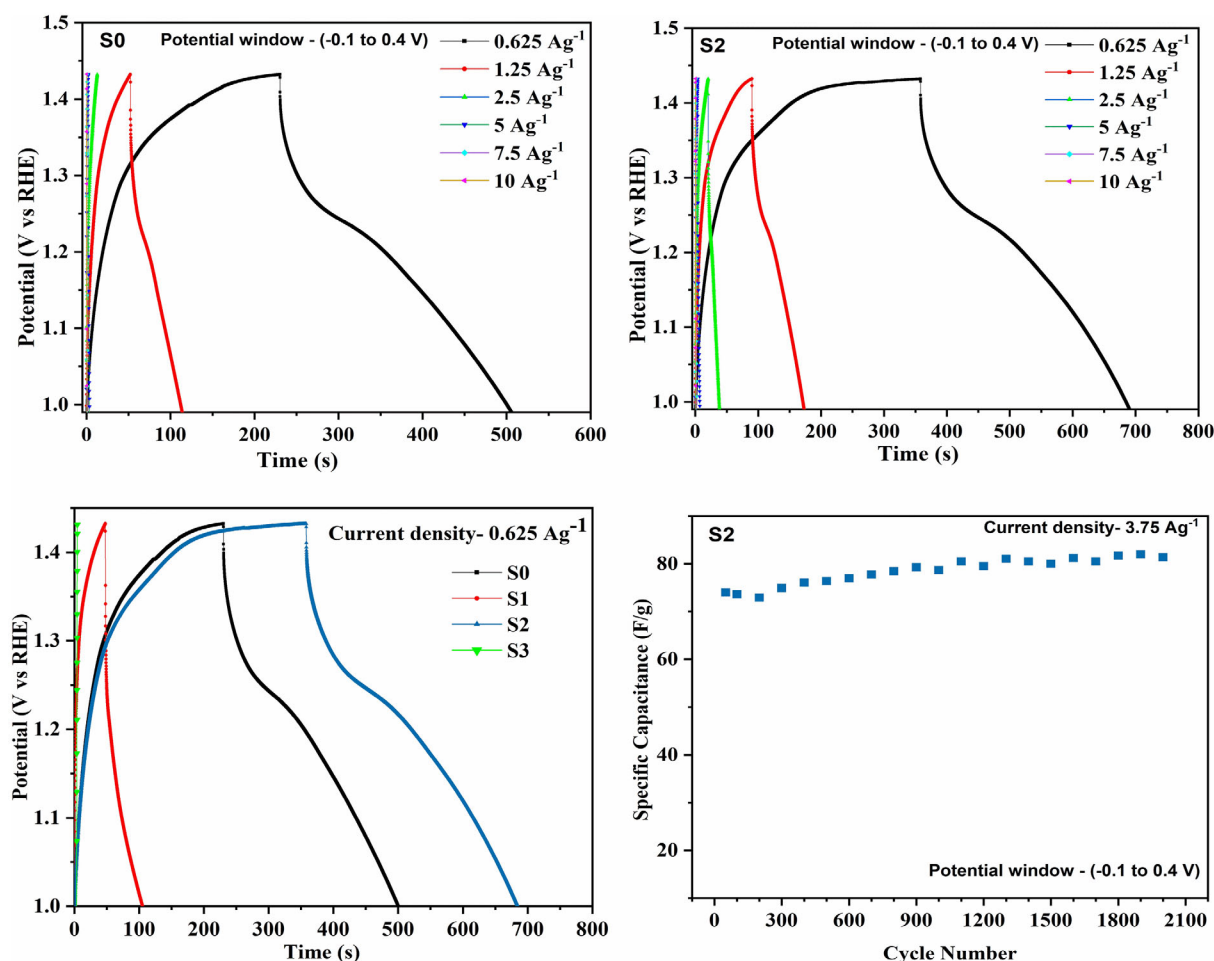


Figure 7. GCD curves and the stability of electrodes. Supporting electrolyte (1 molar aqueous KOH solution).

its initial specific capacitance and retained its initial mass undercharging/discharging testing up to 2000 cycles at an applied 3.75 Ag^{-1} current density.

3. Conclusion

In this work, we used a straightforward sol-gel process to synthesize powders of bare and different Cu-doped NiTiO_3 materials. We demonstrated that the intrinsic charge carrier pairs in NiTiO_3 can be efficiently separated by creating a static lattice deformation. The distortion and subsequent modification of the optoelectronic properties are directly attributed to a large radius size and doping quantity of a degenerate Cu dopant (replacing Ni-sites). Under an optimum static lattice distortion, the photocatalytic and electrocapacitive performance of NiTiO_3 is greatly enhanced by a 2% Cu doping in its rhombohedral unit cell. This substantial and durable enhancement ($\approx 35\%$) in catalytic performance is attributed to an efficient separation of charge carrier pairs. Significantly improved catalytic performance for photocatalytic, electrocatalytic, and electrocapacitive reactions might be achieved by synthesizing the same materials with large surface areas and regulated particle morphologies.

4. Experimental Section

Materials: Until unless specified, all materials were purchased from commercial sources and utilized as received. The following were used: nickel (II) acetate tetrahydrate (Merck life science; 99.95%), copper (II) acetate monohydrate (LOBA India; 98%), titanium (IV) isopropoxide (Sigma-Aldrich; 99.99%), 2-methoxy propanol (SRL India; 99.98%), polyvinylidene fluoride (PVDF; Thermo-Scientific US, 99.9%), N-methyl-2-pyrrolidone (NMP; SRL, extra-pure, 99.5%), conductive graphite sheet (CGS; Nanoshel), activated carbon (SRL; Granular extra pure), a cationic methylene blue (MB) trihydrate dye (green color; Alfa-Aesar), and tripled deionized water (Merk Millipore, resistivity $\approx 18.2 \text{ M}\Omega \text{ cm}$).

Methods: In a typical synthesis of powder material, at ambient room conditions, a light green transparent precursor solution was made inside a Pyrex glass beaker (100 mL) by dissolving the 7 mmol ($\approx 1.724 \text{ g}$) of nickel acetate in 2-methoxy propanol (30 mL) under a constant magnetic stirring (300 rpm, 1 h). Then, a stoichiometric molar amount of titanium (IV) isopropoxide (7 mmol, $\approx 2.07 \text{ mL}$) was quickly and directly injected into the solution which later turned into a transparent gel. After $\approx 3 \text{ h}$, this gel was converted into a green powder by placing it onto a standard hot plate (100°C , 24 h). This powder was then directly annealed in a muffle furnace (ramp rate 5°C min^{-1} , 600°C , air, 6 h), and the furnace was left to cool naturally. The collected powder was gently ground ($\approx 5 \text{ min}$) using a hand with the help of a pestle and mortar. To prepare a Cu-doped NiTiO_3 , an appropriate amount of copper acetate was dissolved in 2-methoxy

propanol prior to adding its counterpart nickel acetate. The rest of the synthesis procedure remains the same.

To fabricate the working electrodes, powder (8 mg), a conducting agent (activated carbon, 1 mg), and a binder (PVDF, 1 mg) were mixed using a pestle-mortar for 1 min duration and then 1 drop (0.1 mL) of solvent (NMP) was added to form a slurry, which was then pipetted, and pasted onto half of the portion of CGS sheet and dried at 80 °C for 12 h in a laboratory oven.

Characterization Techniques: The phase, purity, crystallite size, optical absorbance, diffuse reflectance, bandgap energy, charge-pair separation characteristics, particle size/shape morphology, elemental state, and chemical composition of powders were mapped out by using techniques like XRD (Panalytical X'Pert-Pro, Cu-K α , $\lambda = 1.5415$ Å), UV-vis spectroscopy (Cary-spectrophotometer WinUV-5000, Agilent Technologies), PL spectroscopy (RIMS spectrometer; excitation source LED laser, 385 nm), X-Ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific USA; Al-K α radiation source, 1486.6 eV; calibrating reference C1s peak at 284.6 eV), SEM (Carl Zeiss EVO-18), and SEM-EDX.

Photocatalytic Test: Photocatalytic activity of powders was tested by measuring the degraded amount of MB dye under continuous light illumination (Techinstro vision; Hg-lamp, 250 W, $\lambda > 355$ nm). An aqueous solution containing MB dye (10^{-5} mol L $^{-1}$) was used for photocatalytic test. The powder (10 mg) was added to this solution (100 mL) under mild stirring, and this dispersion was agitated in the dark condition (30 min) to achieve the adsorption-desorption equilibrium of MB molecules onto particle surfaces. After 30 min, the dispersion was then continuously kept under light illumination for the period of 4 h. For a fixed time interval, the absorption spectra of the supernatant liquid (5 mL) extracted through the centrifuge process (3000 rpm, 3 min) from the above dispersion were analyzed using a UV-vis spectrophotometer (Shimadzu UV-1800).

Electrochemical Tests: The electrochemical characterization of electrode was carried out using CV, GCD, and Nyquist plot of electrochemical impedance spectroscopy (EIS) techniques. All electrochemical tests were repeated at least twice to check the reproducibility using a standard three-electrode configuration (Potentiostat, EC-Lab Express software, VSP-300) in a standard 1 M aqueous KOH electrolyte solution (pH = 14). KOH is used as it has a small desolvation energy of K ions, a faster diffusion of K ions over electrode/electrolyte interface, and a lower standard potential of a redox electrolyte (K/K $^{+}$). In the working electrode, the mass (m) and the area of active solid material in direct contact with electrolyte solution were 0.8 mg and 0.25 cm 2 respectively. Platinum wire and Ag/AgCl (3.5 M KCl) are used as counter and reference electrodes respectively. The potentials reported in this work were converted to the reversible hydrogen electrode (RHE) using the equation. $E_{RHE} = E_{Ag/AgCl} + 0.205 + 0.059 \times \text{pH}$.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

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

Keywords

carrier separations, electrocatalysts, lattice distortions, optoelectronics, photocatalysts

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