Engineered Electronic States of Transition Metal Doped TiO₂ Nanocrystals for Low Overpotential Oxygen Evolution Reaction

Nitish Roy,† Youngku Sohn,‡ Kam Tong Leung,§ and Debabrata Pradhan*†

†Materials Science Centre, Indian Institute of Technology, Kharagpur 721 302, W.B., India
‡Department of Chemistry, Yeungnam University, Gyeongsan, Gyeongbuk 712-749, Korea
§Department of Chemistry, University of Waterloo, Waterloo N2L 3G1, Ontario Canada

ABSTRACT: Electrochemical oxygen evolution reaction (OER) involves high overpotential at the oxygen evolving electrode and thereby suffers significant energy loss in the proton exchange membrane water electrolyzer. To reduce the OER overpotential, precious ruthenium and iridium oxides are most commonly used as anode electrocatalyst. Here we report marked reduction in overpotential for the OER using transition metal (TM) doped TiO₂ nanocrystals (NCs). This reduction in overpotential is attributed to d-orbitals splitting of the doped TMs in the TM-doped TiO₂ NCs and their interactions with the oxyradicals (intermediates of OER) facilitating the OER. The d-orbital splitting of TMs in TM-doped TiO₂ NCs is evident from the change in original pearl white color of undoped TiO₂ NCs and UV–vis absorption spectra.

1. INTRODUCTION

TiO₂ is a prototype oxide material that has extensive applications in the field of photocatalytic degradation of organic contaminants, water splitting, pigments, self-cleaning, and dye sensitized solar cells.¹⁻⁵ Although TiO₂ is widely considered as a stable and potential catalyst for photochemical water-splitting reaction, it is poorly active for electrochemical oxygen evolution reaction (OER) and thus scarcely studied. Nonetheless, TiO₂ is a self-doped n-type material that has oxygen vacancy within its crystal. Such oxygen vacancy affects the physicochemical properties of TiO₂. In particular, oxygen vacancy reduces the band gap and hence increases the light absorption property.⁶,⁷ In addition, surface oxygen vacancy serves as an electron donor center, an active site for heterogeneous catalysis, and enhances the electrical property, which has strong influences on the photocatalytic and photoelectrochemical properties of TiO₂.⁸ One of the simple ways to tune the oxygen vacancy is doping the metals or transition metals (TMs) within the crystal without changing the TiO₂ crystal structure and hence keeping the characteristics feature of TiO₂ intact while enhancing the aforesaid properties. For example, Nb-doped TiO₂ has recently been reported as a cathode catalyst for the oxygen reduction reaction of polymer electrolyte membrane (PEM) fuel cells.⁹ Chevallier et al. demonstrated high stability with Nb-doped TiO₂ based catalyst support materials for the oxygen reduction reaction in a PEM fuel cell.¹⁰ However, there are fewer studies on TiO₂ as electrocatalyst for OER.

One of the major challenges for a PEM water electrolyzer is to find an inexpensive electrocatalyst to replace commonly used precious metal oxides such as Ir₂O₃ and RuO₂ in the anode to reduce the overpotential of OER.¹¹⁻¹⁴ Thus, in recent years, attention has been focused on the preparation of inexpensive and non-noble metal oxide catalysts that could reduce the OER overpotential and improve the electrocatalytic activity.¹⁵ This includes perovskites,¹⁶ metal oxides,¹⁷ and metal hydroxides/oxyhydroxides.¹⁸,¹⁹ In particular, recently Hu et al. reported improved OER activity of IrO₂/Nb-TiO₂ catalyst as compared to unsupported IrO₂ catalyst.¹¹ This suggests the potential for TiO₂ as an electrocatalyst in addition to its advantageous properties of high thermal and chemical stability, lost cost, and commercial availability. Recently, Cai et al. reported enhanced OER with Co-doped TiO₂ nanowires synthesized by the sol–flame process.²⁰ A few other recent reports also confirm the reduction of OER overpotential with TM-doped TiO₂.²¹,²² However, the exact rationality behind such improved performance remains unclear. Here we report reduced overpotential of OER using TM-doped TiO₂ nanocrystals (NCs) synthesized by a facile low-temperature hydrothermal technique. This reduced overpotential is attributed to d-orbital splitting of TMs in TiO₂ NCs producing midgap energy states as confirmed from the UV–vis absorption spectroscopy. The d-orbital splitting of three TMs (Fe, Co, and Cu) and their role in OER overpotential is discussed in the present report.

Received: August 21, 2014
Revised: December 2, 2014
Published: December 3, 2014
2. EXPERIMENTAL DETAILS

2.1. Materials. All the chemicals were analytical grade and were used as received without further purification. Titanium tetraisopropoxide (TTIP) (98.999%), Cu(NO₃)₂·3H₂O, Fe(SO₄)₂·7H₂O, Co(NO₃)₂·6H₂O, tetraethyl ammonium hydroxide (TBAH) [(C₂H₅)₄NOH in 0.1 N aqueous], and diethanolamine (DEA) were purchased from Merck.

2.2. Synthesis of TM-Doped TiO₂ NCs. In a typical synthesis, 3 mmol of TTIP was added to a mixture of TBAH (40 mmol) and DEA (160 mmol), and the solution was stirred for 5 min at room temperature. Then the viscous solution was transferred to a Teflon-lined stainless steel autoclave and heated at 225 °C for 24 h. After the heat treatment, the autoclave was allowed to cool to room temperature naturally and the product was collected by centrifuge and washed with water and ethanol several times. The final product was dried in air at 60 °C for 24 h. The overall yield of the product was 90–95%. TM-doped TiO₂ NCs was synthesized by adding the corresponding salt of TM (2 mol %) to the solution of TBAH and DEA. Then the solution was sonicated for 30 min to completely dissolve the TM salt. The rest of the procedure was kept the same. All the samples were calcined at 500 °C for 2 h in air before the characterization and electrochemical measurements.

2.3. Material Characterization. The microstructure of the as-synthesized products was examined with a JEM-2100 (JEOL) Transmission Electron Microscope (TEM) operated at 200 kV. The crystallographic phases of the as-synthesized products was obtained by a PANalytical high resolution powder X-ray diffractometer (HR-XRD) [PW 3040/60] operated at 40 kV and 30 mA, using Cu Kα X-rays. UV–vis absorption measurements were carried out with a Cary 5000 UV–vis–NIR spectrophotometer (Agilent Tech.). The Raman measurements were carried out with a SENTERRA dispersive Raman microscope (BRUKER) at room temperature. The X-ray photoelectron spectroscopy (XPS) study was performed with use of a Thermo-VG Scientific ESCALab 250 microprobe and PHI 5000 VersaProbe II Scanning XPS Microprobe with a monochromatic Al Kα source (1486.6 eV).

2.4. Electrocatalytic Study. Electrochemical measurements were carried out with a Bipotentiostat (CH Instruments, Model: 760E) in a three-electrode system, using 1 M H₂SO₄ and in 0.1 M KOH electrolyte. The pristine and TM-doped TiO₂ NCs coated glassy carbon was used as the working electrode. Platinum wire and Ag/AgCl served as counter and reference electrodes, respectively. The potential scale was calibrated to a standard hydrogen electrode (SHE) using a 1 MH₂SO₄ electrolyte.

3. RESULTS AND DISCUSSION

The TM doping into the TiO₂ NCs was confirmed by XRD analysis, Raman scattering, and optical measurements. Figure 1 shows the XRD patterns of pristine or undoped and TM-doped TiO₂ NCs. The diffraction features are well matched and indexed as per reference pattern (JCPDS: 00–002–0387) of pure tetragonal anatase TiO₂ suggesting that the anatase crystal structure of TiO₂ NCs does not change upon TM doping. The absence of diffraction features from TM indicates no precipitate formation of doped metal inside the NCs. In all the samples, the (101) diffraction feature is found to be the strongest indicating the major crystal growth along the same plane of undoped TiO₂. Moreover, apparent shift in 2θ values (inset, Figure 1) is ascribed to TM doping. The major diffraction from the (101) Bragg plane shifted to lower 2θ, i.e., 25.55° for undoped TiO₂ NCs to 25.35° for Cu-doped TiO₂ NCs due to the lattice expansion. As the ionic size of Ti(IV) is smaller than that of corresponding TMs (II) in the same series of the periodic table, TM doping increases the crystal volume resulting in the downward shift of 2θ values.

The TM doping introduces heterogeneity (due to difference in elemental property of TM and Ti in the TiO₂ crystal) in the pristine TiO₂ crystal system which has a direct effect on the band length, bond energy, as well as bond polarizability. Therefore, Raman scattering is a useful technique to analyze the TM-doped TiO₂ NCs. Figure 2 shows the Raman spectra of undoped and TM-doped TiO₂ NCs. All six active Raman modes (A₁g + 2B₁g + 3Eg) in anatase TiO₂ are assigned and shown in Figure 2. The Raman peak at 141 cm⁻¹ is due to the symmetric stretching of Ti–O–Ti bonds whereas peaks at 379 and 514 cm⁻¹ are due to symmetric and antisymmetric bending vibrations, respectively. As shown in the inset of Figure 2, an obvious shift in Raman scattering is observed for the strongest Eg(1) mode of Cu-doped TiO₂ NCs which is shifted to a higher frequency. In particular, the Eg(1) Raman mode of Cu-doped TiO₂ NCs is significantly shifted to 153 cm⁻¹ from 141 cm⁻¹ for undoped TiO₂ NCs (inset, Figure 2). This shift is due to the change in bond polarizability and strength of the Ti–O bond upon TM doping.

XPS analysis was carried out to further ascertain the doping of TM into TiO₂ NCs and their oxidation states. Figure 3a shows the Ti 2p XPS region spectra of undoped and TM-doped TiO₂ NCs. The Ti 2p₃/₂ and 2p₁/₂ photoelectron peaks of undoped TiO₂ NCs are symmetric in nature and their binding energy (BE) positions are at 459.46 and 465.20 eV, respectively, revealing the Ti⁴⁺ state. The spin–orbit splitting energy of 5.74 eV matches the literature value. The Ti 2p peaks of Ti in TM-doped TiO₂ NCs are also identical with the
undoped one except for a slight positive shift in BE (0.14 eV for 2p3/2 and 2p1/2) suggesting the substitution of Ti(IV) by TMs.28,29,31,32 This BE shift is due to the movement of electron cloud toward electronegative TMs. For example, as the Fermi levels of copper oxides are lower than that of TiO2, electrons cloud would shift toward the Cu atom in the lattice. This would create a slight positive charge on the Ti atom leading to positive shift in BE of Ti 2p for the doped sample.33 A similar positive shift in BE was found in the case of O 1s BE of TM-doped TiO2 NCs (Figure 3b−e).34 Figure 3b shows the O 1s XPS region spectrum of undoped TiO 2 NCs. The O 1s feature is deconvoluted to two peaks, centered at 530.62 and 531.49 eV, which can be assigned to the lattice oxygen of oxide and the adsorbed oxygen at the surface, i.e., hydroxide, respectively. Similar O 1s XPS features are observed for the TM (Fe, Co, and Cu)-doped TiO2 NCs (Figure 3, c, d, and e, respectively). The absence of additional O 1s features in the TM-doped TiO2 NCs suggests that TM-oxide cluster formation did not occur in the doped samples.28 On the contrary, the BE position of O 1s is found to be shifted from 530.62 to 530.90 eV revealing the formation of skeleton −O−TM−O−TM−/−O−TM−O−Ti−. This positive shift of O 1s BE (of 0.28 eV) is due to the heteroneighbor atoms [(Fe(II), Co(II), and Cu(II)]] in the skeleton. The positive shift of the O 1s BE position in the TM-doped TiO2 NCs is found to follow the order Fe-TiO2 < Co-TiO2 < Cu-TiO2 as electronegativity increases with increase in the atomic number of TM (Figure 3b−e).

The oxidation states of the doped-TMs are further obtained through the XPS analysis. Panels f, g, and h of Figure 3 show the Fe 2p, Co 2p, and Cu 2p XPS region spectra of the corresponding TM-doped TiO2 NCs, respectively. The BE positions of Fe 2p3/2 and 2p1/2 of Fe-TiO2 NCs are found at 709.44 and 722.89 eV, respectively, confirming the Fe(II) state.35 The Fe region XPS spectrum shows a broad satellite peak around 716 eV, i.e. 6.5 eV above the 2p3/2 position, further suggesting the Fe(II) state in Fe-TiO2 NCs.36−38 The BE of Co 2p photoelectron peaks are found at 780.95 eV (2p3/2) and 796.56 eV (2p1/2), which suggests the Co(II) chemical state in Co-TiO2 NCs.24 The XPS region spectra of Co displays satellite peaks at ~787 and ~802 eV revealing the high spin Co(II) state with complex transitions.24,39,40 The Cu 2p XPS spectrum (Figure 3h) shows Cu(II) 2p3/2 (932.67 eV) and 2p1/2 (952.83 eV) BE matching the reference values.32,41 The XPS analysis revealed that all the doped TMs in the TiO2 NCs are in the +2 oxidation state.

The morphology, size, and shape of TiO2 NCs were further characterized by TEM and high resolution TEM (HRTEM) analysis. Figure 4 shows representative TEM and HRTEM images of TiO2 and Cu-TiO2 NCs. The size of the undoped

Figure 2. Raman shifts of undoped and TM-doped TiO2 NCs depicting different vibrations of anatase TiO2. The inset shows the shift of Eg(1) peak indicating change in Ti−O bond polarizability of TM-doped TiO2 NCs.

Figure 3. (a) Ti 2p XPS region spectra of undoped and TM-doped TiO2 NCs. O 1s region spectra of (b) undoped TiO2 NCs, (c) Fe-TiO2 NCs, (d) Co-TiO2 NCs, and (e) Cu-TiO2 NCs. XPS region spectra of (f) Fe 2p of Fe-TiO2 NCs, (g) Co 2p of Co-TiO2 NCs, and (h) Cu 2p of Cu-TiO2 NCs.
TiO$_2$ NCs (Figure 4a) varies in the range of 20–40 nm. Figure 4b shows a HRTEM image clearly revealing the single crystalline nature of the NCs. The lattice fringe spacings were measured to be 0.48 and 0.35 nm corresponding to (002) and (101) planes of anatase TiO$_2$, respectively.$^{12,43}$ Figure 4c shows the Cu-doped TiO$_2$ NCs, which reveals that the morphology of NCs does not change significantly upon doping, although the average size of the Cu-TiO$_2$ NCs increases from 30 to 40 nm. The increase in size could be due to the incorporation of TM salts into the reaction mixture and thereby increases the hydrolysis rate. The HRTEM image (Figure 4d) of Cu-TiO$_2$ NCs shows continuous lattice fringes further suggesting that the crystallinity remains with doping of Cu(II) in the lattice of TiO$_2$ NCs. Similar larger sized nanoparticles (30–50 nm) are obtained for Fe-doped (Figure S1(a,b), Supporting Information) and Co-doped (Figure S1(c,d), Supporting Information) TiO$_2$ NCs. The HRTEM images (Figure S1(b,d), Supporting Information) of Fe- and Co-TiO$_2$ NCs further suggest their highly crystalline nature.

The optical properties of TM-doped TiO$_2$ NCs were characterized by UV–vis absorption spectroscopy. The white color of undoped TiO$_2$ is found to be changed upon doping the TMs as shown in the digital photographs (top panel of Figure S). The Fe$^\text{2+}$, Co$^\text{2+}$, and Cu$^\text{2+}$-doped TiO$_2$ NCs powder appear reddish, olive, and sky-blue, respectively. This change in color is ascribed to doping of TM as confirmed by peak shift in the XRD, Raman scattering, and XPS analysis. Figure 5a shows the UV–vis absorption spectra of undoped and TM-doped TiO$_2$ NCs revealing their light absorption properties. Absorbance sharply increases at ~400 nm for the undoped TiO$_2$ NCs, due to the electronic transition from valence band (VB) to conduction band (CB) matching the band gap (~3.1 eV) of TiO$_2$ and absorption remains low at higher wavelength (~400 nm). However, in addition to increased absorbance below 400 nm, TM-doped TiO$_2$ NCs absorb substantially in the visible region with the broad absorption maxima at around 500 (Fe-TiO$_2$), 525 (Co-TiO$_2$), and 600 nm (Cu-TiO$_2$ NCs). The absorption in the visible region indicates multiple midgap states transitions in the TiO$_2$ NCs. The transitions in the visible region can be explained on the basis of d-orbital splitting of TM in the doped TiO$_2$.44 Panels b, c, and d of Figure 5 show the UV–vis absorption spectra of Fe-, Co-, and Cu-doped TiO$_2$ NCs and their deconvoluted absorption peaks with fit factor values. The fit factor value ($R^2$) of greater than 0.99 suggests the well-fitted deconvolution plots in all the cases.

UV–vis absorption spectra of TM-doped TiO$_2$ NCs clearly reveal the multiple electronic transitions. The VB and CB of TiO$_2$ are composed of multiple energy levels in TiO$_2$ NCs.45 The VB of TiO$_2$ NCs is composed of Ti–O σ, Ti–O π, and O π molecular orbitals (MOs). On the other hand, there are two theoretical CBs (lower and upper).46 The lower CB is composed of Ti–Ti σ, Ti–Ti σ*, Ti–Ti π, Ti–Ti π*, and Ti–O π* MOs while the upper CB has Ti–O σ* MO.47 Although the VB and CB are made up of different MOs, VB and CB have significantly different energy levels.47 This is due to the higher electronegativity of O 2p than that of Ti 3d orbitals. The doped TM or nonmetal thus interacts with different MOs of TiO$_2$, resulting in a change in the optical properties of TiO$_2$. For example, in the nitrogen- or carbon-doped TiO$_2$, 2p states of carbon or nitrogen produce a localized state above the VB of TiO$_2$.48,49 Similarly, TMs [e.g., Cu(II), Fe(II), or Mn(II)] produce the energy states above the VB and below the CB, thereby narrowing the energy gaps between the different energy levels.47,50 The 3d-orbitals of the dicaticonic TMs in between the VB and CB of TiO$_2$ NCs can split if the geometry of the host crystal is maintained.51 Interaction of 3d orbitals of TMs with O$^{2-}$ of TiO$_2$ in an
The octahedral field is known to produce three sets of MOs: (a) $\pi^*$ due to interaction of the $T_{2g}$ level of TM with the O $p_z$ orbital, (b) $\sigma^*(1)$ due to interaction of the $d_{x^2}$ of TM and the O $p_z$ orbital, and (c) $\sigma^*(2)$ due to interaction of the $d_{x^2-y^2}$ of TM with the O $p_z$ orbitals. The energy level of $\pi^*$ orbitals of TM-doped TiO$_2$ NCs shifts toward the VB maxima with an increase in atomic number of TM, i.e., the energy level of $\pi^*$ follows the order Cu(II) < Co(II) < Fe(II).55 On the other hand, energy levels of $\sigma^*(1)$ and $\sigma^*(2)$ are shifted upward and downward, respectively, as the atomic number of the dopant TM increases. The different electronic transitions obtained in the UV–vis spectra are therefore due to the formation of MOs which are formed upon interaction of 3d orbitals of TM with the O 2p orbitals of TiO$_2$ in the octahedral field. The probable energy levels of these MOs [$\sigma^*(1)$, $\sigma^*(2)$, and $\pi^*$] are displayed in Scheme 1. The absorptions at ~840 (1.4 eV), 800 (1.5 eV), and 700 nm (1.7 eV) are assigned to the electronic transition $\pi^* \rightarrow \sigma^*(1)$ for Fe-, Co-, and Cu-doped TiO$_2$ NCs, respectively, correlated with UV–vis absorption spectra (Figure 5). It should be noted that the energy of the peak positions in the UV–vis absorption spectra is within the ±0.1 eV of transition energies marked in Scheme 1 for TM-doped TiO$_2$ NCs. This could be due to the slight change in VB and CB positions upon doping and/or bigger size of the dicationic TMs which introduces a slight distortion in geometry with respect to the pristine TiO$_2$.52 The reddish (Fe-TiO$_2$), olive (Co-TiO$_2$), and sky-blue (Cu-TiO$_2$) colors can therefore be explained on the basis of deconvoluted absorption peaks (Figure 5b–d) of TM-doped TiO$_2$ NCs. The strongest absorption at 540 nm (2.3 eV) for Fe-TiO$_2$ NCs corresponds to the $\pi^* \rightarrow \sigma^*(2)$ transition (Figure 5b, Scheme 1b) correlating blue-green light and the complementary violet-reddish color is observed for the Fe-doped TiO$_2$ powder (Figure 5a,b, top panel). However, Co-TiO$_2$ shows two equally strong absorption peaks at 475 (2.6 eV) and 600 nm (2.1 eV) corresponding to $\pi^* \rightarrow \text{CB}$ and VB $\rightarrow \sigma^*(1)$ or $\pi^* \rightarrow \sigma^*(2)$ transitions, respectively (Figure 5c, Scheme 1c). These two absorption peaks correspond to blue and orange light with their complementary emission colors yellow and blue producing an olive Co-TiO$_2$ powder. The Cu-TiO$_2$ NCs show a strong and broad absorption peak at 600 nm (orange light) corresponding to VB $\rightarrow \sigma^*(1)$ or $\pi^* \rightarrow \sigma^*(2)$ transition (Figure 5d, Scheme 1d) and thereby the complementary blue Cu-TiO$_2$ NCs powder was obtained (Figure 5a,d, top panel). Thus, the origin of TM-doped TiO$_2$ NCs powder color can be explained by the d-orbitals splitting and the formation of midgap states in between the VB and CB of TiO$_2$ NCs.

The TM-doping in TiO$_2$ NCs substantially changes its optical and electronic properties that have strong correlation to the photocatalytic properties. To find the role of TM doping, we studied the electrocatalytic properties (i.e. OER) of present low temperature hydrothermally synthesized TM-doped TiO$_2$ NCs. Figure 6a shows the typical Mott–Schottky plots obtained with 1 M H$_2$SO$_4$ at 500 Hz. The positive slopes confirm the n-type nature of both the undoped and TM-doped TiO$_2$ NCs. The donor density ($N_d$) of undoped and TM-doped TiO$_2$ NCs were estimated by using the following equation, $N_d = [2/(\varepsilon_e \varepsilon_0 A C^2)](E - E_FB - (kT/\varepsilon))$, where $\varepsilon$ is the charge of an electron, $C$ is the electrode capacitance, $\varepsilon$ is the dielectric constant of TiO$_2$ (55), $\varepsilon_0$ is the vacuum permittivity, $E$ is the applied potential, $E_{FB}$ is the flat band potential, $k$ is the Boltzmann constant, $T = 298 K$, and $A$ is the electrode area in cm$^2$ (0.07 cm$^2$).54 The slope of the curve measures the extent of doping concentration. The lower the slope, the higher is the doping concentration (Figure 6a). The donor densities are estimated to be ~9.4 × 10$^{18}$ (undoped TiO$_2$ NCs), 1.3 × 10$^{20}$ (Fe-TiO$_2$ NCs), 1.6 × 10$^{20}$ (Co-TiO$_2$ NCs), and 2.5 × 10$^{20}$ cm$^{-3}$ (Cu-TiO$_2$ NCs). Figure 6b shows linear sweep voltammetry curves for undoped and TM-doped TiO$_2$ NCs, depicting the OER activity. The OER begins at ~1.45 V ($\eta = 0.22$ V) for undoped TiO$_2$ NCs with respect to the standard hydrogen electrode (SHE), where $\eta$ is the overpotential. This potential for OER is found to be drastically reduced to ~1.12 V ($\eta = -0.11$ V) for the TM-doped TiO$_2$ NCs due to the decrease in the overpotential of 0.33 V. Similar reduction in overpotential of 0.31 V was also observed in 0.1 M KOH electrolyte (not shown). This improved electrocatalytic property is ascribable to the change in electronic band position of TM-doped TiO$_2$ NCs. Recently Shi et al. reported improved...
representative well-known oxidation potentials for different moieties in OER for Cu-TiO2 NCs and its electronic energy band positions of midgap states, i.e. $\sigma^*(1)$ and $\sigma^*(2)$ (based in Scheme 1), which are formed due to TM (Cu) doping with respect to SHE.66–68 The $\sigma^*(1)$ and $\sigma^*(2)$ MOs are axis directed in an octahedral field and their energy levels lie near the peroxide and water oxidation potentials. Therefore, they are likely to interact with the $\sigma$ orbitals of the intermediate species (OOH*, OH*, and O*) thereby reducing the overpotential of OER. The decrease in OER overpotential with the TM-doped catalyst is therefore attributed to the formation of midgap states in between the CB and VB of TiO2 NCs due to d-orbital splitting of TMs. Furthermore, current densities obtained with TM-doped TiO2 NCs are higher than that of undoped TiO2 NCs. The higher current densities with TM-doped TiO2 NCs can be attributed to higher electronic conductivity with increase in their carrier concentrations upon doping as confirmed from the Mott–Schottky plots.

4. CONCLUSIONS

In conclusion, we demonstrate here the improved optical and electrocatalytic properties of hydrothermally synthesized TM-doped TiO2 NCs. The deviation of pearl white pristine TiO2 NCs color for the TM-doped TiO2 NCs is ascribed to the d-orbital splitting of TM and its interaction with the O p orbitals forming MOs [$\pi^*$, $\sigma^*(1)$, $\sigma^*(2)$], in between the VB and CB of TiO2. Such splitting and formation of midgap states significantly increases the light absorption properties in the visible range and improved the electrocatalytic properties due to the interaction of split energy levels with intermediate peroxide species of water oxidation. In particular, TM-doped TiO2 NCs exhibit marked reduction in the overpotential of OER as compared to the undoped TiO2 NCs. Thus, the present study demonstrates that the tuning of energy levels in between the VB and CB is one of the key parameters to the performance of TiO2 NCs as an anode electrocatalyst in PEM water electrolyzers.


