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Nitrogen Doped Reduced Graphene Oxide Based Pt–TiO2 Nanocomposites for Enhanced Hydrogen Evolution

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Supporting Information

ABSTRACT: Electrochemical hydrogen production from water is an attractive clean energy generation process that has enormous potential for sustainable development. However, noble metal catalysts are most commonly used for such electrochemical hydrogen evolution making the process cost ineffective. Thereby design of hybrid catalysts with minimal use of noble metals using a suitable support material is a prime requirement for the electrolys is of water. Herein, we demonstrate the superior hydrogen evolution reaction (HER) activity of the platinum nanoparticles (Pt NPs) supported on faceted titanium dioxide (TiO2) nanocrystals (Pt–TiO2) and nitrogen doped reduced graphene oxide (N-rGO) based TiO2 nanocomposite (Pt–TiO2–N-rGO). The ternary Pt–TiO2–N-rGO nanocomposite exhibits a superior HER activity with a small Tafel slope (~32 mV·dec⁻¹), exchange current density (~0.22 mA·cm⁻²), and excellent mass activity (~3116 mA·mgpt⁻¹) at 300 mV overpotential. These values are better/higher than that of several support materials investigated so far. The excellent HER activity of the ternary Pt–TiO2–N-rGO nanocomposite is ascribed to the presence of Ti(III) states and enhanced charge transportation properties of N-rGO. The present study is a step toward reliable electrochemical hydrogen production using faceted TiO2 nanocrystals as support material.

1. INTRODUCTION

Hydrogen evolution from water by means of electrolysis in alkaline or acid media is of great interest due to the present energy crisis. The potential of hydrogen energy lies in its characteristic features of the lightest molecular weight, high diffusion coefficient, highly ignitability, and easily convertibility into electrical or mechanical energy.1−5 Platinum (Pt) has so far been recognized as an invincible catalyst for the electrochemical hydrogen evolution reaction (HER). Pt shows promising HER activity with very low overpotential, small Tafel slope (~30 mV·dec⁻¹), and high exchange current density (10⁻³ A·cm⁻²).4 However, high cost and scarcity of Pt in the Earth’s crust limit its large scale applications. In recent years, a few noble metal-free catalysts such as MoS2, Ni-based alloys, metal pyrites, and graphene/carbon nanotube composites have been employed for HER.6−9 Generally, these noble metal-free catalysts are found to exhibit a large overpotential and Tafel slope with a small exchange current density.5 In particular, Yoon et al. reported graphene-carbon nanotubes supported molybdenum based composites for stable HER with Tafel slope >50 mV·dec⁻¹ and exchange current density ~10⁻³ A·cm⁻².10 Yu et al. showed the layer dependence HER activity of MoS2 sheets with a Tafel slope ~140 mV·dec⁻¹ and exchange current density of ~10⁻⁷ A·cm⁻².11 There are a few more studies on the noble metal-free catalysts for HER but all of those associated with large overpotential and Tafel slope with a low exchange current density (~10⁻⁵ A·cm⁻²). Although noble metal-free catalysts are highly desirable for cost effectiveness, the large Tafel slope and small exchange current density make them not suitable for practical applications. Therefore, Pt is indispensable and the most attractive catalyst for HER. Pt shows the smallest Tafel slope (29 mV·dec⁻¹), almost zero overpotential, and high exchange current density.1 To improve the cost effectiveness of the system, one of the strategies is to reduce the use of Pt content while achieving high exchange current density with small Tafel slope to increase its mass activity. The mass activity of Pt can be enhanced primarily by (a) nanaoresizing,12 (b) making alloys with the non-noble metals,13 and (c) depositing the subnanometer size Pt nanoparticles (NPs) on suitable support material.14 Recently, a few studies have demonstrated enhanced HER mass activity with the noble or rare-earth based metal catalyst supported on oxide.15 In particular, Khdary et al. reported Pt–SiO2 nanomaterials with mass activity 11.9 A·mgpt⁻¹·mV⁻¹ (or 11.9 mA·mgpt⁻¹·mV⁻¹) at overpotential >250 mV vs saturated calomel electrode (SCE) in 1 M H₂SO₄ solution.15 Zhang et al. reported HER activity of 40 mA·cm⁻² at overpotential 300 mV vs normal hydrogen electrode (NHE) in 0.1 M H₂SO₄ with Pt–SnO2 flower-like nanostructures. They also reported a Tafel slope of 111 mV·dec⁻¹ and exchange current density of 0.46 mA·cm⁻² toward HER.16 Ham et al. studied the Pt NPs decorated W2C microspheres which achieved a mass activity of 476 mA·mgpt⁻¹ and current density...
15.8 mA cm\(^{-2}\) at 10 mV overpotential vs NHE in 1 M H\(_2\)SO\(_4\).\(^{17}\) They reported the Tafel slope of 103 mV dec\(^{-1}\) and enhanced exchange current density of 2.08 mA cm\(^{-2}\).\(^{17}\) In the present study, titanium dioxide (TiO\(_2\)) is demonstrated as a potential and superior support oxide material for Pt NPs that has shown much higher mass activity than that of recently reported works.\(^{3–19}\)

TiO\(_2\) is a well-known self-doped n-type semiconductor catalyst for water splitting reaction whose conduction band (CB) lies just above the HER potential with respect to the standard hydrogen electrode (SHE).\(^{20–22}\) The electronic states in TiO\(_2\) can be tuned in various ways such as reducing its surface,\(^{23,24}\) changing the stoichiometry,\(^{25}\) doping,\(^{26}\) and/or forming composites.\(^{27}\) Among the different strategies used by researchers to modify the electronic states and thus the properties of TiO\(_2\) reduction has recently attracted enormous attention. This is due to the formation of Ti(III) state, which lowers the CB of Ti(IV) by an extent of \(\sim 0.5–1\) eV thereby reducing the band gap.\(^{25,24}\) Ti(III) state in the reduced TiO\(_2\) is reported to show enhanced visible light photoelectrochemical hydrogen production.\(^{23,24}\) In addition, the Ti(III) state in reduced TiO\(_2\) is recently found to exhibit enhanced electrochemical activity toward the electrochemical redox reaction.\(^{28,29}\) Taking advantage of the Ti(III) state of reduced TiO\(_2\) near the HER potential, we synthesized reduced Pt–TiO\(_2\) as potential catalyst material for HER. Furthermore, RGO or doped rGO has recently been shown as a promising support material for improved HER performance.\(^{30–53}\) Hence, several combinations of Pt, TiO\(_2\), and nitrogen (N) doped hydrothermally reduced graphene oxide (N-hrGO) such as TiO\(_2\) on N-hrGO (TiO\(_2\)–N-hrGO), Pt NPs deposited on N-doped reduced graphene oxide (Pt–N-rGO), Pt NPs deposited on TiO\(_2\) NCs (Pt–TiO\(_2\)), and Pt NPs deposited on TiO\(_2\)–N-hrGO nanocomposite (Pt–TiO\(_2\)–N-rGO) hybrid nanomaterials were prepared to study the HER activity. Our findings show an excellent HER performance (very high mass activity, small Tafel slope, and large current density) with ternary Pt–TiO\(_2\)–N-rGO nanocomposite suggesting its potential for hydrogen production. The possible mechanism behind the superior electrocatalytic performance of Pt–TiO\(_2\) and Pt–TiO\(_2\)–N-rGO nanocomposite is discussed in the present article.

2. EXPERIMENTAL SECTION

Materials. Titanium tetraisopropoxide (TTIP) (99.999%), tetrabutyl ammonium hydroxide (TBAH) [(C4H9)4NOH in 0.1 M aqueous], diethanolamine (DEA), graphite fine powder, potassium permanganate (KMnO\(_4\)), sodium borohydride (NaBH\(_4\)), sulfuric acid 98% (H\(_2\)SO\(_4\)), hydrochloric acid 30% (HCl), ethanol (C\(_2\)H\(_5\)OH), isopropyl alcohol (C\(_3\)H\(_7\)OH), and hydrogen peroxide 30% (H\(_2\)O\(_2\)) were purchased from Merck, India. Platinum acetylacetone [Pt(acac)\(_2\)] and 20% Pt/Vulcan (Pt/C) were purchased from Sigma-Aldrich. All the chemicals were used as received.

Synthesis of Graphene Oxide (GO). GO was synthesized by modified Hummers method.\(^{34}\) In a typical synthesis, 2 g of fine graphite powder was added to a concentrated solution of H\(_2\)SO\(_4\) (70 mL, 98%), sonicated for 30 min, and stirred at a temperature below 15 °C. Then 6 g of KMnO\(_4\) was added slowly to the reaction mixture, it was heated in an oil bath at 40 °C for 30 min, and 200 mL of water was added. The reaction temperature was then raised to \(\sim 80\) °C and stirred for another 30 min prior to cooling to room temperature and addition of 500 mL of water. Then \(\sim 8\) mL of 30% H\(_2\)O\(_2\) was added slowly until the color of the reaction mixture turned yellow from dark brown. After addition of H\(_2\)O\(_2\), the reaction mixture was stirred for another 15 min. Then the product was filtered and sequentially washed with DI water, dilute HCl (5%), and DI water. After filtering, the product was dried in vacuum.

In Situ Synthesis of Hydrothermally Reduced Nitrogen Doped GO–TiO\(_2\) (N-hrGO–TiO\(_2\)) Nanocomposites. In situ synthesis of N-hrGO–TiO\(_2\) nanocomposite was performed by taking \(\sim 20\) wt % of as-synthesized dry GO. In a typical synthesis, 40 mg of vacuum-dried GO was dispersed in 40 mL of TBAH and DEA (mol ratio 2:5) mixture and sonicated for 30 min. Then 1 mL of TTIP was added to the above mixture and stirred for a few minutes at room temperature. Then the reaction mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 225 °C for 24 h. After the hydrothermal heat treatment, the autoclave was allowed to cool naturally and the product was collected, washed thoroughly with dilute HCl (5%), water, and ethanol, and finally dried in vacuum.

Synthesis of Hydrothermally Reduced Nitrogen Doped Graphene Oxide (N-hrGO). In order to confirm the N doping in hydrothermal heat treatment of TBAH and DEA with GO, chemically synthesized GO was allowed for hydrothermal heat treatment. In a typical synthesis, 200 mg of GO was added to a mixture of TBAH (20 mL) and DEA (20 mL) and sonicated for 30 min. Then the reaction mixture was transferred into a Teflon-lined stainless steel autoclave and heated at 225 °C for 24 h. After hydrothermal heat treatment, the black colored N-hrGO product was collected and washed in water and isopropyl alcohol. The product was finally dried at 60 °C for 24 h in air.

Deposition of Pt Nanoparticles (NPs) on Cuboid TiO\(_2\) NCs, N-hrGO, and N-hrGO–TiO\(_2\) Nanocomposites. Pt NPs were deposited on the N-hrGO, TiO\(_2\) NCs, or N-hrGO–TiO\(_2\) nanocomposite using Pt(acac)\(_2\) as Pt precursor. Twenty milligrams of TiO\(_2\) or N-hrGO–TiO\(_2\) was taken in 60 mL of water, sonicated for 30 min, and then kept under UV light for 3 h to excite the TiO\(_2\) NCs. Then 30 mL of isopropyl alcohol solution containing 0.5 mg mL\(^{-1}\) Pt(acac)\(_2\) was added to the TiO\(_2\) or N-hrGO–TiO\(_2\) dispersed solution and stirred for another 1 h under UV light. Then 5 mL of freshly prepared aqueous NaBH\(_4\) solution (5 mg mL\(^{-1}\)) was added to the above reaction mixture. After addition of NaBH\(_4\), the reaction mixture was found to turn black from pearl white (for pristine TiO\(_2\) sample only) indicating the formation of Pt NPs. After 1 h of UV light irradiation, an additional 2 mL of NaBH\(_4\) was added to reduce the partially reduced N-hrGO for the N-hrGO–TiO\(_2\) sample. To deposit Pt on N-hrGO, the reaction mixture was not irradiated under UV light, but 20 mg of N-hrGO was dispersed in 50 mL water and sonicated for 30 min. Then 15 mg of Pt(acac)\(_2\) dissolved in 30 mL of isopropyl alcohol was added with constant stirring. Then 5 mL of freshly prepared aqueous NaBH\(_4\) was added and stirred overnight at room temperature to obtain Pt–N-rGO composite.

Characterization. The surface morphology and energy dispersive X-ray (EDX) analysis and microstructure of the products were examined by Carl Zeiss SUPRA field emission scanning electron microscope (FESEM) and TECNAI G2 (FEI) transmission electron microscope (TEM) operated at 200 kV, respectively. The crystallographic phases of the as-synthesized products were obtained by a PANalytical high-resolution powder X-ray diffractometer (HR-XRD) [PW 3040/ 60] operated at 40 kV and 30 mA using Cu K\(_\alpha\) X-rays. The
Raman study was carried out with a SENTERRA dispersive Raman microscope (BRUKER) with an excitation wavelength of 532 nm. The XPS measurement was performed by a Thermo-VG Scientific ESCALab 250 microprobe or a PHI 5000 VersaProbe II Scanning XPS Microprobe with a monochromatic Al Kα source (1486.6 eV).

**Electrochemical Testing.** The electrochemical HER activity of the different nanocomposite samples was tested using a CH Instrument (760 D) bipotentiostat with Pt wire as the counter electrode, Ag/AgCl saturated with KCl as the reference electrode, and disc glassy carbon (GC) electrode as the working electrode. Before the catalyst was loaded onto the disc GC electrode, the electrode surface was washed by sonicating in Millipore water. After the sonochemical cleaning, a slurry of presonicated dispersed catalyst in isopropyl alcohol (10 mg·mL$^{-1}$) was coated onto the GC disc electrode (50 μL) by drop casting. The coating was made with care for uniform thickness of the slurry on GC disc and allowed to dry in vacuum overnight. The electrochemical testing was then carried out in a three-electrode system in 0.1 M H$_2$SO$_4$. The scan rate for all the HER activity testing was 100 mV·s$^{-1}$ unless mentioned. The potential was calibrated with respect to standard hydrogen electrode (SHE) by adding 0.19 V to the

![Figure 1](image1.png)

**Figure 1.** FESEM images of (a) GO, (b) cuboid shaped TiO$_2$ NCs, (c) TiO$_2$–N-hrGO, and (d) Pt–TiO$_2$–N-rGO nanocomposites. Inset of (c) shows magnified FESEM image of the corresponding sample showing TiO$_2$ NCs in between the N-hrGO sheets.

![Figure 2](image2.png)

**Figure 2.** (a, b) TEM images of Pt–N-rGO nanocomposite depicting the sheet structures of N-rGO decorated with chemically reduced Pt NPs. (c) TEM image of Pt–TiO$_2$ NCs showing the selective photodeposition of <5 nm Pt NPs majorly at the edges of the cuboid shaped TiO$_2$ NCs. (d, e, f) Ternary nanocomposite of Pt–TiO$_2$–N-rGO shows the TiO$_2$ NCs in between the N-rGO sheets and deposition of Pt NPs on both TiO$_2$ NCs and N-rGO sheets.
chemical reduction of platinum acetylacetonate [Pt(acac)_2] and − TEM images of Pt found to deposit at the edges of cuboid TiO2 NCs by On the other hand, much smaller size Pt NPs (<5 nm) are The diameter of individual Pt NPs is measured to be 2 on the N-rGO sheets both as individual and as agglomeration. photoreduction under UV light irradiation (Figure 2c) and Figure 1c points to N-hrGO sheet. Figure 1d shows that the Pt in the magnified FESEM image shown as the inset of Figure 1c. The arrow in the inset FESEM image of Figure 1c points to N-hrGO sheet. Figure 1d shows that the Pt NPs are deposited not only on N-rGO but also on TiO2 NCs. The diameter of Pt NPs is found to be extremely small (<5 nm) as marked by the circles in Figure 1d.

TEM analysis was carried out to precisely measure the diameter of Pt NPs and the distribution of the different component in the nanocomposite. Figure 2a and 2b show the TEM images of Pt–N-rGO nanocomposite synthesized by chemical reduction of platinum acetylacetonate [Pt(acac)_2] and N-hrGO. The Pt NPs are found to be nonuniformly deposited on the N-rGO sheets both as individual and as agglomeration. The diameter of individual Pt NPs is measured to be 2–10 nm. On the other hand, much smaller size Pt NPs (<5 nm) are found to deposit at the edges of cuboid TiO2 NCs by photoreduction under UV light irradiation (Figure 2c) and simultaneous coreduction, i.e., photoreduction and chemical reduction by NaBH4 (Figure 2d–f) of Pt(acac)_2 on the pristine cuboid TiO2 NCs without any agglomeration as shown in measured potential obtained with KCl saturated Ag/AgCl reference electrode.

3. RESULTS AND DISCUSSION

Morphology. Figure 1 shows the FESEM images of GO, cuboid TiO2 nanocrystals (NCs), TiO2–N-hrGO, and Pt– TiO2–N-rGO nanocomposites. The GO prepared by the modified Hummers method is found to have sheetlike morphology with uniform exfoliation as shown in Figure 1a. The length and width of the GO sheets vary in the range 1 μm to a few micrometers. Figure 1b shows an FESEM image of hydrothermally synthesized cuboid faceted anatase TiO2 NCs with a size range 100–150 nm along the diagonal with uniform surface morphology.35 Figure 1c and 1d show the FESEM images of TiO2–N-hrGO and Pt–TiO2–N-rGO nanocomposites, respectively. The TiO2 NCs are found to be deposited on N-hrGO and also intercalated in between the N-hrGO sheets as clearly observed in the magnified FESEM image shown as the inset of Figure 1c. The arrow in the inset FESEM image of Figure 1c points to N-hrGO sheet. Figure 1d shows that the Pt NPs are deposited not only on N-rGO but also on TiO2 NCs. The diameter of Pt NPs is found to be extremely small (<5 nm) as marked by the circles in Figure 1d.

XRD and Raman Analysis of the Nanocomposites. The phase analysis and conversion of graphite powder to GO were analyzed by XRD and Raman spectroscopy. Figure 3a shows the XRD patterns of GO and in situ hydrothermally synthesized TiO2–N-hrGO nanocomposite. The diffraction peak at 10.2° in the XRD pattern of GO is assigned to be its intercalated (001) planes.36 In the XRD pattern of TiO2–N-hrGO, the absence of any Bragg signature in the 2θ region of 10–15° suggests the conversion of GO to N-hrGO upon hydrothermal heat treatment during the TiO2 NCs synthesis.36 However, a separate peak for N-hrGO at around ~26° is not distinguishable due to the overlap of strong (101) diffraction peak of anatase TiO2.36,37 All the diffraction features in the XRD pattern of TiO2–N-hrGO nanocomposite is matched with the pure anatase TiO2.3 This suggests that incorporation of GO in the reaction mixture and subsequent hydrothermal heat treatment do not induce any phase transformation to TiO2. To confirm the reduction of GO via hydrothermal heat treatment, GO synthesized by modified Hummers method was hydrothermally treated with only 0.1 N aqueous tetrabutylammonium hydroxide (TBAH) and dieth-
anatase phase of TiO2 (JCPDS: 00-002-0387). Figure 3d shows the Raman spectra of pure graphite powder (Figure 3b). All the Bragg reflections in graphite powder are found to match with the JCPDS reference number 00-025-0284 of graphite. The (002) peaks of N-hrGO and TiO2−N-hrGO are found to shift to a lower Bragg angle (2β) compared to 26.8° in the case of graphite powder. A very weak signature at 210 cm−1 (due to presence of small edge defects in the fine graphite powder) is observed at 2717 cm−1 (D*) and 2937 cm−1 (D + G), and 3246 cm−1 (G*). The D, G, D*, and G* bands of GO are found to be red-shifted due to the introduction of defects in the exfoliated GO sheets (Table 1). These defects are introduced because of multilayers of GO sheets that can be further analyzed using the intensity ratio of I_G/I_D (2.4) ratio is found to be much lower for GO than that of pure graphite (I_G/I_D = ~13) revealing the formation of a multilayer GO sheets synthesized via the modified Hummers method. The D band of N-hrGO in TiO2−N-hrGO nanocomposite is shifted downward to an extent of 30 cm−1 compared to GO (Table 1). This shift could be due to the N doping and/or bonding with TiO2 NCs which induce strain and defects in N-hrGO.40 In addition to imposed defects and strain by doping, this red shift could also be ascribed to the downward shift of Fermi level (E_F) of N-hrGO as compared to GO.40,41 The different Raman modes of TiO2 are assigned for TiO2−N-hrGO in Figure 3d. All the Raman modes of TiO2 in TiO2−N-hrGO are found to shift ±5 cm−1 compared to the reported values; e.g., E_g(1) peak shifts from 141 to 145 cm−1, E_g(2) peak shifts from 637 to 632 cm−1, A_{1g} peak shifts from 397 to 394 cm−1, and (A_{1g} + B_{1g}) peak shifts from 514 to 520 cm−1.40

**Surface Composition of the Nanocomposites.** X-ray photoelectron spectroscopy (XPS) is employed to measure the surface composition and chemical states of the element present and the nature of bonding in the as-synthesized nanocomposites. Figure S1 in the Supporting Information shows the survey spectra of pristine TiO2, Pt−TiO2, Pt−TiO2−N-hrGO, and TiO2−N-hrGO samples. The binding energy (BE) of photoelectron peaks were calibrated with C 1s peak at 284.5 eV. In addition to the expected elements present, the samples containing rGO show N 1s XPS peak (Figure S2) indicating the N-doping/bonding in rGO. It is to be noted that DEA and TBAH were used in the synthesis of TiO2-based rGO nanocomposites (TiO2−N-hrGO and Pt−TiO2−N-rGO). It is evident that hydrothermal heat treatment reduces the GO to rGO which is also confirmed by XRD analysis (Figure 3b) in the present work.42 Although nitrogen is not doped in TiO2 NCs, it can be doped into the GO sheets upon hydrothermal heat treatment.35,43 In order to confirm the N-doping in GO containing nanocomposites, XPS analysis was carried out on the N-hrGO and compared with GO as shown in Figure S3. Part (a) of Figure S3 shows the XPS survey spectra of GO and hydrothermally treated GO, i.e., N-hrGO. The atomic % of oxygen is found to decrease from 29% (for GO) to 23% (for N-hrGO) suggesting that hydrothermal heat treatment leads to

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<th>Table 1. Peak Positions of D and G Bands and Their Overtones in the Graphite, GO, and TiO2−N-hrGO Nanocomposite</th>
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Figure 4. (a, c, e) Ti 2p and (b, d, f) O 1s region XPS spectra of (a, b) TiO2−N-hrGO, (c, d) Pt−TiO2, and (e, f) Pt−TiO2−N-rGO nanocomposites.
partial reduction of GO to N-hrGO which is in accord with the XRD analysis (Figure S3a and Figure 3b). In addition, N-doping occurs as revealed by the presence of N 1s photoelectron peak in the surface survey of N-hrGO (Figure S3a). The details on the type of bonding are further confirmed by the C 1s and N 1s XPS region spectra (Figure S3b–d). Parts (b) and (c) of Figure S3 in the Supporting Information show the C 1s region spectra of GO and N-hrGO, respectively. The C 1s of GO shows two different distinct photoelectron peaks at 284.5 eV (C-1) and 286.7 eV (C-3), which can be assigned to the C-C sp$^3$ and C-O/C=O and/or O=C=O photoelectron peaks, respectively. The deconvolution of C 1s of N-hrGO exhibits three different photoelectron features which are assigned to C-C at 284.5 eV (C-1), C-N/C=O at 285.9 eV (C-2), and C=O/O=C=O at 286.5 eV (C-3). Similarly, deconvoluted N 1s region spectra shows three different photoelectron peaks at 399.1, 399.8, and 401.3 eV in N-hrGO, which are assigned to pyridinic-N (N-6), pyrrolic-N (N-5), and quaternary-N (N-Q), respectively (Figure S3d).

Figure 4a, c, e and 4b, d, f show the XPS region spectra of Ti 2p and O 1s, respectively, in TiO$_2$–N–hrGO, Pt–TiO$_2$, and Pt–TiO$_2$–N–rGO nanocomposites. The BE of Ti 2p photoelectron peaks in TiO$_2$, N–hrGO nanocomposite is found to be broader (full width at half-maximum (FWHM) of Ti 2p$_{3/2}$ peak is 2.2 and 2.4 eV, respectively) than that of Ti 2p of TiO$_2$–N–hrGO nanocomposite (FWHM is 1.3 eV) (Figure 4a, c, e). Due to the nonsymmetric nature of Ti 2p feature of Pt–TiO$_2$ and Pt–TiO$_2$–N–rGO nanocomposites, it is deconvoluted as shown in Figure 4c, e. The BE at 459.6 and 462.5 eV are assigned to the 2p$_{1/2}$ and 2p$_{3/2}$ peaks of Ti(IV) states, while the photoelectron peaks at 458.7 and 464.2 eV can be assigned to the 2p$_{3/2}$ and 2p$_{1/2}$ peaks of Ti(III) in Pt–TiO$_2$ nanocomposite (Figure 4c). It should also be noted that the Ti 2p photoelectron peaks of Ti(IV) in Pt–TiO$_2$ nanocomposite are found at higher BE than that of Ti 2p peaks of Ti(IV) state in TiO$_2$–N–hrGO nanocomposite (2p$_{3/2}$ = 458.9 and 2p$_{1/2}$ = 464.6 eV). Similarly, BE at 459.5 and 465.2 eV reveals the Ti(IV) state, and 458.3 and 463.9 eV reveals the Ti(III) state of the sample Pt–TiO$_2$–N–rGO nanocomposite. The higher BE of 2p electrons of Ti(IV) in Pt–TiO$_2$ nanocomposite is due to the positive shift of BE of Ti(IV) in Pt–TiO$_2$ with respect to that of TiO$_2$, which is in accord with the increase in O$_2$ feature of the corresponding samples (Figure 4e, f). The increase of Ti(III) state in Pt–TiO$_2$–N–rGO nanocomposite compared to Pt–TiO$_2$ is due to the excess use of NaBH$_4$ during the deposition of Pt NPs for the synthesis of Pt–TiO$_2$–N–rGO. The reduction of TiO$_2$ surface is ascribed to the fact that the excited TiO$_2$ NCS surface could take up electrons from the reducing agent (NaBH$_4$) thereby reducing the surface Ti(IV) to Ti(III) states of TiO$_2$. Figure S4 shows the XPS spectra of Pt 4f photoelectron peaks of Pt–TiO$_2$ and Pt–TiO$_2$–N–rGO nanocomposites. The BE of Pt 4f peaks are well matched with the reported values with a spin orbit splitting of ∼3.3 eV in both the Pt–TiO$_2$ and Pt–TiO$_2$–N–rGO nanocomposites.

**HER Activity.** HER activity of the as-synthesized samples was tested in 0.1 M H$_2$SO$_4$ at a scan rate 100 mV s$^{-1}$. Figure 5a shows the linear sweep voltagammetry (LSVs) presenting the current density as a function of applied potential (vs. SHE) and overpotential ($\eta$) for different catalyst samples. As these composite catalysts were coated on the glassy carbon (GC) electrode by drop casting, the HER activity was also measured with bare GC for comparison. It is found that the ternary Pt–TiO$_2$–N–rGO nanocomposite exhibits a maximum current density of 126 mA cm$^{-2}$ at an overpotential of 300 mV. Overall the Pt-based catalysts exhibit higher current density than TiO$_2$–N–rGO as expected. Figure 5b shows the Tafel plots in the linear portion of HER. The average Tafel slopes for Pt–N–rGO, Pt–TiO$_2$, Pt–TiO$_2$–N–rGO, and Pt/C nanocomposites are measured (from the linear portion of Figure 5b) to be in the range 29–32 mV dec$^{-1}$, i.e., the potential required to increase the current density 10 times. The Tafel slope value suggests information about the HER mechanism. The slope in the range of ∼29 mV dec$^{-1}$ and 38–42 mV dec$^{-1}$ were reported to follow the atom combination and atom ion combination mechanism for HER, respectively. The smaller slopes (29–32 mV dec$^{-1}$) obtained with Pt/C, Pt–N–rGO, Pt–TiO$_2$, and Pt–TiO$_2$–N–rGO nanocomposites in the present work suggest that these catalysts follow an atom combination mechanism. The ternary Pt–TiO$_2$–N–rGO nanocomposite exhibits the exchange current density of 0.22 mA cm$^{-2}$ while Pt–TiO$_2$ and Pt–N–rGO exhibit exchange current density of 0.19 mA cm$^{-2}$ and 0.38 mA cm$^{-2}$, respectively (exchange current densities were measured by the intercepts of X-axis of the inverse slope of Tafel plots). Furthermore, the mass activity of Pt–TiO$_2$–N–rGO nanocomposite is estimated to be the highest (3116 mA·cm$^{-2}$).
mg$^{-1}$) among all the catalysts synthesized in the present work at an overpotential of 300 mV. In order to estimate the mass activity, the wt % of Pt in the as-synthesized samples was first measured using EDX. The Pt wt % in Pt–TiO$_2$–N–rGO, Pt–TiO$_2$, and Pt–N–rGO were measured to be 6.33%, 7.36%, and 6.84%, respectively (Figure S5). The mass loadings of the corresponding samples are estimated to be 2.83, 3.2, and 3.05 $\mu$g while the mass loading of 20 wt % Pt/C is 8.94 $\mu$g. The Tafel slope, current density, mass activity, and exchange current density of the as-synthesized Pt–based catalysts are summarized in Table 2 and compared with 20 wt % Pt on Vulcan carbon (Pt/C). The scan rate dependent HER activity and stability of the ternary Pt–TiO$_2$–N–rGO nanocomposite are shown in Figures S6 and S7, respectively. It is found that the current density decreases from 126 to 115 mA cm$^{-2}$ upon decrease in scan rate from 100 to 50 mV s$^{-1}$. The ternary Pt–TiO$_2$–N–rGO nanocomposite is found to be stable even in 100th run. After a 100th cycle, the overpotential is found to increase by 1.2 mV at current density of 86 mA cm$^{-2}$ (Figure S7).

The HER mechanism here involves two steps: (1) adsorption of proton on the catalytically active sites of the electrode coupled with an electron transfer and (2) desorption of two adsorbed protons to produce hydrogen gas. This atom combination HER mechanism (or Volmer–Tafel mechanism), which proceeds through the above two steps, is illustrated in Scheme 2. The proton-couple electron transfer is reported to occur on reduced TiO$_2$ surface.$^{52,53}$ Furthermore, the Ti(III) states are known to be electrochemically active and decrease the overpotential for the electrochemical reduction by effective electron transfer from the Ti(III) states.$^{28}$ XPS analysis in the present study reveals the presence of the Ti(III) state in Pt–TiO$_2$ and Pt–TiO$_2$–N–rGO nanocomposites. The Ti(III) state on the electrode surface is thus attributed to higher HER activity of ternary Pt–TiO$_2$–N–rGO and Pt–TiO$_2$ than that of Pt–N–rGO nanocomposite (Table 2). It is also important to note that the Ti(III) states not only increase the n-doping degree of TiO$_2$ and thus improve the conductivity but also increase the protonation that facilitates the HER as shown in Scheme 2.$^{28,53,54}$ The superior HER activity of the Pt–TiO$_2$–N–rGO in spite of the larger size of Pt NPs (5–10 nm) compared to Pt NPs (2–5 nm) on Pt–TiO$_2$ can be attributed to following two major factors: (i) increase in the Ti(III) states by an extent of 33% for Pt–TiO$_2$–N–rGO as compared to Pt–TiO$_2$ as confirmed by XPS analysis and (ii) the enhanced charge transportation due to the presence of N–rGO in the Pt–TiO$_2$–N–rGO nanocomposite.$^{55}$ In addition, the HER activity of the Pt–N–rGO is found to be slightly higher than the Pt–rGO composite (not shown). This suggests the higher electrical conductivity and active sites for HER in Pt–N–rGO due to N-doping, which can be considered as another factor for enhanced HER activity. The HER activity of as-synthesized catalysts is compared with the literature values and presented in Table 3.

4. CONCLUSIONS

In this study, we demonstrate the synthesis of TiO$_2$-based nanocomposite catalysts with different combination of TiO$_2$ NCS, N–rGO, and Pt NPs for HER. The Pt NPs deposited on TiO$_2$ NCS by photo reduction are smaller and more uniform than that deposited on GO by chemical reduction. The ternary Pt–TiO$_2$–N–rGO nanocomposite exhibits a maximum current density (126 mA cm$^{-2}$ at 300 mV overpotential) with a small Tafel slope ($\sim$32 mV dec$^{-1}$), high mass activity (3116 mA mg$_{Pt}$$^{-1}$), and high exchange current density (0.22 mA cm$^{-2}$). The small Tafel slope indicates that the HER mechanism...
follows the atom combination discharge process. The excellent electrocatalytic behavior of ternary Pt–TiO$_2$–N-rGO nano-composite toward HER is attributed to the synergistic effect of Ti(III) state of reduced TiO$_2$ NCs and N-rGO with Pt NPs. The Ti(III) state enhances the hydrogen discharge process and N-rGO facilitates the charge transfer from electrode to catalyst surface which lead to increase in the HER activity. The present study is an attempt toward reducing the Pt content and demonstrating TiO$_2$ as a suitable inexpensive support oxide material for the production of hydrogen energy.

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acs.jpcc.5b03870](http://pubs.acs.org/doi/10.1021/acs.jpcc.5b03870).

XPS surface survey, region spectra, EDX spectra, and cyclic voltammograms for HER (PDF)

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#### Notes

The authors declare no competing financial interest.

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