Synthesis, Characterization and Electrocatalytic study of Pd supported on CeO₂ doped on N, S-rGO towards Hydrogen and Oxygen Evolution

Mengistu Woldetinsay

Jimma University College of Engineering and Technology: Jimma University Institute of Technology

Tesfaye Soreta

Addis Ababa Institute of Technology

Krishnamurthy Palani

SRMIST: SRM Institute of Science and Technology

Thandavarayan Maiyalagan

SRMIST: SRM Institute of Science and Technology

Femi Emmanuel Olu (✉ foluemm@gmail.com)

Jimma University <https://orcid.org/0000-0002-6069-7968>

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Abstract

The sustainable production of hydrogen and oxygen through electrolysis of water requires the development of an efficient electrocatalyst. Herein, we synthesized Pd nanoparticles dispersed on CeO₂/N, S-rGO by hydrothermal method followed by chemical reduction of Pd nanoparticles. Electrochemical measurements towards hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) show a high electrocatalytic activity of the catalyst. Among the synthesized electrocatalysts Pd/CeO₂/N, S-rGO exhibits lower overpotential (75 mV and 240 mV) at 10 mAcm⁻² and lower Tafel slope value (44 mV dec⁻¹ and 42 mV dec⁻¹) for HER and OER, respectively. The chronoamperometric and linear sweep voltammetry (LSV) of the electrocatalyst shows a negligible decrease in the current density for twelve hours and a minor change in the polarization curve after 10,000 cycles, respectively. The high electrocatalytic activity and superior stability of the synthesized electrocatalyst could be attributed to the synergetic effect between Pd nanoparticles and CeO₂/N, S-rGO support. This work demonstrates a facile way to develop effective and stable electrocatalysts by exploiting the Pd/Metal oxide interface.

Introduction

The electrochemical water splitting in acidic polymer electrolyte water electrolyzers (PEWEs) has many advantages over the alkaline system. This includes higher kinetics of the cathodic hydrogen evaluation reaction, high electrolyte conductivity, and higher pressure above 50 bar [1].

Hydrogen has been a promising clean energy source for the future [2]. The production of hydrogen through water splitting sustainably by using an effective electrocatalyst is attracting more attention [3, 4].

Pt and Pt-based electrocatalyst are mostly used for hydrogen production [5]. However, the low natural abundance of Pt hinders large-scale applications. These limitations forced the research community to find a non-Pt or less Pt content electrocatalyst [6, 7] or Pt alloys with other metals such as Pd [8,9], Ni [10,11], etc. Pd and Pd-based electrocatalysts attract more attention because Pd has a similar property with Pt, relatively more abundant and lower cost compared to Pt. It is also less poisonous during processing [12]. Moreover, Pd has very close adsorption energy and exchange current density to Pt towards HER, as Norskov et al. [13] calculated.

Pd and Pd-based electrocatalyst are mostly used in catalytic reactions related to hydrogen [14,15]. However, Pd and hydrogen's strong binding energy in Pd-H bonding makes the Pd electrocatalyst inactive towards hydrogen evolution reaction. Many strategies have been employed to alter hydrogen binding energy on the Pd surface [16]. This includes Pd's combination with heteroatomic metallic elements that could affect the lattice strain [17] and the dispersion of Pd on high surface area support that could weaken the bond between Pd and Hydrogen [18, 19].

An additional reason for the special attention given to Pd based materials towards hydrogen evolution reaction is because of its fast adsorption kinetics, selectivity, and reversible hydrogen formation [20]. However, the desorption of hydrogen from the palladium catalyst surface is very difficult. The hydrogen evolution performance of Pd nanoparticle can be improved by modifying the electronic properties and crystal parameters, which could be achieved by reducing Pd's size.

The noble metal content in the electrocatalyst can be reduced without compromising the HER performance using support materials with a higher surface area and good electrical conductivity [21]. Good electrical conductivity, higher surface area, optimum porosity, and higher stability in an acidic environment are the main characteristics of good support material. They should also possess high energy density and corrosion resistance under oxidizing conditions [22, 23].

The morphology, size, structure, and nature of the support materials may influence the metal nanoparticles' catalytic activity. In addition to these, the low coordination of metal nanoparticles, quantum size effect, and better metal support interactions could have a more significant impact [24]

Among the carbon support materials, graphene can best fit the above criteria [25, 26]. However, due to the Van der Waals attraction between graphene nanosheets, the effective surface area and conductivity could be affected [27, 28]. To solve this problem, doping of electron-rich species on graphene is the best option to help the carbon π electrons conjugate with an electron of doped element and increase the material's donor properties [29].

Generally, various carbon-supported catalysts have significant limitations, such as low electrocatalytic stability due to the rapid depletion of carbon [30]. Many attempts have been devoted to overcoming this problem, such as the incorporation of heteroatom example, nitrogen, and sulfur that coordinates with different N.P.s [31, 32]

Doping of a small amount of cerium oxide CeO_2 can improve the catalytic activity of metal catalyst [33, 34], for example, Au- CeO_2 [35], Ag@ CeO_2 [36], and Pt@ CeO_2 [37]. This is due to the high capability of CeO_2 in adsorbing OH-species, which is closely related to the redox process between the different possible oxidation states of cerium (Ce) [38-40].

To increase both the activity and stability of metal- CeO_2 suitable support that can disperse metal N.P. is required. In this respect, reduced graphene oxide (rGO) is the best choice due to its high surface area, good conductivity, and thermal and chemical stability [41, 42]. Combining N, S-rGO, and CeO_2 may optimize both the dispersion and catalytic activity of Pd nanoparticles and stability.

Recently, we reported M@Pd(M=Ni, Cu, Co) core-shell nanostructures supported on N, S-rGO [43] and Pd/ MOS_2 /N, S-rGO [44] to demonstrate a higher electrocatalytic activity with small overpotential, stability, and lower Tafel slope value towards hydrogen evolution reactions due to the synergetic effect between Pd nanoparticles and supports.

This report synthesized Pd/CeO₂/N, S-rGO, and Pd-Ni/CeO₂/N, S-rGO by hydrothermal, and wet chemical reduction method followed by characterization of the composite and its application in electrochemical activities towards hydrogen evolution reaction and oxygen evolution reaction. Among the synthesized electrocatalysts, Pd/CeO₂/N, S-rGO demonstrated the highest electrocatalytic activity than Pd-Ni/CeO₂/N, S-rGO, and CeO₂/N, S-rGO.

Experiment

Reagents

All chemicals used for this analysis were analytical grade and utilized without further purification.

Graphite powder; Nickel nitrate hexahydrate(Ni(NO₃)₂·6H₂O); Cerium nitrate Ce(NO₃)₃·6H₂O Ethylene glycol was purchased from SRL, India; Palladium chloride(PdCl₂, 98%, Sigma-Aldrich); hexadecyltrimethylammonium bromide(CTAB); Sulfuric acid (H₂SO₄, ≥ 95-98%, Fischer Scientific Ltd.); Potassium permanganate (KMnO₄); Sodium nitrate (NaNO₃) and Thiourea (N₂H₄SC) were purchased from SRL, India; Ethanol (98%); Hydrogen peroxide (H₂O₂, ≥ 30%) were obtained as a gift from Merck. De-ionized water (using Labaqua Bio ultrapure di-ionizer) was used for all aqueous sample preparation.

Method

G.O. and N, S-rGO Synthesis

Graphene oxide was synthesized from graphite powder by the modified Hummer method as our previous report [44]. N, S-rGO was synthesized by the hydrothermal method as our previous report [44]. Briefly, G.O. (70 mg) was added to de-ionized water (70 ml), followed by sonication for an hour. Thiourea (1 g) was added to the above mixture as a source of both N and S, followed by sonication for 30 minutes. The mixture was transferred into a 100 ml Teflon lined stainless steel autoclave for the hydrothermal reaction at 180 °C for 12 h. Finally, the product was collected by washing with de-ionized water and ethanol, followed by drying at 60 °C for 12 h.

CeO₂/ N, S-rGO Synthesis

CeO₂/ N, S-rGO was synthesized by following the procedure reported by G.Tengyang et al. [45]. Briefly, Ce(NO₃)₃·6H₂O (10.1 g) dissolved in 250 ml of de-ionized water and N, S-rGO (4 g) was added to the above solution, followed by sonication of the whole solution for 30 minutes. The solution's pH was adjusted to neutral value using 0.1 M KOH, followed by stirring the solution for 2 h. Finally, the product was collected by filtration and washed with de-ionized water until the pH becomes neutral and dried at 60 °C. The powder was further heated in a tube furnace at 250 °C for two hours.

Pd/CeO₂/ N, S-rGO and Pd-Ni/CeO₂/ N, S-rGO Synthesis

Palladium nanoparticle anchored on CeO₂/ N, S-rGO, was synthesized using the method reported by G.Tengyang et al. [45]. Accordingly, CeO₂/ N, S-rGO (500 mg) was dissolved in 100 ml of de-ionized water followed by vigorous stirring (for one hour) and sonication (for 30 minutes). K₂PdCl₄ (0.17 g) solution in 20 ml of de-ionized water was added to the above mixture under stirring and stirred for an additional one hour. The solution's pH was adjusted by adding 2 ml of 2.5 M KOH solution dropwise, followed by 15 ml of Ethanol (1 ml /min). The whole solution was heated for one hour at 80 °C. Finally, the product was collected by cooling, filtering, and washing until the pH becomes neutral and dried at 60 °C. The Pd-Ni/CeO₂/ N, S-rGO composite was synthesized by co-reduction of the metal salts.

Physicochemical characterization

X-ray diffraction (XRD) was used to investigate the crystalline structure of the crystals using Shimadzu powder XRD-600 with Cu K α radiation. Horiba-Jobin Raman spectra (model: - LabRAM HR Evolution) with 633 nm Ar Laser source was used to evaluate the prepared sample's defect structure. HRTEM image was taken with JEOL JEM 2100(200kv) with a LaB₆ electron gun (manufactured in Japan). The X-ray Photoelectron Spectroscopy (XPS model PHI 5000 Versa Probe III) and XPSPEAK4.1 software were used to analyze the synthesized sample's surface chemistry. A field emission scanning electron microscope (FESEM) (FEI, Quanta 200) was used to study the surface morphology.

Electrode fabrication

The glassy carbon electrode was polished with different particle size alumina polishing slurry. The geometric area of the electrode was 0.0706 cm². The Pd loading amount on the glassy carbon was 0.14 mg/cm². The catalyst ink was prepared by dissolving 5 mg of electrocatalyst sample in water/ethanol (1:1) and 10 μ l 5% Nafion solution (used as a binder). The suspension was ultrasonicated for 30 minutes. The ink (5 μ l) dropped cast on the polished glassy carbon.

Electrochemical measurement

All electrochemical measurements were carried out using a potentiostat (Biologic SP-300 using software EC-Lab V11.10) with a three-electrode configuration. The electrocatalyst modified glassy carbon electrode was used as a working electrode, Ag/AgCl (saturated KCl) as a reference electrode. A graphite electrode was used as a counter electrode in N₂ saturated 0.5 M H₂SO₄ for hydrogen evolution and in 0.1M KOH for oxygen evolution.

The electrocatalytic performance evaluated using linear sweep voltammetry (LSV) measurement due to the ohmic resistance (iR) the current measured may not indicate the intrinsic behavior, so iR correction was done using LSV measurement. Stability is an essential criterion for practical applications. Commonly there are two ways to study the stability of electrocatalyst. One way is measuring the change in current with time (i.e., the I-t curve). In this case, the current was set at a current density of 10 mA cm⁻² for twelve hours. The second method was by conducting a cycling experiment for 10,000 cycles at 25 °C

in 0.5 M H₂SO₄ and 0.1 M NaOH, for HER and OER, respectively. The electrochemical impedance spectroscopy (EIS) was used to evaluate the solution's charge transfer resistance, which was conducted at a frequency range of 100 kHz to 0.01 HZ at open circuit potential with perturbation 5 mV. All the potential mentioned in this report converted to RHE by using

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059\text{pH} + E^{\circ}_{\text{Ag/AgCl}}(0.197)$$

Result And Discussion

The XRD pattern was used to analyze the crystalline nature of the synthesized sample. Accordingly, the diffraction peak of the electrocatalyst displayed in Fig. 1(a) shows strong diffraction at 39.61, 46.05, and 66.94 for Pd/CeO₂/N, S-rGO and 39.7, 46.6, and 67.9 for Pd-Ni/CeO₂/N, S-rGO those peaks correspond to Pd(111), Pd(220) and Pd(200) plane of palladium respectively. The diffraction peak of Pd/CeO₂/N, S-rGO, was relatively lower than Pd-Ni/CeO₂/N, S-rGO. This could be due to the highest degree of the desperation of Pd in the former case. The interaction between Pd_{NP} and CeO₂ can occur either by a spillover effect or reverse spillover effect. The presence of Pd peak and the absence of PdO peak indicate the interaction occurs through the reverse spillover effect in which electrons are donated from Pd_{NP} to CeO₂. The diffraction peak of Ce at 29.76 corresponds to miller indices Ce (111) in CeO₂/N, S-rGO, which indicates the higher crystalline nature of the sample. Ce's characteristic peak at 29.76 was diminished in Pd/CeO₂/N,S-rGO composite that could result from the interaction between Pd and Ce.

The Raman spectroscopy was used to analyze the defect in the synthesized sample in a non-distractive way. The presence of more defects in the Nano composite structure helps form a more active site for electrochemical reactions.

The two band in the Raman spectrum are D-band, which is related to out of plane vibration of SP² bonded carbon associated with a structural defect, and G-band due to in-plane vibrations of SP² bonded carbon. Moreover, the ID/IG ratio indicates the degree of defect in the synthesized sample. The Raman analysis result of the electrocatalyst displayed in Fig.1 (b) shows a peak at (1322.6) corresponding to D-band and (1594.2) G-band for Pd/CeO₂/N, S-rGO and a peak at (1337.2) corresponding to D-band and (1596.3) G-band for Pd-Ni/CeO₂/N, S-rGO and a peak at (1341.3) corresponding to D-band and (1602.5) G-band for CeO₂/N, S-rGO. The increase in intensity ratio (ID/IG) after incorporating heteroatoms related to rGO indicates more defects in the synthesized sample.

Table 1; Raman parameter for the synthesized electrocatalyst			
Electrocatalyst	D-band	G-band	ID/IG
rGO	1338	1597	0.83
N,S-rGO	1340	1600	0.91
CeO ₂ /N,S-rGO	1341.3	1602.5	1.24
Pd/CeO ₂ /N,S-rGO	1322.6	1594.2	1.25
Pd-Ni/CeO ₂ /N,S-rGO	1337.2	1596.3	1.22

The X-ray Photoelectron Spectroscopy (XPS) measurement was done to study the composite elements' chemical state. The XPS of the best performing electrocatalyst displayed in Fig.2 Shows the presence of Palladium (Pd), Cerium (Ce), Carbon (C), Nitrogen (N), Sulfur (S), and Oxygen (O). The XPS spectrum of palladium (Pd) displayed in Fig.2(a) shows peak around 336.6 eV and 341 eV corresponding to Pd 3d_{3/2} and Pd 3d_{5/2} level of Pd⁰, respectively [46,47]. The observed increase in Pd's binding energy in Pd/CeO₂/N, S-rGO, could be due to the strong interaction between Pd and CeO₂, which resulted from electron transfer between Pd and CeO₂[48]. The Peak at 337.0 eV and 342.2 eV corresponds to palladium (II). The higher intensity of the former peak indicates the higher dispersion of palladium nanoparticles.

The XPS spectrum of Ce3d is displayed in Fig.2 (b). The highest peaks at 905.3 eV and 886.1 eV is associated with Ce (Ce⁴⁺). The satellite peaks relatively lower binding energies are related to trivalent Ce (Ce³⁺). The peak at 284.7 of C 1s shown in Fig.2(c) corresponds to graphitic carbon due to distortion in the sp³ carbon structure. The peak at 289.4 eV corresponds to the oxygen-containing carbon functional group (O-C=O)[49]. The XPS spectrum of S 2p is displayed in Fig.2 (d) with a peak at 162.3 eV, and 163.03 eV corresponds to S 2p_{3/2} and S 2p_{5/2}. The N 2p XPS spectrum shown in Fig.2(e) shows major peaks around 398.6 eV and 399.0 eV associated with nitrogen bonded to Sp²- hybridized carbon (C-C=N-C) [50,51]. The XPS analysis confirms the successful incorporation of N and S.

The HRTEM and FESEM analysis was conducted to study the morphology and microstructure of the best performing electrocatalyst Pd/CeO₂/N, S-rGO. The result shows uniform dispersion of Pd_{N.P.} on CeO₂/N, S-rGO support with fringe calculated lattice spacing (0.21 nm) that corresponds to Pd (111), and a fringe of CeO₂ with lattice spacing (0.32 nm) corresponds to CeO₂(111) plane. The result suggests the nanocomposite was formed by transferring an electron from Pd_{NP} to CeO₂ by reverse spillover effect [52], which agreed with the XRD and XPS results.

Electrochemical activity measurement

The electrochemical HER activity was investigated in 0.5 M H₂SO₄. Fig.5 shows the iR-corrected polarization curve (LSV) of the synthesized electrocatalyst. The CeO₂/N, S-rGO exhibit very weak activity with an onset potential of 261 mV and overpotential of 197 mV at 10 mA cm⁻². Pd/CeO₂/N, S-rGO demonstrates the highest HER activity with the onset potential of 45 mV, overpotential of 55 mV at 10 mA cm⁻², resulting from the strong interaction between Pd and CeO₂. Comparatively, Pd-Ni/CeO₂/N, S-rGO exhibited lower HER activity than Pd/CeO₂/N, S-rGO with an onset potential of 75 mV, overpotential of 105 mV at 10 mA cm⁻² under the same condition. This could be related to the availability of less active sites for an electrocatalytic reaction.

The Tafel slope value derived from the polarization curve indicates the rate of increase in current against overpotential. The increase in current density with a small change in overpotential signifies faster electrocatalyst kinetics and is also used to estimate the hydrogen desorption mechanism from the electrocatalyst's surface. Accordingly, Pd/CeO₂/N, S-rGO reveals 49 mV dc⁻¹, Pd-Ni/CeO₂/N, S-rGO 64 mV dc⁻¹ and CeO₂/N, S-rGO 101 mV dc⁻¹. Therefore, the hydrogen evolution follows the Volmer-Heyrovsky mechanism in which the desorption of hydrogen was the rate-determining step.

The EIS was measured in 0.5 M H₂SO₄ with a frequency range from 100 kHz to 0.01 HZ and displayed in Fig.5(e) the smallest semicircle obtained for Pd/CeO₂/N, S-rGO indicates the high kinetics of HER resulted from strong metal-support interactions.

Electrochemical measurement of oxygen evolution reaction activity

Oxygen evolution reaction (OER) involves a complex process in which the O-H bond is broken, and the O = O bond is formed through the transfer of four electrons. The synthesized electro catalysts' OER activity was evaluated using linear sweep voltammetry (LSV) in N₂-saturated 1M KOH solution at a scan rate of 5 mVs⁻¹. As displayed in Fig.6. Pd/CeO₂/N, S-rGO demonstrate lower overpotential and Tafel slope value 0.24 V at 10 mAcm² and 42 mv dec⁻¹ respectively. The incorporation of Ni resulted in less OER activity than the former (0.29 V and 44 mv dec⁻¹) due to the availability of a less active site for electrochemical reaction. The least electrochemical activity was observed for CeO₂/N, S-rGO (0.41 V and 78 mv dec⁻¹). Moreover, the chronoamperometric stability study shows good stability for 12 h, and EIS measurement was conducted in 0.1 M KOH with a frequency range from 100 kHz to 0.01 HZ and amplitude 5 mV. The small semicircle demonstrated by Pd/CeO₂/N, S-rGO, shows a faster electron transfer rate.

Table 2. Comparison of HER electrocatalytic performance of the electrocatalyst in 0.5 M H ₂ SO ₄				
Electrocatalyst	Onset potential(mv)	Over potential(mv)	Tafel slope (mv.dec ⁻¹)	Reference
Pd/CeO ₂ /N,S-rGO	64	75	49	This work
Pd-Ni/CeO ₂ /N, S-rGO	69	105	64	This work
GO-Au ₄₈ Pd ₅₂	80	130	149	[53]
rGO-Fe ₄₈ Pd ₅₂	140	250	370	[53]
PdNiMo film	85	110	227	[54]
Co@Pd/N,S-rGO	94	58	54	[43]
Pd16-CoCNTs	-	120	79	[55]
Pd/MoS ₂ /CB		78	57	[56]
Pd/g-C ₃ N ₄		105	69	[56]

Conclusion

In this study, we synthesize Pd/CeO₂/N, S-rGO, Pd-Ni/CeO₂/N, S-rGO and CeO₂/N, S-rGO successfully by hydrothermal, followed by chemical reduction. The Pd/CeO₂/N, S-rGO, demonstrates a higher electrocatalytic activity than Pd-Ni/CeO₂/N, S-rGO, and CeO₂/N, S-rGO. The observed decrease in electrocatalytic activity after incorporating Ni in Pd/CeO₂/N, S-rGO, could be due to decreased active site for electrochemical reactions. The strong interaction between Pd_{NP} and CeO₂ confirmed by HRTEM, XRD, and XPS analysis leads to higher electrocatalytic activity. Furthermore, CeO₂ and N's coexistence, S-rGO support was beneficial for anchoring and stabilizing the metal nanoparticles. It is also evident interaction in the nanocomposite metal with the support). This study could help investigate the further improvement of the catalytic activity of non-Pt electrocatalyst through Pd/Metal oxide interface.

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Declarations

All the authors of this research declared that we have no known competing financial interests or personal relationships with each other that could have appeared to influence the work reported in this paper. Therefore, there is no conflict of interest between all the authors of this research.

Signed

Dr. Olu Emmanuel Femi

Corresponding Author

Figures

Figure 1

(a) XRD pattern for the catalysts Pd/CeO₂/N,S-rGO, Pd-Ni/CeO₂/N,S-rGO and CeO₂/N,S-rGO respectively. Fig. 1 (b) the Raman shift spectra for the catalysts Pd-Ni/CeO₂/N,S-rGO, Pd/CeO₂/N,S-rGO and CeO₂/N,S-rGO respectively.

Figure 2

XPS plot for Ni@Pd/N, S-rGO nanostructure (a) Pd3d, (b) Ce3d (c) C1s, (d) S 1s (e) N 1s, (d) (f). Pd/CeO₂/N,S-rGO

Figure 3

HRTEM image with two different magnification (a) at 20 nm, (b &c) at 50 nm, Pd/CeO₂/N,S-rGO nanocomposite.

d

Element	At.No.	Mass%	Mass Norm	Atom%
Ce	58	24.01	32.32	5.08
C	6	21.72	29.24	53.66
O	8	18.66	25.12	34.61
Pd	46	7.01	9.44	1.96
N	7	1.70	2.28	3.59
S	16	1.18	1.59	1.10
		74.28	100	100

Figure 4

FESEM analysis result of Pd/CeO₂/N,S-rGO (a) 500nm, (b) 5μm , (c) EDX and (d) corresponding elemental ratio table

Figure 5

(a) HER polarization curves for $\text{Pd}/\text{CeO}_2/\text{N}, \text{S-rGO}$, $\text{Pd-Ni}/\text{CeO}_2/\text{N}, \text{S-rGO}$ and $\text{CeO}_2/\text{N}, \text{S-rGO}$ in 0.5 M H_2SO_4 with scan rate 5 mVs^{-1} . (b) The corresponding Tafel plot derived from the polarization curve, (c) and (d) are the stability test of $\text{Pd}/\text{CeO}_2/\text{N}, \text{S-rGO}$ by Linear Sweep Voltammetry (LSV) and chronoamperometry respectively (e) electrochemical impedance spectroscopy of the prepared catalysts. (f) Comparison of overpotential at 10 mA/cm^2 for the prepared catalysts.

Figure 6

(a) OER polarization curves of the Pd/CeO₂/N, S-rGO, Pd-Ni/CeO₂/N, S-rGO, and CeO₂/N, S-rGO in 0.1 M KOH at a scan rate of 5 mVs⁻¹. (b) The corresponding Tafel plot derived from the polarization curve, (c) the stability test of Pd/CeO₂/N, S-rGO by Chronoamperometry for 12 hours in 0.1 M KOH (d) Nyquist plot of electrochemical impedance spectroscopy of the prepared catalysts in 0.1 M KOH (e) Comparison of overpotential at 10 mA for the prepared catalysts.