

Modification of mesoporous titanium dioxide with cobalt oxide electrocatalyst for enhanced oxygen evolution reaction

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Abstract

Water electrolysis is an attractive approach for hydrogen production process and has enormous potential for sustainable clean energy development. This work demonstrates a controllable and reliable method for in-situ decorating of mesoporous titanium dioxide (*m*-TiO₂) support with low loading (0.1- 2.1 wt. %) of cobalt oxide for an efficient electrocatalytic oxygen evolution (OE) in alkaline solution. The ordered (*m*-TiO₂) support modified with cobalt oxide and having uniform mesopores (3-5 nm pore diameter) and a crystalline framework is successfully prepared via soft-template strategy using Pluronic® F127 triblock copolymer as a mesopores template. Compared to the pure TiO₂ mesoporous, the entire Co oxide doped (Co(x)/*m*-TiO₂) catalysts exhibit greatly enhanced OE activity in spite of the low loading of Co oxide electrocatalyst. The Co(2.1)/*m*-TiO₂ catalyst with 2.1 wt. % of Co oxide was the OER most active robust electrocatalyst with a mass activity of 31.5 mA cm² mg⁻¹, the specific activity of 12.6 mA cm⁻² at $\eta = 350$ mV and 200 mV decrease in overpotential (η) compared to bare *m*-TiO₂. The enhanced OE activity of (Co(x)/*m*-TiO₂) catalysts was attributed to the existence of a uniform distribution of Co oxide electrocatalyst supported on a highly porous structure of the TiO₂ substrate. Copyright © 2019 VBRI Press.

Keywords: Mesoporous, titanium dioxide, cobalt oxide, oxygen evolution.

Introduction

The production of oxygen (O₂) and hydrogen (H₂) fuel via water electrolysis or solar-driven photoelectrochemical water electrolysis is an attractive technology toward clean and renewable energy sources. The hydrogen gas has been recognized as a prominent energy carrier and can be used directly in internal combustion engine and as fuel to generate the electricity in a fuel cell [1, 2, 3, 4, 5]. Also, hydrogen used mostly in various chemical industry processes such as Fischer–Tropsch synthesis, petroleum refining and can be used in the Haber–Bosch synthesis of ammonia for fertilizer [6]. The majority of hydrogen gas is currently produced from steam-reforming of fossil fuels, which is accompanied with CO₂ gas emission as a byproduct [2, 5, 6]. The hydrogen produced from water through electrolysis or renewable sources of energy, such as wind or solar is considered as an appropriate fuel due to avoiding harmful CO₂ emissions, but this methodology must have increased energy efficiency and decreased the costs to be comparable to conventional fuels and compete with fossil hydrogen sources. On the other hand, the oxygen evolution reaction (OER) during the water-electrolysis process at

the anode in both acidic (2H₂O → O₂ + 4H⁺ + 4e⁻) and basic (4OH⁻ → O₂ + 2H₂O + 4e⁻) solution, is inherently more complex and has sluggish kinetics. Since it takes place through a four-electron transfer with the removal of four protons reaction from water molecules to produce one oxygen molecule which needs large overpotential to facilitate the reaction efficiently [7, 8, 9]. Therefore, the development of effective and stable OER electrocatalysts is of great interest to facilitate the water oxidation kinetics and reducing the overpotential, and thus improve the energy-conversion efficiency. It is well documented that noble metal oxides of Ru, Ir and Rh are a highly active catalyst for OER [10, 11], however, their scarcity and high cost greatly prevent their utilization in large-scale commercial applications. Recently, substantial research interests have been devoted to preparing and develop an earth-abundant transition metal oxides hydroxides and phosphate for highly active and durable electrocatalysts for water splitting electrolysis [12, 13, 14, 15, 16]. Nevertheless, the OER performance of the transition metal oxide is still needed further improvement to make them highly competitive and stable in comparison with their noble-metal catalysts and useful for practical applications.

Titanium dioxide (TiO_2) has been intensively studied as a robust and photocatalyst for water splitting because its unique electronic, optical and chemical stability characteristics [17, 18, 19, 20, 21]. However, TiO_2 is regarded as a poor electrocatalyst for (OER) because it's high electrical resistivity (105 to 102 $\Omega \cdot \text{cm}$) [22]. More recently, the modification of TiO_2 semiconductor with various cations or anions has been extensively studied to improve its electronic, chemical, optical and magnetic properties for a better photo- and electrocatalytic performance in water splitting and energy storage applications [23, 24, 25, 26, 27, 28]. Yang *et al.* for example demonstrated that TiO_2 nanowires modified with 2.0 wt. % transition metal leads to enhancing the OER efficiency and decreased the overpotential required for water electrolysis [23]. In another study by Park *et al.* [24] reported an enhanced OER performance of at transition metals doped TiO_2 nanocrystal catalysts as compared to bare TiO_2 . Cai *et al.* studied the OER at TiO_2 nanowires modified with Co oxide prepared by the sol-flame process [25]. A few other recent reports also confirm the reduction of OER overpotential with transition metal-doped TiO_2 [26-28]. Furthermore, in situ doping of transition metals such as Co, Fe, Ni and Mn into the mesoporous TiO_2 crystalline frameworks without changing the TiO_2 crystal structure and disruption of the mesoporous structure face challenges when doping mesoporous since dopants will unavoidably affect the cooperative assembly with the TiO_2 precursor, leading to different morphology and distortion of the mesoporous structure frameworks. This suggests the role of the doping with transition metal as promising techniques for improving the activity of TiO_2 based electro-catalysis and photo-electrolysis cells.

Recently, ordered mesoporous materials have attracted a lot of attention in energy conversion and storage applications owing to their extraordinarily high surface areas and large pore volumes [29, 30, 31, 32]. These features may improve the performance of materials in terms of energy and power density, lifetime and stability. There are various synthetic procedures to prepare mesoporous materials and can be classified as soft-templating based on sol-gel processes involving surfactants as templates, hard-templating using mesoporous silica or carbon and template-free approaches. Among of these methods, soft-templating employs amphiphilic molecules as a structure-directing agent has been the most extensively investigated since mesoporous materials synthesized using this method have advantages such as high purity, homogeneity, different compositions and pore sizes. However, sometimes it's difficult to control the fabrication of non-siliceous mesoporous oxides, due to the high reactivity hydrolysis-condensation behaviour of the inorganic precursors [30, 33]. Recent studies show that the co-assembly of organic and inorganic species can be well controlled by introducing ligands such as acetylacetone and citric acid [34, 35, 36]. Following these reports, we utilized a soft-templating method to

synthesize ordered and crystalline transition metal doped mesoporous TiO_2 catalyst by using tetrabutyl titanate as Ti precursor and the triblock copolymer Pluronic® F127 as the template. We also employ acetic acid as a chelating agent during the self-assembly process to control the hydrolysis and condensation of the TiO_2 precursor by stabilizing the hydrolyzed Ti precursor by chelation. The obtained mesoporous cobalt oxide doped TiO_2 were utilized in electrochemical water splitting and showed high electrocatalytic activity with a significant negative shift in the onset potential of oxygen evolution reaction. Moreover, an optimal amount of Co oxide dopant is established for improving the OER activity and stability.

Experimental

Materials and chemicals

Titanium tetra-butoxide and Triblock copolymer Pluronic® F127 ($M_w = 12600$, $\text{PEO}_{106}\text{PPO}_{70}\text{PEO}_{106}$) and were obtained from Aldrich Corp. Cobalt nitrates, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was purchased from Alfa Aesar and ethanol, HCl, acetic acid. Conductive fluorine-doped tin oxide (FTO) glasses (Wuhan Geo Corp., China) were used as working electrode which was cleaned sequentially by sonicating in acetone, isopropanol and deionized water for 20 min each. Deionized water (DI) used in all experiments was purified with a Milli-Q Ultrapure Water purification system. The chemicals were used as received without extra purification.

Synthesis of cobalt oxide doped mesoporous TiO_2

The crystalline ordered CoO-doped TiO_2 mesoporous were prepared by chelating assisted evaporation-induced self-assembly (EISA) approach in an ethanolic/Pluronic® F127 /HCl/Acetic acid (HOAc)/Titanium tetrabutoxide (TBOT) mixed solution. In a typical synthesis, 2.0 g of Pluronic® F127 was dissolved in a mixture consist of 20 ml of anhydrous ethanol and 2.4 g of concentrated HCl (37%). The mixture was vigorously stirred for 30 min at 40 °C to form a transparent solution. Then a certain weight percent of cobalt nitrate equals 0.1, 0.5, 1.0 and 2.1 wt.% which is equivalent to Co/Ti mole ratio of 0.001, 0.005, 0.01 and 0.021, respectively, was poured into above solution with continuous vigorous stirring at 40 °C to obtain a clear homogeneous solution. Sequentially, 3.4 g of tetrabutyl titanate and 2.4 g of acetic acid were added with vigorous stirring for 2 h at 40 °C to obtain a homogeneous solution. After that and to evaporate the solvents the mixture was placed in Petri dishes and left at room temperature for 40 min, then heated at 100 °C for 24 h to completely remove the solvents and obtained the inorganic-polymer hybrids. Then, the obtained film was heated and treated with a ramp of 1 °C min^{-1} to 350 °C in N_2 and held for 3.0 h, resulting in the carbon-supported amorphous CoO-doped TiO_2 oxide powder. Finally, the carbon was removed and crystallization of the CoO-doped TiO_2 oxides structure

was carried by subsequent heat treatment with a ramp of $1\text{ }^{\circ}\text{C min}^{-1}$ to $400\text{ }^{\circ}\text{C}$ in air for another 3 h to get the mesoporous CoO-doped TiO_2 oxide. The obtained products were assigned as $\text{Co}(x)/m\text{-TiO}_2$, where x equals 0.1, 0.5, 1.0 and 2.1 wt.% and corresponding to the molar ratios of Co/Ti of 0.001, 0.005, 0.01 and 0.21 respectively, in the synthetic mixture. The non-porous $\text{Co}(2.1)/\text{bulk-TiO}_2$ catalyst was synthesized via a similar route as used for $\text{CoO}(x)/m\text{-TiO}_2$, but in absence of the triblock copolymer Pluronic[®] F127 templates and used as control catalyst.

Characterizations and measurements

Wide angle X-ray diffraction (XRD) patterns were executed with a Rigaku Mini Flex 600 irradiation X-ray diffractometer using $\text{Cu K}\alpha$ radiation (40 kV, 15 mA). The JEM-2100F transmission electron microscopy (TEM, Japan) operating at 200 kV was used to identify the materials mesoporous structures. For TEM measurement, the samples were dispersed in ethanol then a drop of the mixture was applied and dried on Cu grid. The SEM characterization was performed by Field emission scanning electron microscopy (FESEM, Hitachi Model S-4800). The Nitrogen adsorption-desorption isotherms were obtained at $77\text{ }^{\circ}\text{K}$ using NOVA 2200e surface area analyzer (Japan). The samples were heated under vacuum for at least 6 h at $180\text{ }^{\circ}\text{C}$ to remove the moisture before the measurement, the specific surface area was estimated using the Brunauer-Emmett-Teller (BET) method, while the the Barrett-Joyner-Halenda (BJH) method was employed to calculate the pore size and pore volume distribution using the adsorption branch.

Electrochemical measurements were carried out with a potentiostat (BioLogic SAS, model) in a three-electrode system, using a coiled Pt wire as a counter electrode, and SCE electrode as a reference electrode. The working electrode of CoO modified mesoporous TiO_2 was deposited on FTO substrate by electrophoretic deposition (EPD). In the atypical procedure, 1.0 ml of (iodine 40 mg, Alfa-Aesar, 15 ml acetone mixture) and (15 mg of mesoporous $\text{CoO}(x)/m\text{-TiO}_2$) powder were dispersed in a certain amount of acetone and sonicated by the ultrasonic probe for 20 min to get a uniform dispersion of mesoporous catalyst. The FTO substrate ($1 \times 1\text{ cm}^2$) was immersed in parallel with the FTO electrode at ca. 1 cm distance in the solution. Then +10 V of bias was applied between them for 4 min using a potentiostat (BioLogic SAS, model). The electrocatalyst particles coated on negative electrode were then rinsed with deionised water, dried in air and calcined at $350\text{ }^{\circ}\text{C}$ for 30 min under a flow of N_2 gas. The average weight of all mesoporous catalyst deposited on FTO was (0.4mg). The electrolyte was an aqueous solution of 1.0 M KOH ($\text{pH} = 14$). The potential scale was normalized to the reference hydrogen electrode (RHE) using the equation, $E_{\text{RHE}} = E_{\text{SCE}} + 0.244\text{ V} + 0.059\text{ pH}$ at $25\text{ }^{\circ}\text{C}$. The electrochemical impedance spectroscopy (EIS) was

operated in the frequency range of 10^{-2} to 200kHz with an AC voltage amplitude of 20 mV at a dc bias of 0.5 V vs. the saturated calomel electrode (SCE) in a 1.0 M KOH electrolyte.

Results and discussion

Synthesis of mesoporous CoO doped TiO_2 in the soft-templating synthesis procedure of ordered mesoporous $\text{Co}(x)/m\text{-TiO}_2$ catalysts the Pluronic[®] F127 is used as templating agent while the acetic acid as assisted chelating agent and the cobalt nitrate salts, TOBT as cobalt and Ti precursor respectively. The F127 triblock copolymers is co-assemble with the acetic acid-stabilized Ti precursor to form composite micelles during the solvent evaporation process. The hydrophilic PEO segments of F127 with associated metal salts precursor was co-assembled to form rod-like micelles in ethanolic solution. After solvent evaporation by heating at $100\text{ }^{\circ}\text{C}$ for 24 h, the resultant composite film was scraped and crushed into a powder which was subjected to calcination at $350\text{ }^{\circ}\text{C}$ in nitrogen for 3 h followed by heating at $400\text{ }^{\circ}\text{C}$ in the air for 3 h. **Fig. 1** shows the optical images of the pure $m\text{-TiO}_2$ and $\text{CoO}(x)/m\text{-TiO}_2$ catalysts after the annealing process. Clearly, there is a significant colour change from white of pure $m\text{-TiO}_2$ to greenish for $\text{CoO}(x)/m\text{-TiO}_2$ catalysts.

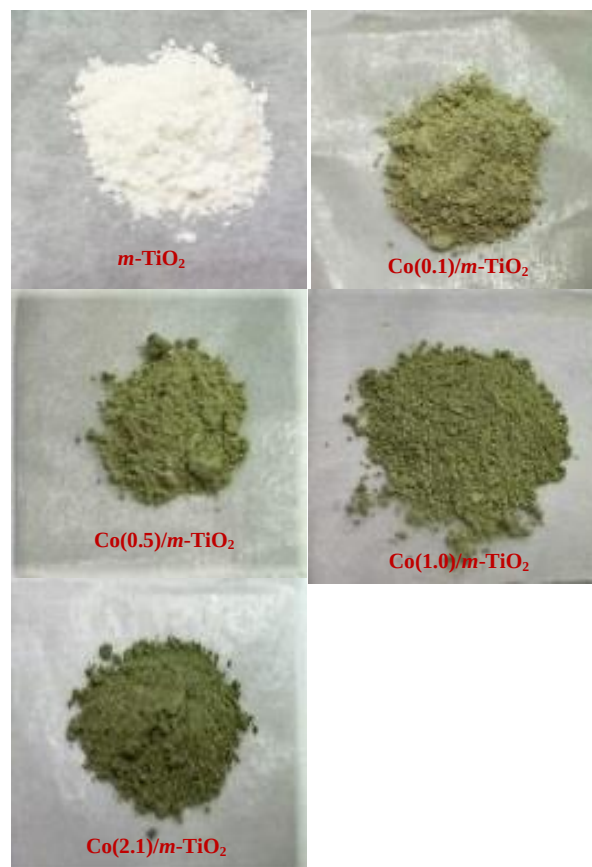


Fig. 1. Optical images showing the colour changes of $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts.

Fig. 2 shows the surface morphology and composition of Co(2.1)/*m*-TiO₂ catalyst as analyzed by scanning electron microscopy SEM and energy-dispersive X-ray spectroscopy (EDX) mapping respectively. The SEM image and corresponding EDX mapping of Co(2.1)/*m*-TiO₂ samples show the even distribution of the cobalt within the mesoporous TiO₂ support.

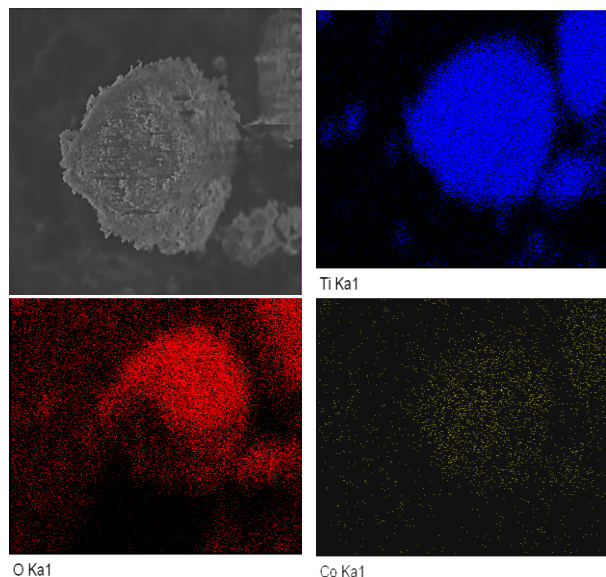


Fig. 2. Scanning electron microscopy SEM image and energy-dispersive X-ray spectroscopy (EDX) mapping of Co(2.1)/*m*-TiO₂.

The fine mesoporous structure and lattice spacing Co-doped TiO₂ catalyst were directly observed by HRTEM analysis as shown in **Fig. 3**. The TEM images show that all the Co(*x*)/*m*-TiO₂ have a highly and well-ordered mesoporous hexagonal channels with an average pore size reaches of 2.5 nm in consistent with the pore size of the pure *m*-TiO₂. The HRTEM images in **Fig. 3c** shows that all the pure mesoporous TiO₂ and Co(*x*)/*m*-TiO₂ (*x* = 0.002-0.025 Co: Ti molar ratio) are crystalline with the same lattice fringe spacing as the pure anatase *m*-TiO₂, suggesting that the lattice of *m*-TiO₂ doesn't change upon Co doping. The lattice fringes spacing were estimated to be (0.29, 0.32, and 0.35 nm) corresponding to (001), (100) and (101) planes of anatase TiO₂, respectively [37, 38]. The electronic diffraction pattern recorded on the at the TiO₂ wall shows a well-resolved diffraction rings and spots (**Fig. 3c**, inset) further confirming a crystalline anatase wall.

The effect of the Co-doped amount on the crystal structure of TiO₂ was studied by XRD and N₂ adsorption-desorption isotherms. **Fig. 4** shows the XRD of Co(*x*)/*m*-TiO₂ catalysts as compared with those of pure mesoporous TiO₂ and pure Co₃O₄ reference catalyst. The reference Co₃O₄ powders were synthesized by the same procedure, in which the amounts of cobalt nitrate and tetrabutyl titanate were 2.4 and 0 g, respectively.

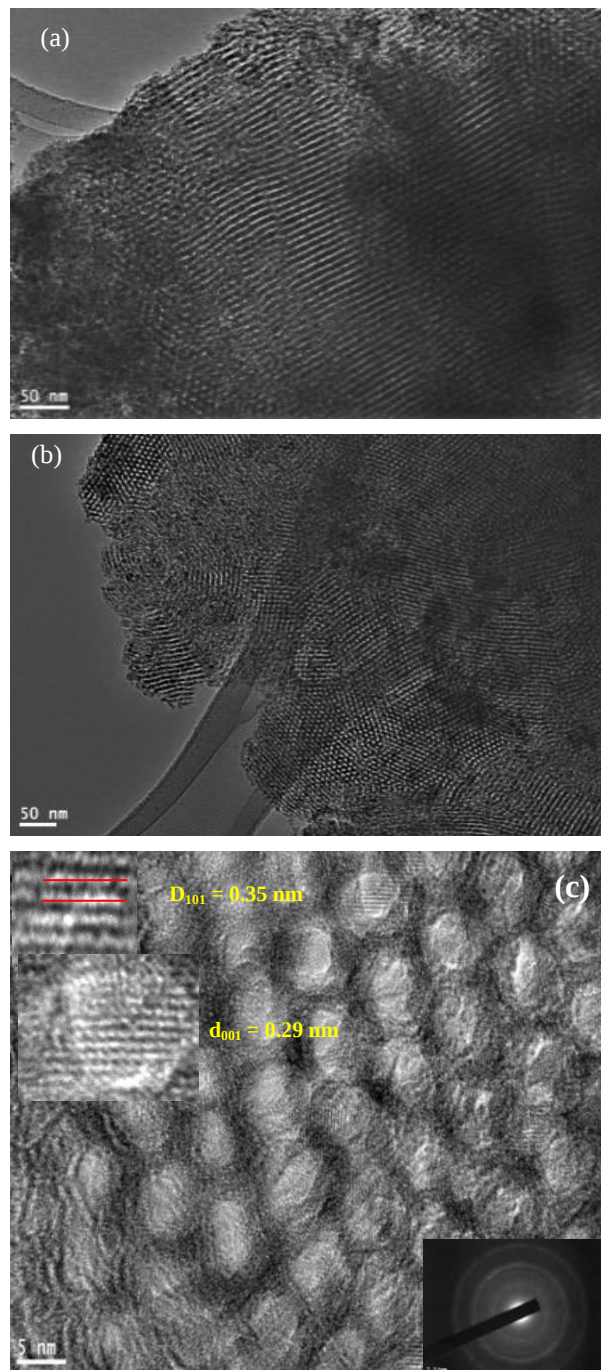


Fig. 3. TEM images of (a) pure *m*-TiO₂, (b) Co(2.1)/*m*-TiO₂ and (c) HRTEM of Co(2.1)/*m*-TiO₂ with the corresponding crystal lattice parameters, the inset is the electronic diffraction pattern.

As shown in **Fig. 4**, the XRD patterns clearly show that the Co(*x*)/*m*-TiO₂ catalysts display a crystalline anatase TiO₂ phase (JCPDS card No. 01-086-1157; Space group I41/amd) and have diffraction peaks that are identical to those of pure *m*-TiO₂ with no separate cobalt oxide peaks can be observed or matches with those of the pure Co₃O₄ reference. These results suggest that the incorporation of cobalt oxide does not change the crystal structure of the pure *m*-TiO₂. Moreover, the increase in cobalt oxide content neither modifies the

crystallinity of the mesoporous TiO_2 support nor leads to the appearance of the cobalt oxide diffraction peaks.

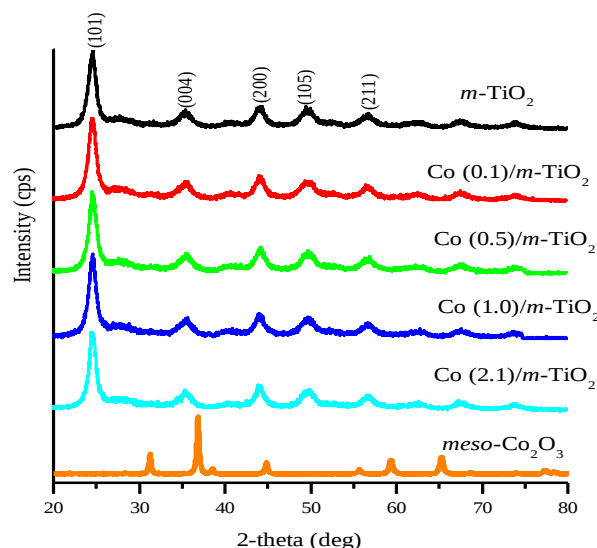


Fig. 4. Wide-angle XRD pattern of pure $m\text{-TiO}_2$, $\text{Co}(x)/m\text{-TiO}_2$ samples, and reference Co_3O_4 mesoporous.

The enlarged (101) diffraction peak of the pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts (Fig. S1) indicates no shift in 2θ values and the (101) diffraction feature which is evidence for the crystal growth of cobalt oxide proceeds along the same plane of anatase TiO_2 support [39].

The specific surface area and texture properties of the mesoporous $\text{Co}(x)/m\text{-TiO}_2$ catalysts were characterized by the N_2 -physisorption technique as shown in **Fig. 5**. The N_2 -adsorption-desorption isotherm of all catalysts exhibit the characteristic type IV curves with H1 hysteresis loops and capillary condensation steps which are the typical characteristic of the mesoporous materials according to the IUPAC classification [40, 41]. As shown in **Fig. 5a** the distinct capillary condensation at $P/P_0 = 0.4\text{--}0.8$, indicating the existence of cylindrical mesoporous pores, which is consistent with the TEM results. **Fig. 5b** shows the pore size distribution of pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts was calculated from the adsorption data using the Barrett–Joyner–Halenda (BJH) method. Moreover, the textural parameters of the specific surface area, mesopore volume and pore diameter of pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts obtained from the N_2 adsorption-desorption isotherms and Barrett–Joyner–Halenda (BJH) method are reported in **Table 1**. All the catalysts have a large specific surface area ($202\text{--}229\text{ m}^2/\text{g}$), big pore volume and uniform pore size range from 2 to 2.7 nm. Clearly, the introduction of CoO into the mesoporous TiO_2 mesoporous leads to a decrease in the pore volume as well as the pore size, presumably, due to the mesoporous wall structures becomes less porous and more crystalline on the addition of CoO. In contrast the $\text{Co}(x)/m\text{-TiO}_2$ catalysts exhibit more significant surface area than $\text{Co}(x)/\text{bulk-TiO}_2$ ($42\text{ m}^2/\text{g}$).

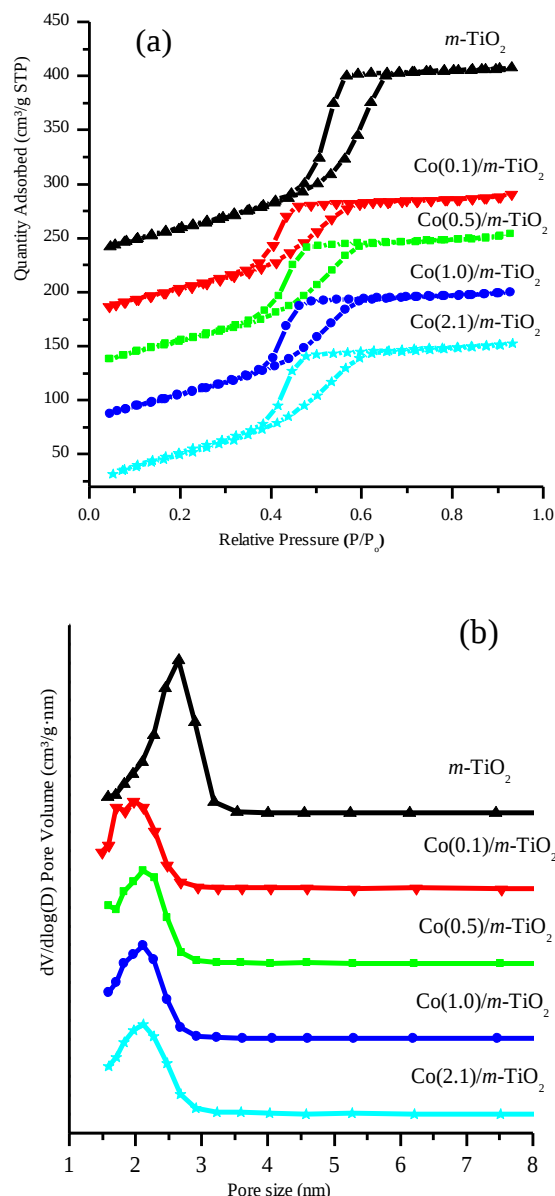


Fig. 5. (a) N_2 absorption-desorption isotherms of pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts, (b) the corresponding pore size distributions of $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts.

Table 1. Molar ratio and textural parameters of pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts.

Samples	Co, wt. %	S_{BET} (m^2/g) ^a	Pore volume (cm^3/g)	Pore size (nm)
$m\text{-TiO}_2$	0.0	218	0.33	2.65
$\text{Co}(0.1)/m\text{-TiO}_2$	0.1	202	0.21	2.0
$\text{Co}(0.5)/m\text{-TiO}_2$	0.5	207	0.22	2.12
$\text{Co}(1.0)/m\text{-TiO}_2$	1.0	225	0.21	2.11
$\text{Co}(2.1)/m\text{-TiO}_2$	2.1	229	0.22	2.11
$\text{Co}(2.1)/\text{bulk-TiO}_2$	2.1	42	0.025	1.50

The surface analysis of Co(x)/*m*-TiO₂ catalysts was performed by XPS spectra analysis to further ascertain the doping of Co into mesoporous TiO₂ support and its oxidation states [42, 43]. **Fig. 6** shows the XPS fine survey of pure *m*-TiO₂ and Co(2.1)/*m*-TiO₂ catalysts. In **Fig. 6a** the Ti 2p_{3/2} and 2p_{1/2} photoelectron peaks of pure *m*-TiO₂ are symmetric in nature and their binding energy (BE) positions are at 459.55 eV and 465.29 eV respectively, implying the Ti⁴⁺ oxidation state [44]. The value of spin-orbit splitting energy of those two peaks is 5.74 eV which is consistent with the reported literature value [45]. As Co loading increased, the Ti 2p_{3/2} peaks of Ti in Co(x)/*m*-TiO₂ catalysts are stayed identical to the pure *m*-TiO₂ except a slight red-shifted in BE by 0.15 eV suggesting the substitution of Ti (IV) by Co dopant [42, 43, 46, 47]. **Fig. 6b** and **6c** display XPS core spectra of O 1s region of pure *m*-TiO₂ and Co(2.1)/*m*-TiO₂ catalysts.

The other peak (2) located at 533.64 eV, is related to the OH group adsorbed at the surface of the mesoporous TiO₂. However, the O 1s region of Co(x)/*m*-TiO₂ catalyst (**Fig. 6c**) can be fitted into three Gaussian peaks marked as (1), (2) and (3). The peak located at 530.7 eV assigned to the Ti–O bonding in TiO₂ while the peaks located at 532.3 and 535.8 eV can be ascribed to the Ti–OH bonding and to the presence of Co–O bonding.

The core spectra of Co 2p in **Fig. 6d** displays two peaks at 781.2 and 796.7 eV in addition of two satellites at 786 and 803.6 eV which can assign to Co 2p_{3/2} and Co 2p_{1/2}, in consistent with the well-known characteristics of Co²⁺ species [48]. Moreover, in the Co 2p spectra the presence of small peak at 777 eV suggests the existence of a small account of Co(0) deposit [49].

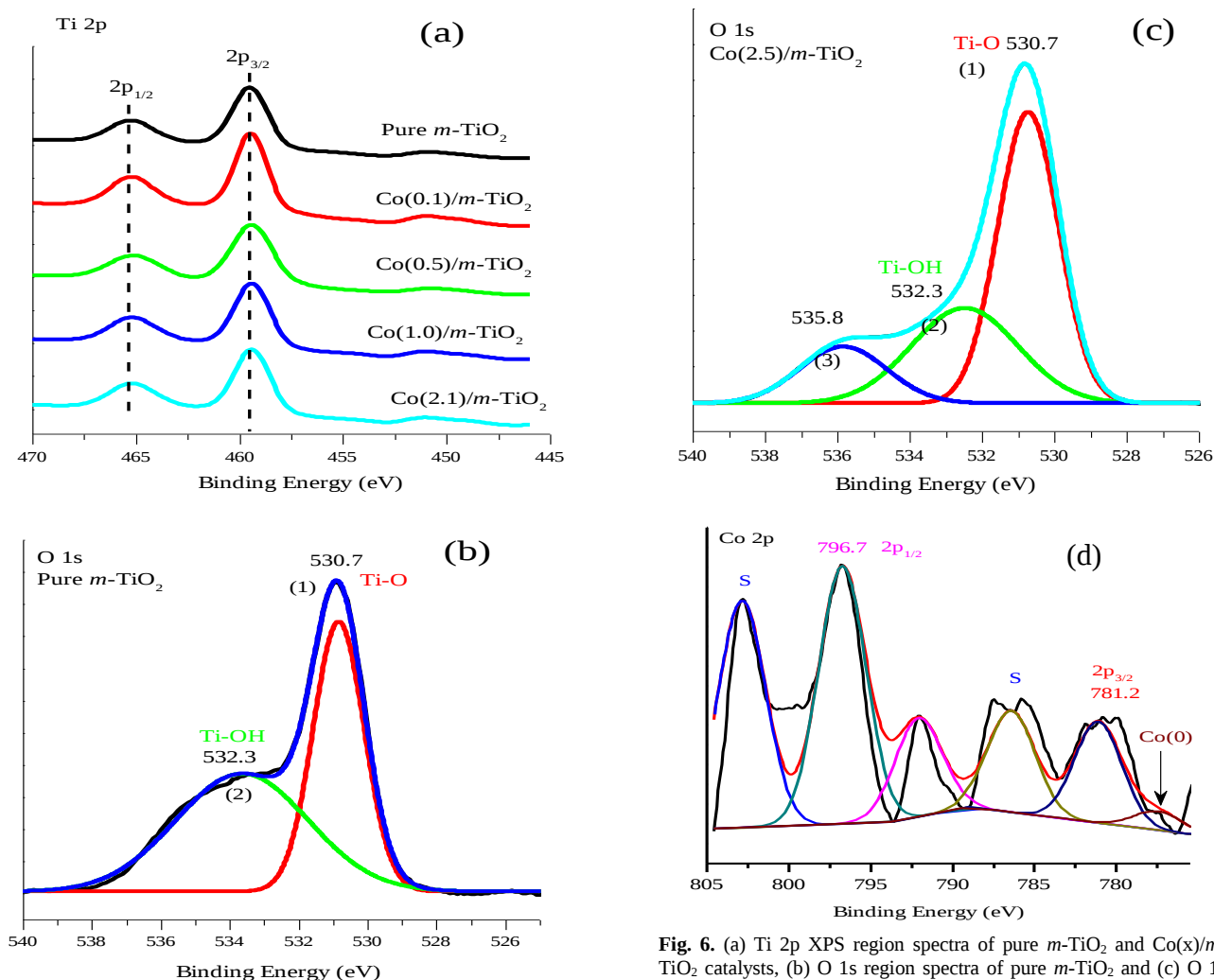


Fig. 6. (a) Ti 2p XPS region spectra of pure *m*-TiO₂ and Co(x)/*m*-TiO₂ catalysts, (b) O 1s region spectra of pure *m*-TiO₂ and (c) O 1s region spectra of Co(2.1)/*m*-TiO₂ and (d) Core spectra for Co 2p.

It is demonstrated that the O 1s of pure *m*-TiO₂ (**Fig. 6b**) which shows two different forms of oxygen. Two fitting Gaussian peaks assigned as (1) and (2) were used to fit the experimental data. The first peak (1) centred at the lower binding energy of 530.8 eV and is assigned to lattice oxygen of the TiO₂.

Electrocatalytic water oxidation activity

The electrocatalytic activity of pure *m*-TiO₂, Co(x)/*m*-TiO₂, Co(x)/*m*-TiO₂ and reference catalysts for oxygen evolution reaction (OER) in alkaline solution was carried out in 1.0 M KOH using standard three

electrodes system. Electrocatalysts were uniformly deposited as thin films on FTO substrates using EPD with a loading of $\sim 0.4 \text{ mg cm}^{-2}$. **Fig. 7 (a)** shows the OER catalytic activity of pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ in comparison to the commercial IrO_2 catalyst. All the $\text{Co}(x)/m\text{-TiO}_2$ catalysts show significantly enhanced OER activity as evidenced by the higher current density and improved oxygen evolution onset potential at approximately (1.55 V) in comparison with IrO_2 (1.48 V) and pure $m\text{-TiO}_2$ (1.8 V vs. RHE) as measured at a current density of 1.0 mA cm^{-2} .

A similar electrochemical behaviour was observed for the series of $\text{Co}(x)/m\text{-TiO}_2$ catalysts (**Fig. 7a**) and in compared to the pure $m\text{-TiO}_2$, the $\text{Co}(2.1)/m\text{-TiO}_2$ electrode afforded the least onset potential for OER at 1.55 V vs RHE among the catalysts tested here.

Fig. 7b shows the plot of the OER overpotential (η) for pure $m\text{-TiO}_2$ and the $\text{Co}(x)/m\text{-TiO}_2$ electrodes at a different current density of 0.5, 2 and 5 mA cm^{-2} as a function of the Co content in wt. %. As the Co concentration in the $\text{Co}(x)/m\text{-TiO}_2$ catalyst increases, the overpotential of the OER at current densities of 0.5, 2, and 5 mA cm^{-2} is decreased, which implies a better OER catalytic activity of the electrocatalyst. The lowest overpotential of 0.285 V is achieved by the $\text{Co}(2.1)/m\text{-TiO}_2$ catalyst, which is lower than the overpotential of 0.613 V of pure $m\text{-TiO}_2$ at 0.5 mA cm^{-2} . For comparison, a similar measurement for both commercial IrO_2 and $\text{Co}(2.1)/\text{bulk-TiO}_2$ catalysts were performed. As shown in **Fig. 7a** and **Table 2**, the IrO_2 catalyst displays a lower onset potential of 1.48 V vs. RHE. However, the $\text{Co}(2.1)/\text{bulk-TiO}_2$ catalyst has 1.55 V which is higher than that obtained for bulk $\text{Co}(x)/\text{bulk-TiO}_2$ catalysts due to the existence of highly ordered mesoporous TiO_2 support. Our $\text{Co}(x)/m\text{-TiO}_2$ catalysts show OER performance comparable with the IrO_2 catalyst particularly at higher polarization and much better activity than bulk $\text{Co}(2.1)/\text{bulk-TiO}_2$ catalyst.

To gain more insight into the enhanced OER activity of the $\text{Co}(x)/m\text{-TiO}_2$ catalysts, **Fig. 7c** shows the Tafel plot and **Table 2** reports the Tafel slope of the studied catalysts. Basically, the Tafel plot describes the relationship between the OE overpotential (η) and the logarithm of the current (I), which can provide useful information about water oxidation activity enhancement of the electrocatalyst [50].

The lower the value of the Tafel slope indicates more favourable OE kinetics. The Tafel slope of $\text{Co}(0.1)/m\text{-TiO}_2$ was the least (53 mV/dec) and it is slightly increased to about 67 mV/dec by adding more cobalt dopant which significantly less than a pure $m\text{-TiO}_2$ catalyst. The mass activity, specific activity and turn over frequency (TOF) of the catalysts are estimated following the method reported in the literature [51] and as described in the supporting information (SI). At $\eta = 0.35 \text{ V}$, the mass activity and specific activity of the best performance catalyst $\text{Co}(2.1)/m\text{-TiO}_2$ were found to be $31.5 \text{ mA cm}^{-2} \text{ mg}^{-1}$ and 12.6 mA cm^{-2} , respectively, (**Table 2**). The calculated TOF of $\text{Co}(2.1)/m\text{-TiO}_2$ at

$\eta = 350 \text{ mV}$ is 1.6, which is higher than TOF values for other catalysts. Again, in comparison to the bulk $\text{Co}(2.1)/\text{bulk-TiO}_2$ catalyst the TOF values of $\text{Co}(x)/m\text{-TiO}_2$ catalysts is at least 30 times more active for OER.

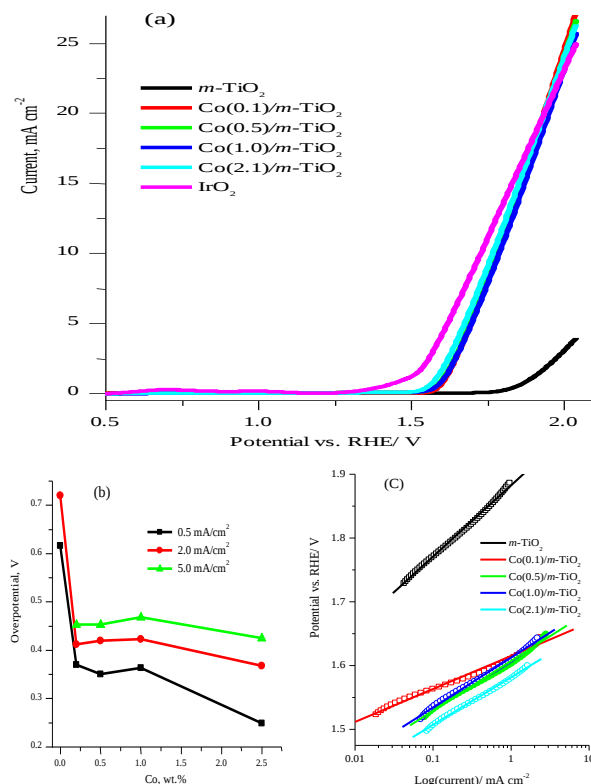


Fig. 7. (a) Linear sweep voltammetry (LSV) curves recorded at 10 mV s^{-1} for pure $m\text{-TiO}_2$, $\text{Co}(x)/m\text{-TiO}_2$ and commercial IrO_2 electrodes in 1.0 M KOH , (b) plot for the OER overpotential as function of Co wt. % content at different current density of $\text{Co}(2.1)/m\text{-TiO}_2$ electrode, (c) Tafel plots of pure $m\text{-TiO}_2$, $\text{Co}(x)/m\text{-TiO}_2$ and commercial IrO_2 electrodes.

Table 2. Summarized water oxidation reaction and OER activities of pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ catalysts.

Catalyst	Onset potential / V	Potential (V) at 10 mA cm^{-2}	mass activity at $\eta = 0.35 \text{ V}$ ($\text{mA cm}^{-2} \text{ mg}^{-1}$)	specific activity at $\eta = 0.35 \text{ V}$ (mA cm^{-2})	Tafel slope mV/dec	TOF
Pure $m\text{-TiO}_2$	1.75	> 2.0	0.625	0.25	110	0.03
$\text{Co}(0.1)/m\text{-TiO}_2$	1.58	1.77	27.3	10.9	53	1.38
$\text{Co}(0.5)/m\text{-TiO}_2$	1.57	1.78	27.3	10.9	72	1.38
$\text{Co}(1.0)/m\text{-TiO}_2$	1.57	1.78	27.3	10.9	73	1.38
$\text{Co}(2.1)/m\text{-TiO}_2$	1.55	1.76	31.5	12.6	67	1.6
IrO_2	1.48	1.72	35.5	14.2	--	--
$\text{Co}(2.1)/\text{bulk-TiO}_2$	1.62	1.70	0.88	0.350	98	0.05

^aOnset overpotential, ^bOverpotential at $j = 0.5 \text{ mA cm}^{-2}$, ^cSpecific activity is normalized to the BET surface area (see Table.1), ^dTafel equation: $\eta = b \log(j/j_0)$, η is the overpotential (measured), defined as $E_{\text{Applied}} (\text{vs. RHE}) - 1.23 \text{ V}$, b is the Tafel slope (mV/decade), j is the current density (measured), and j_0 is the exchange current density, ^e Turnover frequency (TOF), see supporting information for the calculation method.

The electrochemical impedance spectroscopy (EIS) was employed to study the charge-transfer resistance and the reaction kinetics during OER process at the $\text{Co}(x)/m\text{-TiO}_2$ and $m\text{-TiO}_2$ electrodes. **Fig. 8a** shows the Nyquist plots of various $\text{Co}(x)/m\text{-TiO}_2$ and $m\text{-TiO}_2$ electrodes at overpotential of 1.55 V vs SCE in 1.0 M KOH solution. The inset in **Fig. 8a** shows resistor-capacitor (RC) circuit model that obtained by fitting of the impedance spectra. The equivalent circuit elements contains a resistor (R_s) assign to electrolyte resistance between the working and reference electrode; the charge transfer resistance (R_c), corresponding to the charge transfer resistivity of the electrochemical reaction; and the constant phase element (CPE) (Q_2) in parallel to (R), corresponding to the catalyst/ KOH interface, respectively. The fitted values of R_s , R_c , and Q_2 were calculated, and these are summarised in **Table 3**. Clearly, more better OER activity is observed at the $\text{Co}(2.1)/m\text{-TiO}_2$ catalyst in comparison to other studied catalysts. This catalyst has lowest charge-transfer resistance (R_{ct}) and the trend is increase as $m\text{-TiO}_2 < \text{Co}(0.1)/m\text{-TiO}_2 < \text{Co}(0.5)/m\text{-TiO}_2 < \text{Co}(1.0)/m\text{-TiO}_2 < \text{Co}(2.1)/m\text{-TiO}_2$, suggesting that the cobalt doped samples possess smaller charge transfer resistance and better electrochemical OER performance. Furthermore, the result indicates that the modification of mesoporous TiO_2 with cobalt oxide centres accelerate the charge transfer kinetics and acts as effective water oxidation electrocatalyst.

The long-term durability is a significant benchmark to evaluate the electrocatalyst. To examine the catalyst long-term stability of $\text{Co}(x)/m\text{-TiO}_2$ electrodes for OER in alkaline solution, the chronoamperometry measurement ($j-t$) for $\text{Co}(2.1)/m\text{-TiO}_2$ electrode alongside with commercial IrO_2 was carried out at a constant potential of 1.6 V vs. RHE in 1.0 M KOH as shown in **Fig. 8b**. The chronoamperometry response demonstrates a high stability for $\text{Co}(x)/m\text{-TiO}_2$ than a commercial IrO_2 catalyst. Within 4 h of water electrolysis in alkaline solution, the $\text{Co}(2.1)/m\text{-TiO}_2$ catalyst exhibits robust long-term stability and a current gain of about 18% indicating further activation during extended electrolysis. On the other hand, the commercial IrO_2 catalyst shows significant current attenuation of 40% due to its instability in alkaline electrolyte [52].

Table 3. AC impedance parameters of $\text{Co}(x)/m\text{-TiO}_2$ catalysts obtained by fitting the experimental data in Fig. 8a.

Impedance	$m\text{-TiO}_2$	$\text{Co}(0.1)/m\text{-TiO}_2$	$\text{Co}(0.5)/m\text{-TiO}_2$	$\text{Co}(1.0)/m\text{-TiO}_2$	$\text{Co}(2.1)/m\text{-TiO}_2$
R_s (Ω)	29	17	19	18	17
R_{ct} (Ω)	153456	8230	2282	846	188
Q_2 ($\mu\text{F s}^{(a-1)}$)	23	240	320	1810	2100

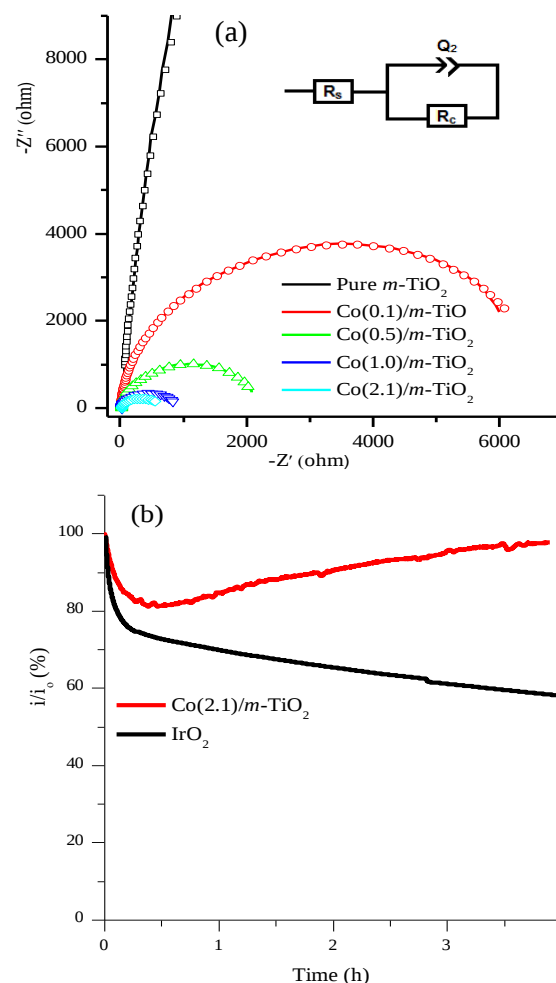


Fig. 8. (a) Nyquist plots with an equivalent circuit for pure $m\text{-TiO}_2$ and $\text{Co}(x)/m\text{-TiO}_2$ electrodes in 1.0 M KOH solution at mV vs. RHE in the frequency range 10^{-2} to 200kHz, (b) Chronoamperometry for $\text{Co}(2.1)/m\text{-TiO}_2$ alongside with commercial IrO_2 electrode at a constant potential of 1.6 V vs. RHE in 1.0 M KOH. The catalyst loading on FTO was 0.4 mg cm^{-2} .

Conclusion

The soft-templating method was utilized to in-situ prepare ordered mesoporous $m\text{-TiO}_2$ decorated with cobalt oxide ($\text{Co}(x)/m\text{-TiO}_2$) catalysts. The $\text{Co}(2.1)/m\text{-TiO}_2$ catalyst with 2.0 wt. % of Co oxide shows the highest OER activity with a 200 mV decrease in overpotential (η), $31.5 \text{ mA cm}^{-2} \text{ mg}^{-1}$, the specific activity of 12.6 mA cm^{-2} at $\eta = 350 \text{ mV}$. Moreover, the $\text{Co}(2.1)/m\text{-TiO}_2$ catalyst exhibits much better stability than commercial IrO_2 during prolonged water electrolysis. Despite the low loading of cobalt oxide electrocatalyst (0.1- 2.1 wt. %), the entire $\text{Co}(x)/m\text{-TiO}_2$ catalysts exhibit significant activity for OER in alkaline media in comparison with the pure mesoporous TiO_2 and bulk $\text{Co}(2.1)/\text{bulk-TiO}_2$ catalysts. This enhanced catalytic performance of $\text{Co}(x)/m\text{-TiO}_2$ catalysts in concentrated alkaline solutions can be attributed to the existence of a highly porous structure of the TiO_2 support that facilitates the mass transport of reactive materials. Moreover, the in-situ dopant method allows

for homogeneous CoO dopant distributions with exhibit higher surface-active sites. This work opens a route to rational synthesis a variety of transition metal electrocatalyst supported onto a mesoporous TiO₂ substrate for various applications in renewable energy production.

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Author's contributions

Conceived the plan: MSA and PA performed the experiments and made the data analysis: AMA, TAA and MAG wrote the results, discussion and finalise the paper submission. Authors have no competing financial interests.

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