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Methane assisted low temperature isothermal thermochemical water splitting over Pt/CeO₂ nanorods

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ABSTRACT

Thermochemical water splitting (TCWS) is a promising route to produce hydrogen using heat, but conventional redox cycles typically require large temperature swings at 800–1400 °C, which limits materials stability and process efficiency. Herein we demonstrate isothermal, methane assisted TCWS at 300 °C using Pt/CeO₂ nanorods as a redox active platform. Catalysts with 1 and 5 wt% Pt were characterised by XRD, HRTEM, H₂-TPR, Raman spectroscopy, XPS and XAS to relate structure and reducibility to oxygen vacancy formation and redox performance. Under isothermal cycling, methane is used as a sacrificial chemical reductant to generate oxygen vacancies at Pt-ceria perimeter sites, while subsequent exposure to H₂O produces H₂ exclusively from water in the oxidation step. At 300 °C, 1 wt% Pt/CeO₂ nanorods reach cumulative H₂ yields of 20 mLg⁻¹ over four redox cycles and 5 wt% Pt/CeO₂ reaches 27.5 mLg⁻¹, with limited loss of nanorod morphology. D₂O labelling experiments at 300 °C confirm that D₂ and HD form only in the oxidation window, whereas H₂ formed in the CH₄ reduction window originates from methane reforming. At 400 °C, the isotopic response shows additional D₂ formation during the CH₄ step and coincides with nanorod sintering and Pt agglomeration, indicating a change in the redox pathway. XPS and Raman analysis indicate that moderate Pt loading increases the accessible Ce³⁺ fraction and defect level in the CeO₂ lattice while preserving a well-defined Pt-ceria perimeter. Although the absolute H₂ productivity is modest and methane is consumed sacrificially, the results establish a low temperature, isothermal TCWS process that exploits Pt-ceria perimeter chemistry at 300 °C and provide a mechanistic basis for designing chemically assisted looping redox cycles hydrogen production.

1. Introduction

Hydrogen is a cornerstone of sustainable energy systems and industrial decarbonization. However, over 95% of global hydrogen is still produced via fossil-based processes such as steam methane reforming, which emit significant CO₂ and rely on high temperatures and natural gas inputs [1–4]. Over the past years, thermochemical water splitting (TCWS) has garnered attention for enabling hydrogen production by cyclically oxidizing and reducing metal oxides [5–8]. In typical cycles, the oxide is reduced at temperatures above 1200 °C, releasing oxygen, and is subsequently re oxidised by steam at around 800 °C to produce hydrogen [6,7]. However, the extreme reduction temperatures (>800–1400 °C) impose thermal stress, accelerate sintering, and

complicate the reactor design [5–10]. Metal oxides have been extensively studied for TCWS because of their excellent redox properties. Their ability to undergo reversible reduction and oxidation makes them ideal candidates for thermal energy driven hydrogen production [12–15]. In general, most of the TCWS cycles are typically performed in this temperature swing mode which decreases the overall efficiency of the hydrogen production due to prolonged heating and cooling times. Efforts to lower operating temperatures have shown limited success, with most isothermal metal oxide-based systems still requiring ≥400 °C. Reports demonstrating stable hydrogen production at low temperature remain scarce, particularly with sustained redox cycling with OVs on metal oxide surface. Achieving efficient oxygen vacancy (OV) generation under low-temperature, isothermal conditions remains difficult due

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to sluggish kinetics. [11].

Among the metal oxides cerium dioxide (CeO_2) is the benchmark TCWS oxide due to its high oxygen mobility and reversible $\text{Ce}^{4+}/\text{Ce}^{3+}$ redox couple [10–15]. CeO_2 can exist in various morphologies, such as cubes, nanorods, and nanowires, each exhibiting different effects on the thermal water splitting reaction performance [16]. Ceria nanorods (CeNRs), owing to their preferential exposure of the reactive [100] and [110] facets, are known to exhibit higher OV densities and improved redox activity. In our prior work, we leveraged this morphology to lower the TCWS temperature to 400 °C, achieving a peak hydrogen yield of 4.7 mLg^{-1} over three redox cycles [16]. However, hydrogen production declined sharply after the first cycle due to sintering of the nanorods which limited OV regeneration. This highlighted a key limitation of bare CeNRs under isothermal operation: despite their favourable redox chemistry, maintaining nanorod morphology requires operation at even lower temperatures, where thermal reduction alone becomes insufficient. This suggests a need of incorporating catalytic metals that can facilitate vacancy formation more effectively or external promotion by introducing reducing agents capable of extracting lattice oxygen [31–40]. Literature reports various strategies such as doping with transition metals (Ni, Fe, Mn, Zr) to enhance its redox performance for TCWS. Such dopants improve lattice oxygen mobility and lower the reduction temperature threshold, thereby facilitating more efficient OV formation. For example, $\text{CeO}_2\text{-ZrO}_2$, $\text{CeO}_2\text{-NiO}$ and $\text{CeO}_2\text{-MnO}$ demonstrated high H_2 production at 1400 (reduction) and 800 °C (oxidation), while $\text{CeO}_2\text{Fe}_2\text{O}_3$ offered excellent cycle stability [17–22]. Among these, incorporating Zr^{4+} improves both reducibility and stability, as seen in $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$, which maintains high redox activity [17–19]. However, these strategies have been largely applied under high-temperature and temperature swing conditions. On the other hand, chemical promotion through external reducing molecules has emerged as a complementary strategy for regenerating oxygen vacancies. This concept stems from studies on CO oxidation over CeO_2 , where it has been shown that CO can effectively abstract lattice oxygen from the oxide surface, thereby reducing Ce^{4+} to Ce^{3+} [33]. Methane behaves similarly to CO in its interaction with ceria both extract lattice oxygen and reduce Ce^{4+} to Ce^{3+} through partial oxidation, enabling vacancy formation without the need for extreme thermal input.

This redox behaviour, observed across a range of temperatures (500–1000 °C) and facilitates more efficient OV regeneration. However, the literature shows that nearly all methane-assisted redox schemes still rely on moderate-to-high temperatures and temperature swings [23]. A comparison of hydrogen production performance from ceria-based redox systems reported in the literature is summarised in Table S1. Most reported studies rely on methane-driven ceria reduction to produce syngas at temperatures $\geq 400\text{--}1127$ °C [23–32]. Only a few studies combine partial methane oxidation with subsequent water oxidation at a different temperature, and these yield only modest hydrogen production with limited selectivity. In contrast, the present work demonstrates a significantly higher hydrogen yield of 27.5 mLg^{-1} at a substantially lower temperature of 300 °C under methane-assisted reduction and isothermal water splitting, highlighting its superior low-temperature redox efficiency of the Pt-ceria perimeter approach. Constant-temperature hydrogen production below 500 °C remains largely unexplored. This ability to reduce CeO_2 has also been widely studied in the context of steam methane reforming (SMR) and dry reforming, where ceria functions both as a support and as an active redox material. Its strong interaction with carbon-containing molecules, particularly under catalytic promotion with metals such as Pt, Cu, Pd, or Fe, makes it a promising candidate for low-temperature chemical promotion of ceria-based systems [32–38].

Building on these insights, this work investigates platinum (Pt)-decorated CeO_2 nanorods (Pt/CeNRs) as a platform for methane-assisted, isothermal thermochemical water splitting. Pt exhibits high activity when supported on ceria creating OVs, attributed to its fine dispersion and stable metallic state, which enhance catalytic

performance [33–35]. This increased concentration of surface OVs improves the redox capacity of ceria under mild conditions. Metallic platinum promotes the reduction of Ce^{4+} to Ce^{3+} in Pt/ CeO_2 systems through several key mechanisms [33–43]. Firstly, electronic interactions between Pt and ceria, particularly direct charge transfer, facilitate electron donation from Pt to ceria. This enhances the ease with which Ce^{4+} is reduced to Ce^{3+} , especially near the Pt-ceria interface [32,33]. While bare CeO_2 typically reduces at temperatures above 500 °C (Surface) and 800 °C (Bulk), the presence of Pt shifts this to much lower temperatures ($\sim 200\text{--}300$ °C), indicating enhanced oxygen mobility and surface activation [34]. Furthermore, bare ceria exhibits limited activity toward methane activation whereas the presence of Pt enables efficient methane dissociation and lattice oxygen abstraction at the Pt- CeO_2 perimeter, which is essential for chemically driven vacancy regeneration. These combined effects explain the enhanced reducibility and material efficiency of Pt/ CeO_2 materials. This combination of low-temperature methane activation and perimeter-mediated lattice oxygen abstraction distinguishes the present use of Pt from its conventional role in CO oxidation or reforming catalysis. Leveraging this behaviour, we introduce controlled amounts of methane during the reduction phase to chemically assist oxygen vacancy generation via the Pt- CeO_2 interface, followed by water splitting in the oxidation phase at a constant temperature of 300 °C. This establishes a low temperature, isothermal TCWS mode in which chemical promotion replaces large thermal swings and provides a conceptually different way to operate redox cycles.

In this work, we evaluate 1 and 5 wt% Pt/CeNRs in methane assisted, isothermal TCWS at 300 °C. We first establish the structural and redox properties of CeNRs and Pt/CeNRs using several characterizations methods, and relate these to oxygen vacancy formation at the Pt-ceria perimeter. We then demonstrate that brief exposure to methane during the reduction phase at 300 °C generates oxygen vacancies that can be refilled by water in the subsequent oxidation phase, yielding hydrogen exclusively from water as confirmed by D_2O labelling experiments. The hydrogen production behaviour and material stability of 1 and 5 wt% Pt/CeNRs are compared over multiple redox cycles at 300 °C and contrasted with operation at 400 °C, where a change in redox pathway coincides with nanorod sintering and Pt agglomeration. Under methane-assisted isothermal operation at 300 °C, Pt/CeNRs deliver cumulative hydrogen yields of 20–27.5 mLg^{-1} over four consecutive redox cycles, demonstrating stable low-temperature thermochemical water splitting in a ceria-based system. Finally, we discuss how Pt-ceria perimeter controlled vacancy cycling can be used as a chemically assisted redox concept for low temperature TCWS and outline limitations and optimisation directions relevant for integrating such schemes into chemical looping and hydrogen production processes.

2. Experimental

2.1. Material and methods

All chemicals were purchased from Sigma-Aldrich and used without further purification. Tetraammineplatinum(II) chloride hydrate [Pt (NH_3)₄Cl₄·xH₂O, 98%], cerium (III) chloride heptahydrate ($\text{CeCl}_3\cdot 7\text{H}_2\text{O}$, 99.9%), and sodium hydroxide (NaOH, 99%) were used as received. Ultrapure argon and methane gases were employed during the TCWS reactions.

2.2. Synthesis of Pt/CeNRs material

First CeNRs were synthesized through a combination of coprecipitation and hydrothermal synthesis. Pt/CeNRs were synthesized via a coprecipitation method with Pt loadings of 1 wt% and 5 wt%. The process began by dissolving $\text{CeCl}_3\cdot 7\text{H}_2\text{O}$ in deionized (DI) water under continuous stirring for 10–15 min. To induce precipitation, 10 M NaOH was gradually added to the solution, followed by an additional 15 min of stirring to ensure homogeneity. In a separate beaker, a calculated

amount of platinum precursor was dissolved in DI water to prepare the platinum solution. This solution was then introduced into the basic cerium precursor mixture. The resulting suspension was transferred to a Teflon-lined autoclave and placed in an oven at 120 °C for 24 h. Afterwards, the material was filtered using DI water in a Büchner funnel until the pH was neutralized, followed by washing with ethanol. The material was then placed in an oven at 100 °C for 24 h to ensure complete removal of residual moisture.

2.3. Reactor setup and product analysis

The TCWS experiments were carried out in fixed bed reactor system (Fig. S1). A quartz tube of 48 cm length, 6 mm outer diameter, 4 mm inner diameter was mounted in a tubular furnace (Nabertherm) furnace at set temperature. Pt/CeNRs powders were pelletized and sieved to 150–300 µm and 148 mg was loaded as a 1–2 cm bed at the centre of the tube secured with quartz wool from both sides. Feed gases were controlled by thermal mass-flow controllers (Bronkhorst), and liquid water was pumped by a syringe pump (New Era Syringe pump inc.) to a heated evaporator coil kept at 120 °C that subsequently connected to a 4-way switching valve. To avoid the water condensation all the lines from 4-way switching valves until the inlet of reactor were heated at 120 °C. Depending on the valve position either pure argon/methane or water steam was passed to the quartz tube. A water condenser connected at the outlet of reactor to condense the unreacted water, whereas the effluent gases were passed to analytical system.

2.4. Reaction conditions and product quantification

Two sets of redox protocols were used: a thermal reduction under argon gas and a methane-assisted chemical reduction. In both cases, the cycle began with a 30-min argon purge (18 mL min⁻¹) to clean the material surface, followed by a 90-min oxidation step using steam carried in argon (water feed: 0.01 mL min⁻¹; Ar: 6 mL min⁻¹). For the thermal reduction cycle, the subsequent reduction phase involved flowing argon alone (18 mL min⁻¹) for 120 min. In contrast, the methane-assisted reduction employed a three-step sequence: a 30-min argon purge (18 mL min⁻¹), 15 min of pure methane exposure (6 mL min⁻¹), and a final 75-min argon purge (18 mL min⁻¹). For isotopic labelling experiments, D₂O was used in place of H₂O during the oxidation phase, with all other conditions held identical. The analytical system consisted of a mass spectrometer (Hiden Analytical QGA) and gas chromatograph with thermal conductivity detector (Thermo Trace GC). The following mass-to-charge ratios were monitored continuously: *m/z* 2 (H₂), 3 (HD), 4 (D₂), 15–16 (CH₄), 18 (H₂O), 20 (D₂O), 28 (CO), and 44 (CO₂) while GC collected the measurements at 3-min intervals for quantitative analysis. GC peak areas were converted to molar flow rates using external calibration curves. Per-cycle H₂ yields were calculated by integrating the H₂ molar flow over the oxidation step, and normalizing by catalyst mass to report hydrogen production in mL g⁻¹.

2.5. Material characterization information

Powder X-ray diffraction (PXRD) were recorded on a Bruker D8 Advance-ECO with CuKα₁ and Kα₂ radiation as the X-ray source. The powdered sample was compactly and evenly placed in a Si sample holder, ensuring it was level with the holder, before being analysed. Transmission Electron Microscopy (TEM) was performed by transmitting a beam of high-energy electrons through the material using JEOL11400 plus instrument. Samples were prepared by adding a small amount of material into a mortar and pestle, crushing it with isopropanol for uniform dispersion, and pipetting it onto a mesh grid, which was transferred into the sample holder. The sample holder was placed into the machine under vacuum conditions, and images were captured using a 4 K camera after fine-tuning the optics. High-angle annular dark-field scanning transmission electron microscopy

(HAADF-STEM) and high-resolution TEM imaging were performed using a JEOL JEM F-200 microscope. For HRTEM, samples were prepared by drop-casting a well-dispersed solution (1.0 mg in 5 mL Ethanol) onto carbon-coated copper grids (200 mesh), and subsequently dried under IR illumination for 1 h. Hydrogen Temperature Programmed Reduction (TPR) experiments were conducted in a fixed-bed reactor equipped with a thermal conductivity detector (TCD). The samples were prepared by adding quartz wool into a quartz reactor, followed by approximately 200 mg of SiC, then 100 mg of the material, and another 200 mg of SiC. The reactor was placed inside the furnace and subjected to reduction using 10% H₂/Ar (hydrogen/argon) gas, with the temperature ramped up to 1000 °C at 10 °C/min heating rate. The peaks obtained at the end of the process identified the temperatures at which reduction occurred. Ex situ X-ray Photoelectron Spectroscopy (XPS) was conducted using a ThermoFisher K-α instrument to determine the oxidation state of the support material. Samples were prepared by placing powdered material onto carbon tape affixed to the sample holder, shaking off excess powder, and transferring the holder into the entry chamber. Once the pressure fell below 10⁻⁷ Pa, the sample was introduced into the analysis chamber, where the difference between the incident X-ray beam's fixed energy and the energy measured after reflection was used to determine the material's binding energy and oxidation state (range of 0 to 1400 eV). XPS experiments under N₂O and argon atmospheres were performed in a custom reaction cell equipped with a gas feeding system operating at 1 bar in Kratos Ultra DLD XPS instrument with a monochromated Al-Kα (excitation energy of 1486.7 eV) X-ray source. XPS spectra were recorded using pass energy of 20 eV and a step size of 0.01 eV. The curve fitting was performed by the CasaXPS using a Gaussian-Lorentzian (30% Lorentzian and 70% Gaussian). Raman spectroscopy was used with visible red laser wavelength of 785 nm as the incident light source, and an external BWtek detector (spectra recorded every 3 min). The Pt/CeNRs sample was diluted with KBr in equal amount. X-ray absorption spectroscopy (XAS) measurements were carried out on the samples filled into 0.7 mm outer diameter quartz capillaries (0.01 mm wall thickness) with a packing height of approximately 1 cm, secured between quartz wool plugs. Due to the highly electrostatic and sticky nature of the powders, sample handling required mild shaking, ultrasonic treatment, and mechanical vibrations to achieve uniform packing. The samples were measured using an air-bearing liquid nitrogen double-crystal monochromator equipped with flat Si (111) crystals. Transmission ion chambers were employed for energy calibration with Pt foil, Cr foil (close to Ce K-edge), and a commercial CeNRs reference. Fluorescence spectra were collected using a Vortex SDD detector coupled with XIA Falcon X fast digital multichannel analyser electronics.

3. Results and discussion

3.1. Material characterization

Powder X-ray diffraction (PXRD) was performed to confirm the crystalline phase and structural integrity of the synthesized CeO₂ nanorods and Pt-loaded samples. As shown in Fig. 1A, the diffraction patterns for pristine CeNRs, 1 wt% Pt/CeNRs, and 5 wt% Pt/CeNRs display peaks corresponding to the cubic fluorite structure of cerium dioxide (space group Fm-3m), with characteristic reflections matching the JCPDS No. 34-0394. These results confirm the phase purity of the CeNRs and demonstrate that the introduction of Pt did not alter the bulk CeO₂ structure. No distinct Pt reflections are observed at 1 wt% Pt loading, suggesting atomic-level dispersion or ultra-small clusters below the detection limit. In contrast, very weak reflections near 40° corresponding to PtO₂ (111) are visible in 5wt. %Pt sample, consistent with small crystallites. The absence of peak shifting or significant broadening across the samples implies that Pt does not cause appreciable lattice distortion or substitutional incorporation into the ceria lattice.

H₂-TPR analysis (Fig. 1B) was performed to assess the reducibility of

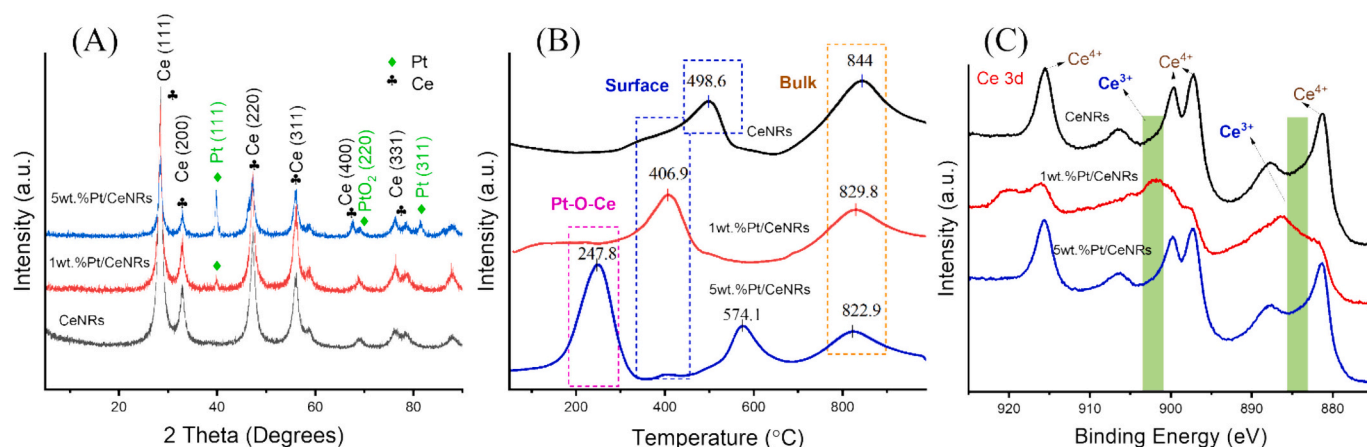


Fig. 1. Structural and redox characterization of CeNRs and Pt/CeNRs. (A) PXRD patterns of CeNRs, 1 wt% Pt/CeNRs and 5 wt% Pt/CeNRs. (B) H_2 -TPR profiles of CeNRs and Pt/CeNRs. (C) Ce 3d XPS spectra and deconvolution showing the evolution of the surface $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio with Pt loading.

CeNRs and Pt-loaded CeNRs. Bare CeNRs exhibited an initial reduction onset near 450°C , typically attributed to the removal of surface oxygen species associated with Ce^{4+} to Ce^{3+} transitions [16]. Upon incorporation of 1 wt% Pt, the main reduction feature shifted to $\sim 300\text{--}400^\circ\text{C}$, assigned to Pt-Ce-O interfacial species, indicating enhanced low-temperature reducibility due to strong metal support interactions. At 5 wt% Pt loading, an additional low-temperature peak emerged near $200\text{--}250^\circ\text{C}$, corresponding to the reduction of surface PtO_x species, as reported in previous studies [36–40]. The progressive shift in reduction temperatures with increasing Pt content reflects the role of Pt in facilitating lattice oxygen removal. This suggests that Pt–Ce interactions play a crucial role in enhancing low-temperature reducibility, potentially supporting sustained OV cycling under isothermal methane-assisted TCWS conditions.

XPS was used to investigate the surface chemical states of Ce and the influence of Pt loading on OV formation. The Ce3d spectra (Fig. 1C) exhibit the expected multiplet splitting characteristic of Ce^{3+} and Ce^{4+} . In the bare CeNRs sample, the spectrum is dominated by Ce^{4+} , consistent with fully oxidised CeO_2 surface. Upon incorporation of 1 wt% Pt, the relative intensity of Ce^{3+} features increases significantly, indicating enhanced surface reduction and a higher concentration of OVs. This qualitative shift indicates a higher concentration of surface OVs consistent with the H_2 -TPR results, which show a reduction temperature shift due to Pt-induced promotion of lattice oxygen removal. At 5 wt% Pt loading, the Ce^{3+} features remain visible but appear less intense than in the 1 wt% sample, potentially due to Pt occupying or passivating surface oxygen vacancy sites. Such behaviour is in agreement with prior studies reporting that excessive Pt loading can mask the ceria surface and suppress vacancy generation. This balance between Pt dispersion and surface accessibility appears critical where low Pt loadings activate the ceria surface and enhance vacancy formation. These findings underscore the synergistic role of Pt in modulating the redox chemistry of CeO_2 at the surface level. The increase in Ce^{3+} content at moderate Pt loadings supports the hypothesis that Pt/CeNRs interfacial interactions enhance OVs formation, which is essential for low-temperature redox cycling in TCWS applications.

The TEM images at different magnifications (Fig. S4) show that pristine CeNRs possess a smooth and uniform rod like morphology with well defined edges. After incorporation of 1 wt% Pt, the nanorods remain clearly identifiable, but their surfaces appear slightly rougher and small, brighter contrasts are visible along the rod facets, consistent with finely dispersed Pt containing particles. In the 5 wt% Pt/CeNRs sample, the rods exhibit more pronounced surface roughness and partial agglomeration; in addition to elongated rods, domains with more cubic like morphology are observed, indicating local structural distortion at higher Pt loading.

High resolution TEM (HRTEM) and fast Fourier transform (FFT) analysis provide further insight into the local structure (Fig. 2 A&A1). For 5 wt% Pt/CeNRs, lattice fringes with a spacing of $\sim 0.19\text{ nm}$ are observed, which can be assigned to the (200) planes of metallic Pt, while fringes with a spacing of $\sim 0.27\text{ nm}$ are consistent with the (010) planes of PtO_2 , confirming the presence of both metallic and oxidic Pt domains at higher loading. The underlying ceria displays fringes with spacings of $\sim 0.28\text{--}0.32\text{ nm}$, which correspond to the (200) and (111) planes of fluorite CeO_2 , respectively. The selected area electron diffraction (SAED) pattern (inset Fig. 2A) exhibits distinct rings that match the cubic CeO_2 phase, confirming that the nanorods retain their crystalline fluorite structure after Pt loading. For 1 wt% Pt/CeNRs, HRTEM images (Fig. 2 B1&B2) show lattice fringes with spacings of $\sim 0.19\text{ nm}$ and $\sim 0.32\text{ nm}$, which can be indexed to the (200) planes of metallic Pt and the (111) planes of CeO_2 , respectively [44]. In this sample, separate PtO_2 domains are not clearly resolved by HRTEM, in line with the absence of distinct PtO_2 reflections in PXRD at 1 wt% loading. The corresponding SAED pattern again shows rings characteristic of fluorite CeO_2 , indicating high crystallinity of the CeNR backbone. HAADF STEM imaging and elemental mapping (Fig. 2 C&D) reveal that Ce and O are distributed throughout the nanorods, while Pt signal is concentrated near the rod surfaces, consistent with Pt nanoparticles decorating the CeO_2 perimeter rather than forming a separate bulk phase. The overlay of Pt, Ce and O maps indicates that Pt is homogeneously dispersed along the nanorod surfaces at 1 wt% loading, supporting the picture of a Pt-ceria perimeter interface that is accessible for redox cycling. The bare CeNRs (Fig. S8a–c) analysis reveal well resolved lattice fringes with interplanar spacings of ~ 0.27 and $\sim 0.29\text{ nm}$, both consistent with the (200) planes of fluorite CeO_2 , where the slight variation from the ideal d spacing ($\sim 0.27\text{ nm}$) can be attributed to minor lattice strain or local oxygen deficiency [45]. The presence of such defects is known to modulate the electronic structure and enhance catalytic activity by facilitating oxygen mobility. The clear periodicity and uniformity of the fringes, together with the SAED pattern (Fig. S8d), confirm the high crystallinity and phase purity of the CeNRs. These observations agree with the PXRD results, which show a single fluorite CeO_2 phase.

The XPS 4f spectrum (Fig. 3A) of fresh 1 wt% Pt sample confirms that Pt is predominantly present in the metallic state (Pt^0) and any higher binding-energy shoulder is weak, showing that oxidised Pt species, if present, are only a very minor fraction at this loading. Pt $\text{L}_{3\text{ edge}}$ X-ray absorption spectroscopy (XAS) was used to probe the oxidation state of Pt in 1 wt% Pt/CeNRs before and after methane assisted TCWS at 300°C (Fig. 3B). The X-ray absorption near edge structure (XANES) of the fresh sample shows an edge position very close to that of metallic Pt foil and a relatively low white line intensity, indicating that Pt is predominantly in the metallic state. After several redox cycles at 300°C under CH_4 and

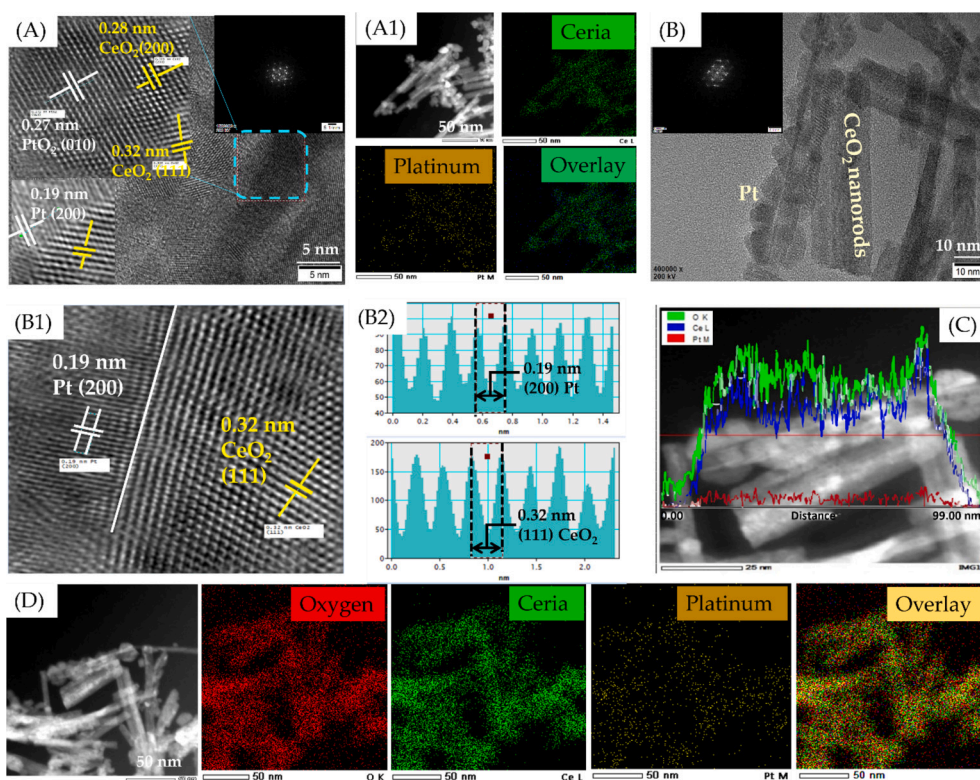


Fig. 2. TEM and STEM analysis of Pt/CeNRs. (A,A1) HRTEM image and corresponding SAED pattern of 5 wt% Pt/CeNRs. (B,B1,B2) HRTEM images and SAED pattern of 1 wt% Pt/CeNRs. (C,D) HAADF-STEM image and elemental maps of Ce, Pt and O for 1 wt% Pt/CeNRs.

H₂O, the XANES spectra of the cycled sample remain essentially unchanged: no significant shift in edge energy and no measurable increase in white line intensity are observed within the experimental uncertainty. Moreover, as shown in the Pt 4f spectrum (Fig. S10) of 1 wt% Pt/CeNRs remains largely unchanged compared to the fresh sample. This behaviour indicates that Pt does not undergo substantial oxidation or restructuring under the low temperature methane assisted TCWS conditions, and remains largely metallic during cycling. Together with the Pt 4f XPS results, the XAS data support a picture of a chemically stable, metallic Pt phase interfaced with the CeO₂ nanorods, which is a prerequisite for sustained perimeter mediated activation of CH₄ and oxygen vacancy cycling at 300 °C. In contrast, for 5 wt% Pt/CeNRs (Fig. S9), the Pt 4f envelope becomes broader and more asymmetric, consistent with a mixture of Pt⁰ and oxidised Pt species, in line with the weak PtO₂ (111) reflection observed by PXRD and the formation of larger Pt/PtO₂ domains in HRTEM likely due to the formation of surface PtO_x clusters at higher loading [33–35].

Raman spectra (Fig. 3C, D) further corroborate the structural stability of the CeO₂ lattice and surface environment under redox cycling. All samples exhibit the prominent F_{2g} vibrational mode at ~465 cm⁻¹, characteristic of the fluorite CeO₂ phase. In addition, a broad band near 590 cm⁻¹, typically associated with OVs and possibly Pt–O–Ce bridging modes, is observed, and its intensity increases with Pt loading. While this band is often used as an indirect indicator of defect concentration, it may also reflect changes in local bonding configurations introduced by Pt, making quantitative interpretation nontrivial. Importantly, no significant shift in the F_{2g} peak position could be found besides only minor variation in the defect band are observed after cycling at 300 °C, indicating that the crystalline structure and surface defect environment are preserved during TCWS. Moreover, the absence of D (~1350 cm⁻¹) and G (~1580 cm⁻¹) bands across all spectra confirms that no carbonaceous residues accumulate, highlighting the clean redox behaviour of the system.

3.2. Methane assisted isothermal TCWS

To evaluate the effect of methane as a chemical reductant, two types of constant-temperature redox cycles were performed: an argon-based cycle (thermal reduction only) and a methane-assisted cycle. Both protocols included a steam-driven oxidation step under identical conditions. The key difference lies in the reduction phase: the argon cycle relies purely on thermal activation, whereas the methane-assisted cycle introduces CH₄ briefly to chemically promote ceria reduction. Unless noted, reported H₂ yields are totals integrated over four oxidation cycles.

Initially, a 30 min treatment at 300 °C was performed under argon to clean the surface and generate OVs. This was followed by a 90 min oxidation step using water. Finally, a 120 min reduction step was performed under argon at the same temperature. The extended reduction period was used to desorb weakly bound hydroxyl groups formed during the water treatment, to partially clean the surface and to create additional vacancies. As shown in Fig. 4A, the blank reactor (without material) produced no detectable H₂ from water alone, confirming that the reactor setup alone does not induce hydrogen formation. Similarly, heating CeNRs under argon in the absence of water led to only trace H₂ evolution, attributable to the decomposition of surface hydroxyl groups. In contrast, hydrogen generation increased substantially under optimized conditions with steam, highlighting the importance of water as the oxidant.

As reported previously, bare CeO₂ nanorods produced ~0.12 mL g⁻¹ of H₂ at 300 °C under the optimized redox conditions as described in Reaction conditions section, which increased to ~5 mL g⁻¹ at 400 °C. Although higher temperatures promoted greater hydrogen production, the nanorod morphology of CeNRs began to degrade above 400 °C due to sintering effects [16]. Additionally, thermal reduction under Ar at 400 °C was insufficient to drive effective redox cycling in bare ceria, indicating the need for chemical promotion. Introducing CH₄ at this stage during the reduction phase altered this behaviour; however,

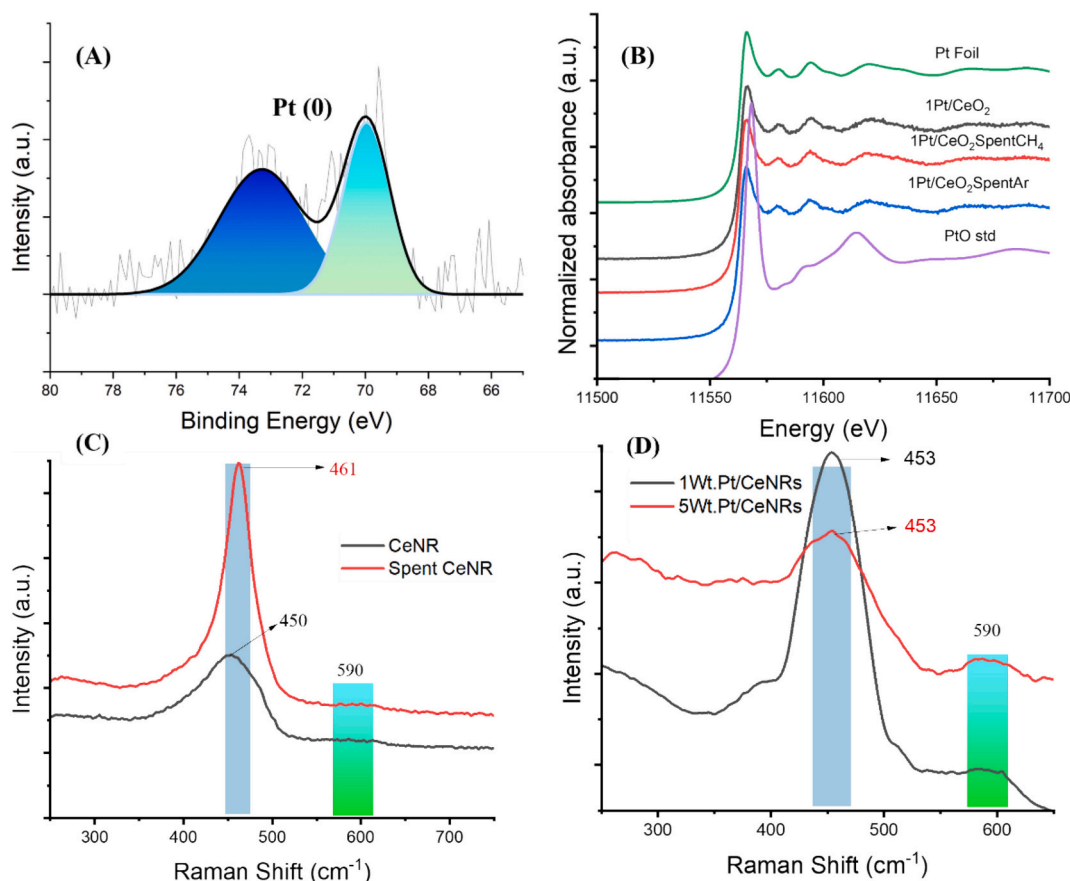


Fig. 3. Pt speciation and lattice structure in Pt/CeNRs. (A) Pt 4f XPS spectra of fresh 1 wt% Pt/CeNRs. (B) Pt L3-edge XANES spectra of fresh and cycled 1 wt% Pt/CeNRs. (C) Raman spectra of fresh CeNRs and Pt/CeNRs. (D) Raman spectra after methane-assisted TCWS at 300 °C.

CeNRs alone did not produce appreciable H_2 , as no active metal sites were present to activate methane. This motivates the incorporation of Pt to facilitate low temperature oxygen vacancy formation and enable methane assisted TCWS.

In contrast, Pt incorporation markedly enhanced performance under purely thermal cycling. At 300 °C, 1 wt% and 5 wt%Pt/CeNRs generated 6.5 and 9.3 $mL\ g^{-1}$ H_2 under argon based redox conditions (Fig. 4B), highlighting the role of Pt in facilitating low-temperature OVs formation. Fresh-spent comparison (Fig. S2 & S3) reveal unchanged diffraction profiles after multiple TCWS cycles at 300 °C, evidencing structural stability, minimal sintering, and morphology retention under isothermal operation (Fig. S5 A & B). As clear from the fresh and spent spectroscopic analyses, the Pt–Ce interface also remained intact at 300 °C.

At 400 °C, a slight increase in H_2 yield was observed for Pt/CeNRs compared to 300 °C, but this gain came at the expense of structural stability. Post reaction TEM images show nanorod sintering and Pt agglomeration (Fig. S5C & D), and the spectroscopic data indicate that the Pt–Ce interface begins to degrade at higher temperature.

Thus, while Pt addition is beneficial in lowering the effective reduction temperature and increasing initial H_2 production relative to bare CeNRs, thermal TCWS under argon still suffers from limited vacancy turnover. As shown in Fig. 4C, the H_2 yield declines across successive cycles, indicating insufficient oxygen vacancy regeneration at constant temperature. To verify this hypothesis, we added CH_4 in inert purge during the reduction step (120 min = 30 min Argon+15 min Methane+75 min Argon), in order to generate CO in situ and chemically assist lattice oxygen abstraction and regenerate OVs. Under this methane assisted conditions at 300 °C, 1 and 5 wt%Pt/CeNRs delivered 20 and 27.5 $mL\ g^{-1}$ H_2 , respectively. An almost stable hydrogen yield was observed with methane over all redox cycles, as evidenced by the

MS data (Fig. 4D), in clear contrast to the declining behaviour under purely thermal cycling. Unless noted otherwise, these yields are calculated only from the H_2 evolved during the oxidation step; any H_2 formed during the CH_4 reduction window (for example, via methane reforming or cracking) is not included in the reported TCWS values. The Pt/CeNRs appeared structurally stable at 300 °C under methane assisted cycling, as shown by post reaction TEM images (Fig. S6 A & B), whereas noticeable morphological changes were observed at 400 °C (Fig. S6 C & D).

The origin of the hydrogen evolved in the oxidation step at 300 °C was further probed using D_2O instead of H_2O during the oxidation phase. In these isotopic labelling experiments, D_2 and HD signal on MS appears only in the oxidation window while H_2 is confined to the CH_4 reduction window (Fig. S11A), confirming water as the sole H source in oxidation and that CH_4 acts only as a redox promoter regenerating OVs. Small, D_2 signals during CH_4 reduction phase likely arise from rapid recombination/desorption of transient OD-derived surface species and limited H-D exchange on Pt upon gas switching and are negligible to D_2 formed during oxidation.

Strikingly, increasing the operating temperature to 400 °C did not lead to a further significant increase in water splitting performance under methane assisted cycling. For 1 wt% Pt/CeNRs, the integrated H_2 yield reached only about 21 $mL\ g^{-1}$, which is only slightly higher than the 20 $mL\ g^{-1}$ obtained at 300 °C. Although more hydrogen was generated during the CH_4 reduction step at 400 °C, this contribution arises from methane reforming and cracking and is not included in the reported TCWS yields, which are calculated solely from the oxidation phase. Thus, raising the temperature to 400 °C does not improve the net water splitting capacity of the system.

Isotopic D_2O labelling at 400 °C (Fig. S11B) reveals a qualitatively different behaviour compared to 300 °C. In addition to D_2 and HD

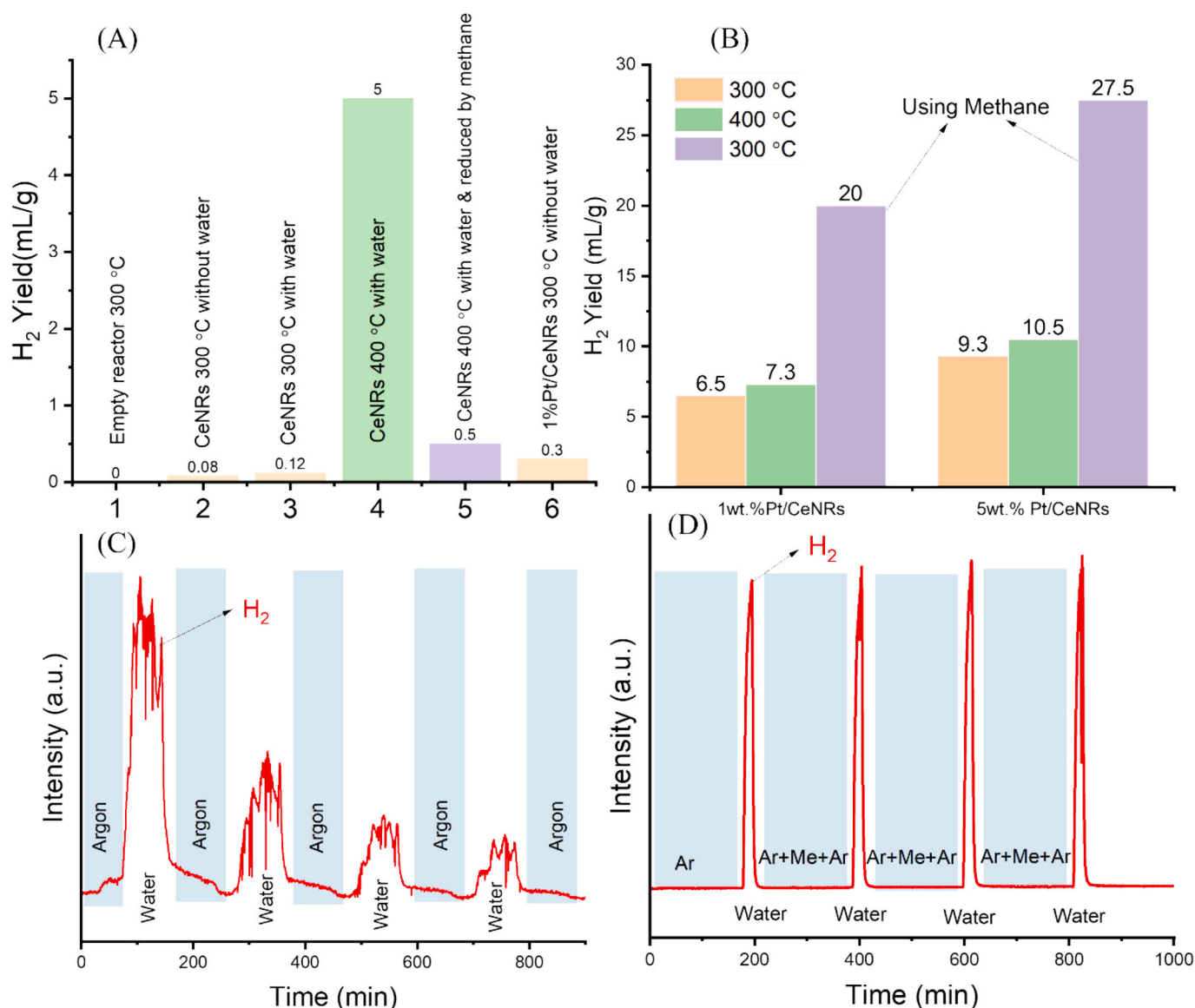


Fig. 4. Isothermal TCWS performance of CeNRs and Pt/CeNRs. (A) Blank experiments and reference TCWS data. (B) H₂ production over 1 wt% Pt/CeNRs and 5 wt% Pt/CeNRs in argon and methane-assisted cycles. (C,D) Time-resolved MS signals (m/z 2, 15, 28, 44) during argon and methane-assisted cycles at 300 °C of 1 wt% Pt/CeNRs.

signals in the oxidation window, a pronounced D₂ signal appears in the subsequent CH₄ reduction window, indicating a change in the redox and isotope exchange pathway relative to the low temperature regime. Together with post reaction TEM images (Fig. S6 C & D and Fig. S7), which show pronounced nanorod sintering and Pt particle agglomeration after cycling at 400 °C, these observations suggest that prolonged operation at 400 °C shrinks the accessible Pt-ceria perimeter and alters the surface hydroxyl and CO_x chemistry. One plausible scenario, consistent with the D₂O experiment and the proposed pathway in Fig. S11B, is that at 400 °C surface OD groups desorb more readily as D₂O and that this D₂O can react with CO via water-gas shift and related H/D exchange processes on Pt during the CH₄ reduction step, leading to additional D₂ formation in that window. In this regime, the proton assisted vacancy cycle becomes less effective and oxygen vacancy regeneration by water is diminished, which caps the overall H₂ yield under methane assisted TCWS at 400 °C.

3.3. Mechanistic insight from XPS under relevant conditions

From the MS profiles in Fig. 4C we concluded that, under argon at 300 °C, both CeNRs and Pt/CeNRs show only limited and progressively declining H₂ production, consistent with incomplete thermal reduction and poor oxygen vacancy turnover. To probe this directly, we performed Ce 3d XPS under conditions mimicking the redox protocol, although using N₂O as an oxidant instead of H₂O due to setup limitations, followed by argon reduction at 300 °C (60 min reduction, 30 min oxidation). This probe scheme allowed us to selectively quantify surface Ce³⁺ formation and consumption under relevant temperature and gas environments.

As shown in Fig. 5, both CeNRs and Pt/CeNRs develop only a modest Ce³⁺ contribution after the first reduction step, and this Ce³⁺ signal decreases further in the second reduction-oxidation cycle. The Ce³⁺ related components in Fig. 5 illustrate that (i) thermal reduction in argon at 300 °C generates only a limited population of oxygen vacancies and (ii) these vacancies are not fully regenerated upon cycling, in line with the declining H₂ yields observed in the argon-only TCWS

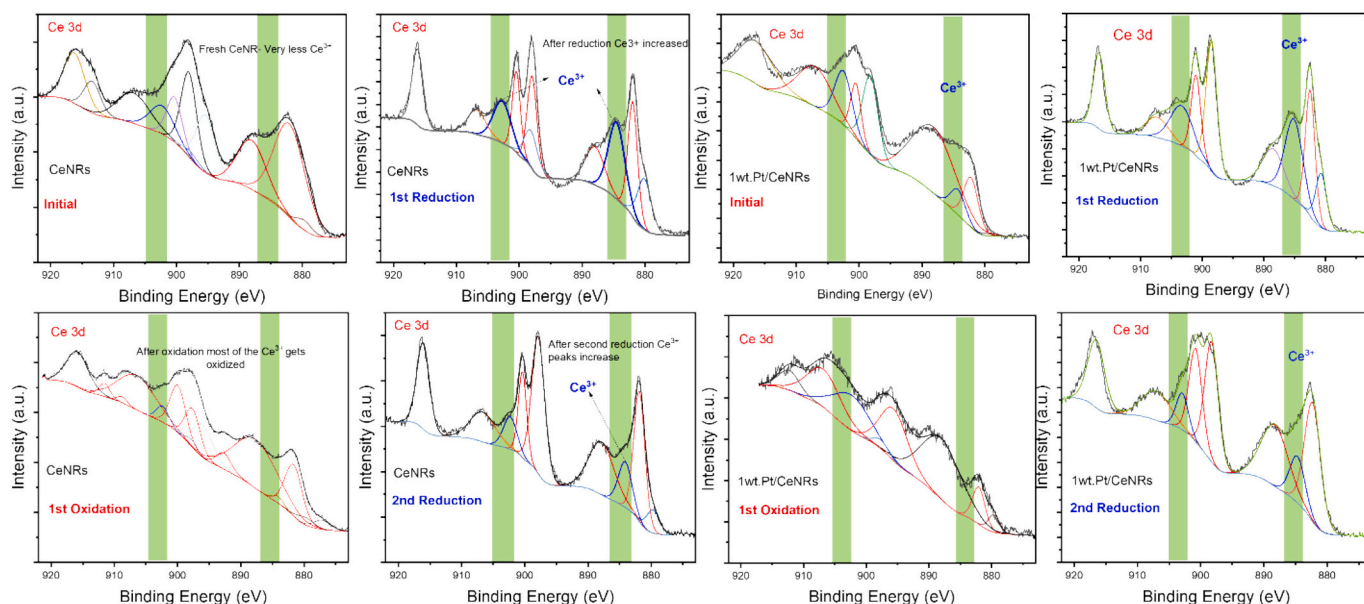


Fig. 5. Ce 3d XPS spectra of CeNRs and 1 wt% Pt/CeNRs after N_2O oxidation and argon reduction at 300°C , showing changes in the surface $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio.

experiments. Even in the presence of Pt, the Ce^{3+} fraction remains relatively low under purely thermal cycling, highlighting the need for an additional chemical driving force to sustain vacancy formation at low temperature.

By combining these XPS results with the TCWS data and structural characterization, we propose a mechanistic picture summarised in Fig. 6. Under thermal treatment in Ar at 300°C , only a fraction of surface hydroxyl groups and labile oxygen species is removed, creating a limited number of OV's (Ce^{3+} sites). Over successive cycles, some of these vacancies become blocked or annihilated by strongly bound hydroxyl or oxide species, so that during the oxidation step less H_2 is produced and the vacancy pool shrinks. This explains why thermal cycling under argon leads to progressively lower H_2 yields and why an external reductant is required to maintain an active vacancy population on ceria.

In the methane assisted regime, Pt provides this additional chemical driving force at 300°C . Metallic Pt^0 sites activate CH_4 to CH_x and hydrogen species that abstract lattice oxygen at the Pt/CeNR perimeter, forming CO_x and generating Ce^{3+} and oxygen vacancies. In the

subsequent oxidation step, water reacts at these vacancies, dissociating to produce H_2 and leaving hydroxyl ($-\text{OH}$ or $-\text{OD}$) groups on the vacancy sites. These hydroxyl species are relatively stable at 300°C and are not completely removed thermally, but can be progressively consumed or transformed in the next methane reduction step via reactions with CH_x and H species at the Pt-ceria interface. The higher Ce^{3+} fraction in 1 wt% Pt/CeNRs (Ce 3d XPS), the shift in reduction onset to lower temperature (H_2 -TPR), the increased defect band in Raman spectra and the D_2O labelling experiments together support this picture of perimeter controlled vacancy cycling, in which methane, activated on metallic Pt, restores the reducibility of the CeNRs at constant low temperature and water supplies hydrogen exclusively in the oxidation phase. The correspondence between structural descriptors (Ce^{3+} fraction, defect density, Pt speciation), the proposed mechanistic cycle (Fig. 6), and the comparative hydrogen yields summarised in Table S1 provides a coherent structure-activity framework for methane-assisted low-temperature TCWS.

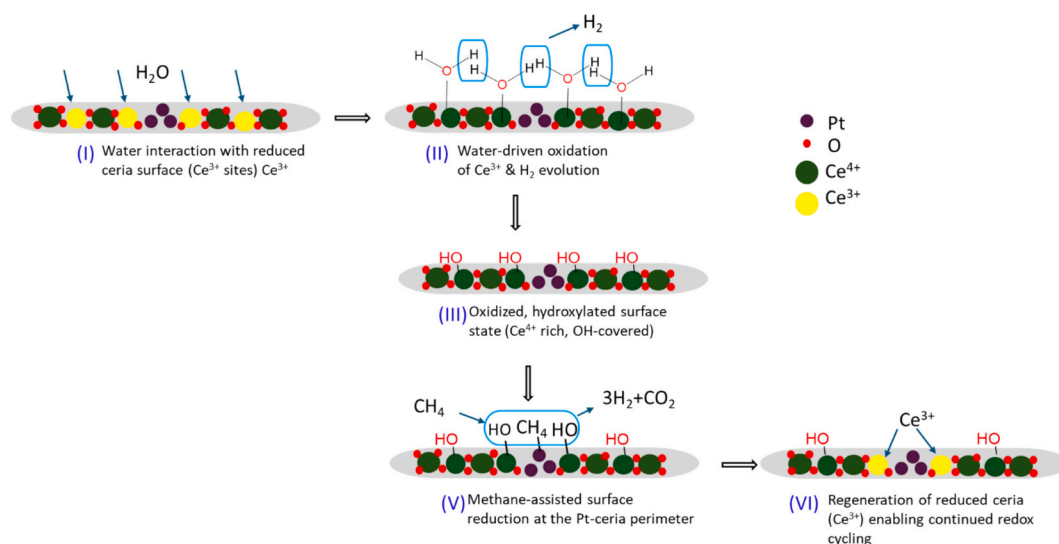


Fig. 6. Proposed schematic illustration of methane-assisted isothermal redox cycling on Pt/CeO₂ at 300°C , where water oxidizes Ce^{3+} sites to an OH-covered Ce^{4+} surface with H_2 evolution, and methane-driven reduction at the Pt-ceria perimeter regenerates Ce^{3+} , enabling sustained cycling.

4. Conclusions

In this work we have demonstrated methane assisted, isothermal thermochemical water splitting at 300 °C over Pt decorated CeO₂ nanorods. Incorporation of Pt substantially improved low temperature redox performance under argon based cycles at 300 °C where 1 and 5 wt % Pt/CeNRs yielded 6.5 and 9.3 mL g⁻¹ H₂, respectively, although the H₂ output declined over successive cycles, indicating incomplete oxygen vacancy regeneration. When methane was introduced during the reduction phase at 300 °C, the H₂ yields in the subsequent oxidation step increased to 20 and 27.5 mL g⁻¹ for 1 and 5 wt% Pt/CeNRs, respectively, and remained nearly constant over multiple cycles, while the CeNR morphology and fluorite structure were preserved.

Together, these results support a picture in which metallic Pt nanoparticles at the Pt-ceria perimeter activate methane to CH_x and hydrogen species that abstract lattice oxygen, generating CO_x and oxygen vacancies at 300 °C. In the subsequent oxidation step, water refills these vacancies and produces H₂, as confirmed by D₂O labelling experiments that show D₂ and HD formation exclusively in the oxidation window at 300 °C, while H₂ formation in the methane reduction window originates from methane reforming and is not counted in the TCWS yield. Increasing the operating temperature to 400 °C did not significantly enhance the net water splitting performance but altered the redox pathway. The integrated H₂ yields in the oxidation step were only slightly higher than at 300 °C, while TEM revealed pronounced nanorod sintering and Pt agglomeration and D₂O experiments showed a D₂ signal appearing in the subsequent methane reduction window, indicative of modified isotope exchange and surface chemistry. These observations suggest that the well-defined Pt-ceria perimeter and associated low temperature vacancy cycle are destabilised at 400 °C, which limits the benefit of operating at higher temperature.

Overall, this study establishes a low temperature, isothermal TCWS regime in which methane, activated on metallic Pt at the Pt-ceria perimeter, serves as a sacrificial chemical reductant to regenerate oxygen vacancies in CeO₂ nanorods at 300 °C, while water is the exclusive hydrogen source in the oxidation phase. Although the absolute H₂ productivity is modest and methane consumption introduces a carbon penalty, the combined TCWS, XPS, XAS, Raman and TEM results provide a mechanistic framework for designing chemically assisted redox cycles that exploit perimeter-controlled vacancy formation at low temperature. More broadly, the results suggest that promoters which retain a metallic state under cycling, facilitate electron transfer to Ce⁴⁺, and preserve nanorod morphology at controlled loading criteria potentially met by metals such as Pd, Rh, or Ru could extend this concept further. This is relevant for the development of low temperature chemical looping and other redox reactor schemes for hydrogen production and related energy conversion processes, where chemical promotion can partly replace high temperature thermal swings.

CRedit authorship contribution statement

Dhanaji R. Naikwadi: Writing – review & editing, Writing – original draft, Methodology, Investigation, Data curation. **Esha Varma:** Methodology, Investigation. **Geeta P. Kharabe:** Writing – review & editing, Methodology, Investigation. **Erdni D. Batyrev:** Writing – review & editing, Methodology, Investigation. **Dragos C. Stoian:** Writing – review & editing, Methodology, Investigation. **Atul Bansode:** Writing – review & editing, Validation, Supervision, Resources, Project administration, Methodology, Investigation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

the work reported in this paper.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.cej.2026.180410>.

Data availability

Data will be made available on request.

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