Hierarchical Heterogeneity at the CeO_x-TiO₂ Interface: Electronic and Geometric Structural Influence on the Photocatalytic Activity of Oxide on Oxide Nanostructures

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Abstract

Mixed oxide interfaces are critical for delivering active components of demanding catalytic processes such as the photo-catalytic splitting of water. We have studied CeO_x - TiO_2 catalysts with low ceria loadings of 1 wt%, 3 wt% and 6 wt% that were prepared with wet impregnation methods to favor a strong interaction between CeO_x and TiO_2 . In these materials the interfaces between CeO_x - TiO_2 have been sequentially loaded (1%, 3% and 6%), with and without Pt (0.5 wt%). The structure and properties of the catalysts were characterized using several X-ray and electron based techniques including XRD, XPS, UPS, NEXAFS, UV-Vis and HR-STEM/STEM-EELS, to unravel the local morphology, bulk structure, surface states and electronic structure. The combination of all these techniques allow us to analyze in a systematic way the complete structural and electronic properties that prevail at the CeO_x - TiO_2 interface. Fluorite structured nanocrystallites of ceria on anatase-structured titania were identified by both XRD and NEXAFS. A sequential increasing of the CeO_x loading led to the formation of clusters, then plates and finally nano particles in a hierarchical manner on the TiO_2 support. The electronic structures of these catalysts indicate that the interaction between TiO_2 and CeO_2 is closely related to the local morphology of nanostructured CeO_2 . Ce^{3+} cations were detected at the surface of CeO_2 and at the interface of the two oxides. In addition, the titania is perturbed by the interaction with ceria and also with Pt. The photocatalytic activity for the splitting of H_2O using UV light was measured for these materials and correlated with our understanding of the electronic and structural properties. Optimal catalytic performance and photo response results were found for the 1 wt% CeO_x - TiO_2 catalyst where low dimensional geometry of the ceria provided ideal electronic and geometrical properties. The structural and electronic properties of the interface were critical for the photocatalytic performance of this mixed-oxide nanocatalyst system.

KEYWORDS: Mixed-metal oxide catalysts, nanostructure materials, photocatalytic water splitting, ceria-titania, transmission electron microscopy, X-ray absorption, X-ray photoelectron spectroscopy

Introduction

Mixed metal oxides are of great interest as effective catalysts for a wide range of applications in industry, including chemical conversion, pollutant decomposition under photo irradiation, and clean energy production (*i.e.* hydrogen generation).¹⁻¹² Mixed oxide systems, such as $\text{MnO}_x\text{-CeO}_2$, $\text{CeO}_2\text{-TiO}_2$, $\gamma\text{-Al}_2\text{O}_3\text{-MgO}$, $\text{SnO}_2\text{-TiO}_2$, $\text{Cu}_2\text{O-TiO}_2$, ZnO-TiO_2 , $\text{Fe}_2\text{O}_3\text{-TiO}_2$, $\text{WO}_3\text{-MoO}_3$, $\text{CuO-CeO}_2\text{-TiO}_2$, $\text{MnO}_x\text{-ZrO}_2\text{-CeO}_2$, $\text{BiVO}_4\text{-SnO}_2\text{-WO}_3$, $\text{CuO-ZnO-Al}_2\text{O}_3\text{-ZrO}_2$, show significantly advantageous synergistic effects due to the formation of either solid solutions or hetero-junctions between two immiscible solid phases.¹¹⁻¹⁸ Mixed oxide systems indispensably generate stimulating and unprecedented features, dramatically enhancing in many cases the performance and applicability of the base materials. Among the most interesting systems, ceria-titania mixed oxides have stood out as a prototype of many interesting textural, physicochemical and electronic properties unobserved in their individual components. On the other hand, the splitting of water under solar light radiation to produce green energy H_2 is one of the most desirable solutions to the global energy problem, although it has been a great challenge to develop practical catalysts with high efficiency. TiO_2 nanostructures with a wide band gap (3-3.2 eV), different geometries, polymorphs and dimensions are known as star photocatalysts for photovoltaics and solar energy conversion. Nonetheless, the promising practical applications are restricted due to low utilization of solar light and fast recombination of photo-generated charge carriers. To overcome these drawbacks, numerous approaches have been employed over the past several decades; including the coupling of TiO_2 with a second metal oxide to obtain an efficient route to greatly improved catalytic performance.

CeO_2 has been extensively investigated in many catalytic processes due to its low cost, earth abundance, unique redox chemistry ($\text{Ce}^{4+} \leftrightarrow \text{Ce}^{3+}$ easily interchangeable), oxygen storage/transport and activation properties.¹⁹⁻²⁸ The combination of TiO_2 with CeO_2 has been predicted to drastically promote the catalytic activity, stemming from its role as a chemical, thermal and mechanical stabilizer of well-dispersed nano- CeO_2 . The interface of such a material is deemed to be the '*sui generis*' site that manifests unique chemical properties. Thus TiO_2 has become an important system to be investigated to unravel the

relationship between the structure and catalytic activity of mixed-metal oxides.^{3-4, 6, 9, 17, 20, 29-40}

As described in previous studies, CeO₂-TiO₂ mixed oxide powders have been prepared with different Ce/Ti ratios, ranging from 0.1 to 0.9. An intermixed solid solution can form when ceria is the predominant component, while separate phases of ceria and titania co-exist when CeO_x is a minor component.^{4, 8, 17, 31, 36, 39-43} Barrio et al.⁴⁴ prepared CeO_x-TiO₂ catalysts by wet impregnation methods with 6 wt% and 15 wt% ceria loadings. Depending on the ceria loading, the interaction between the two metal oxides could lead to unusual coordination modes; nanoparticles with a fluorite structure were observed only at the high ceria loadings. Better reducibility was observed for lower ceria loading, indicating stronger interaction of the CeO_x nanoparticles with the TiO₂ support. Kundu et al.⁴⁵ investigated the electronic properties and structure of Pt dispersed on ceria-modified TiO₂. Interestingly, Ce³⁺ was identified on the surface and at the CeO_x-TiO₂ interface drastically enhancing the formation of electron-hole pairs under visible light irradiation. In this system, the Pt not only played the role of an electron-trapping center, prolonging the charge carrier lifetime, but also increased Ce³⁺ concentration, whereby improving performance for photocatalytic water splitting.

With this background, we were motivated to study lower ceria loading in CeO_x-TiO₂ mixed oxides to gain insight into the nature of mixed metal oxide interface and their catalytic performance. Recently, Johnston-Peck et al.³⁵ demonstrated the growth of complex hierarchical structures of CeO_x interfacially stabilized on TiO₂. The different morphologies of ceria supported on titania (with a nominal mass fraction of 6%) were identified as: 0D clusters, 2D chains/plates and 3D nanoparticles. Defects in the ceria (such as dislocations and surface steps) were observed with HAADF-STEM and DFT calculations were used to unravel the preference for the generation of O vacancies and Ce³⁺ sites at the interface between ceria and titania. However, as all the morphologies were seen simultaneously in one sample, the study of the morphology-dependent properties and catalytic activity remained a significant challenge, which ultimately inhibited the rational design of tunable nanostructured catalysts.

In this manuscript, we extend the investigation of mixed metal oxide interfaces by probing these architectures in samples with lower ceria concentration and isolate nanostructures of ceria on the TiO₂ support. CeO_x-TiO₂ powder catalysts prepared by a wet chemical method with precise nominal ceria loadings from 1 to 6 wt% were studied with several state of the art scattering, spectroscopic and microscopic tools. High-resolution scanning transmission electron microscopy (HR-STEM), *synchrotron* X-ray powder diffraction (XRD)), near edge x-ray absorption fine structure spectroscopy (NEXAFS), x-ray photoemission spectroscopy (XPS) and UV-Visible diffuse reflectance were used to characterize the morphological, structural, optical and electronic properties of the CeO_x-TiO₂ system. For the first time, different morphologies of the CeO_x crystallites were observed sequentially in a series of CeO_x-TiO₂ catalysts with various cerium loadings, in which the evolution of ceria from 0D clusters to 1-2D nanochains and 3D nanoparticles was strongly correlated to a decrease in the Ce³⁺ / Ce⁴⁺ ratio. The isolation of the three morphologies of ceria provided a benchmark to study morphology-dependent properties. Our goal was to further the understanding of the relationship between structure and activity of photocatalysts.

Experiment

Sample preparation and characterization Pre-treatment of the TiO₂ powders (titanium (IV) oxide, catalyst support Alfa Aesar) was performed in a flow of dry air at 500 °C for 4 h. The wet impregnation method was employed to prepare the cerium precursor coated TiO₂ using an aqueous solution of cerium nitrate (Alfa Aesar, Reacton 99.5%) with loadings of 1, 3 and 6 wt %. The titania support was wet with 1 mL of water per gram of support and then an aqueous solution of the appropriate amount of cerium precursor was prepared in a ratio of 5 mL of solution per gram of support. The impregnated solids were stirred for one hour at 70 °C and then dried under reduced pressure to remove the excess of water. Finally they were calcined under air to 500 °C with a heating rate of 2 °C /min. Samples obtained after cerium impregnation were labeled as 1Ce(III)Ti, 3Ce(III)Ti and 6Ce(III)Ti, and correspond to a theoretical coverage of 0.1, 0.25 and 0.5 monolayers, respectively. The as-synthesized samples were then calcined in air at 600 °C for 8 h to obtain the final CeO_x-TiO₂ catalysts, labeled as 1, 3 and 6 wt % CeO_x-TiO₂ (abbreviated

to 1, 3, 6CeTi), respectively. The mixed-metal oxides were loaded with 0.5 wt% Pt, to enable photocatalytic activity, following a similar wet impregnation route as described above through the cerium incorporation and employing H_2PtCl_6 as metal precursor (Johnson-Matthey, 40.78 wt % Pt). After the coating of Pt, the samples were dried at 120 °C for 12 h and then calcined in air at 500 °C to remove the chlorine. The photocatalysts obtained after Pt loading were labeled as Pt/1CeTi, Pt/3CeTi, and Pt/6CeTi, respectively.⁴⁶

XRD patterns of $\text{CeO}_x\text{-TiO}_2$ samples were collected at beam line X7B ($\lambda=0.3196$ Å) of the National Synchrotron Light Source (NSLS). Powder samples of 2-3 mg were loaded in a quartz capillary (0.7mm ID), and the diffraction data was collected through a Perkin Elmer Amorphous Silicon Detector. Detailed information about experimental conditions can be found in reference⁴⁷.

Annular dark-field scanning transmission electron microscopy (STEM) images and energy electron loss spectra (EELS) were collected with a Cs-corrected Hitachi HD-2700C. The microscope was operated with an accelerating voltage of 200 kV and using a probe convergence semi-angle of 23 mrad. The inner collection angle of the annular dark field detector was approximately 53 mrad while the collection angle for energy electron loss spectroscopy was 20 mrad.

NEXAFS spectra of Ti L edge, O-K edge and Ce-M edge were collected at beamline U4B with soft X-ray at the NSLS. A partial electron yield detector with a 250 V bias was employed (to exclude secondary electrons with lower kinetic energy) together with total electron yield measured through the sample drain current. The photon beam was fixed at 45° from the surface normal of the sample. All the NEXAFS spectra were normalized by the incident beam flux, monitored by the mesh and fixing the step of pre-edge and post-edge of “1”, by the Athena software.

X-ray photoelectron spectroscopy (XPS) of the samples was performed using a laboratory based monochromated Al $\text{K}\alpha$ source with a hemispherical analyzer at the Analytical and Diagnostics Laboratory (ADL) at Binghamton University. The core-levels and the valence band region were measured with pass energy of 23.5 eV which

corresponds to an instrumental resolution of 0.51 eV obtained from analyzing both the Au 4f 7/2 and Fermi edge of a Au foil. Electron and argon flood guns were used for charge neutralization.

UV-Vis NIR spectroscopy measurements were performed in diffuse reflection mode using UV-Vis/NIR PerkinElmer Lambda 950 spectrometer located in the Center for Functional Nanomaterials at Brookhaven National Laboratory.

The photocurrent response was monitored on a Basi Epsilon potentiostat using a three-electrode cell and a 150 W Xenon lamp (with IR-cutoff filter) as the excitation source. The reference and counter electrodes were Ag/AgCl and Pt wire, respectively, while 0.1 M HClO₄ aqueous solution was used as the supporting electrolyte. A Toray carbon paper coated with oxide material was employed as the working electrode. The working electrode was prepared by electrophoretic deposition using a Keithley 2410A Electrometer at the Center for Functional Nanomaterials as follows: a suspension of powder sample and ethanol (0.25 wt%) was sonicated for 2 h and two pieces of carbon paper were subsequently submerged in the suspension. The voltage (100 V) was automatically applied during 5 minutes of deposition. After drying at 80 °C, the electrode was finally annealed at 450 °C for 3 h prior to photoelectrochemical analysis. The on-off light-switching measurement was conducted at 1.25 V by irradiating the front side of working electrode.

The photocatalytic water splitting activity was evaluated through the measurement of both hydrogen and oxygen evolution in a closed gas circulation and evacuation system. In a typical H₂ production experiment, 3 mg of powder catalyst was suspended in 3 mL of aqueous methanol solution (20 vol %) in a sealed quartz cell. After evacuation by Argon for 60 min (to remove the dissolved oxygen in the solution and ensure an anaerobic condition), the cell was side-irradiated by the 150-W Xenon arc lamp while being magnetically stirred. The reaction temperature was maintained at 293 K by continuous water circulation. A similar apparatus was used for the photocatalytic O₂ evolution, except with the use of 0.01 M AgNO₃ as a sacrificial electron acceptor instead of

methanol. The amount of evolved gas was determined by a gas chromatograph (GC Agilent 6890N) equipped with FID and TCD detectors using Argon as the carrier gas.

Results and Discussion

A. Bulk and atomic structure of the $\text{CeO}_x\text{-TiO}_2$ systems

Figure 1 shows X-ray powder patterns for the $\text{CeO}_x\text{-TiO}_2$ catalysts with different CeO_x loadings. It is apparent that anatase TiO_2 is found in all samples *via* a series of (101), (004), (200), (105), (211), (213), (116), (220) and (215) diffraction peaks. Cubic fluorite CeO_2 (space group $Fm3m$) features was detected in both 3CeTi and 6CeTi due to the presence of (111), (200) and (311) reflections. The corresponding lattice parameters and chemical compositions obtained from Rietveld refinement of the XRD patterns are summarized in Table 1. The ceria loadings of 3 wt% and 6 wt% have particle sizes of 4.8 and 6 nm, respectively. In the case of a ceria loading of 1 wt%, the diffraction features were too weak and did not allow us to estimate a value for the particle size, suggesting that the ceria particles had a size below 2 nm. For unsupported ceria, we determined a lattice constant of 5.402 (1) Å.⁴⁸ In the supported ceria, the lattice changes from 5.419(2) Å at 3 wt% to 5.413(1) Å at 6 wt% with increasing Ce concentration. This trend and the fact that the supported ceria nanoparticles have a lattice constant somewhat larger than that of unsupported ceria can be explained using the NEXAFS and XPS data discussed later in which one can see significant variations in the content of Ce^{3+} . The size of the cerium cations increases when undergoing a partial reduction from a 4+ to a 3+ oxidation state. The larger the content of Ce^{3+} , the bigger the ceria lattice size. The CeO_x concentration obtained via X-ray fluorescence was 1%(+/-1), 4%(+/-1) and 5.5%(+/-1) for the 1, 3 and 6 wt% samples, respectively. This is consistent with the nominal content within an acceptable error. The XRD data implied that the CeO_x content was predominantly well ordered CeO_x free of amorphous phases which we have attempted to confirm with TEM (presented below).

Table1. Structural parameters obtained from XRD for the CeO_x-TiO₂ samples

Samples	1CeTi	3CeTi	6CeTi	CeO ₂
Ceria size (nm)	< 2 nm	4.8 (5)	6.0 (5)	7 (1)
Ceria lattice (Å)	--	5.419 (2)	5.413 (1)	5.402 (1)
Ceria concentration	--	4.0(1)%	5.5(1)%	100%

Figure 1. Synchrotron X-ray powder diffraction patterns for 1 wt%, 3 wt% and 6 wt% CeO_x-TiO₂ samples.

To probe the short range order and local coordination geometry of the CeO_x-TiO₂ catalysts, we performed experimental pair distribution function (PDF) analysis (processed

using PDFgetX2) for the $\text{CeO}_x\text{-TiO}_2$ catalysts in comparison to two reference samples. The function $G(r)$ describes the probability of finding a pair of atoms at given interatomic distance r . The integrated intensity of $G(r)$ peak depends on the coherent scattering lengths of the elements involved including their multiplicities. In Figure 2, the well-defined maxima located at 1.94, 2.27/2.47 and 3.03 Å are assigned to the mean bond lengths of Ti-O, O-O and Ti-Ti pairs, respectively, of the nearest neighbor coordination shell for TiO_6 octahedral in TiO_2 . Furthermore, the interatomic distances at 2.33 and 3.81 Å match well with the first Ce-O and Ce-Ce coordination shell. It is worth noting that the delicate changes in the intensities of Ti-O and Ti-Ti peaks, concurrent with the strong increase of the first O-O and second asymmetric Ti-Ti/O-O coordination sphere (at 3.78 Å) at higher Ce loading reflects the distortion of the TiO_6 octahedral structure. This is likely due to the contribution of Ce-O distance at the expense of Ti-O and Ti-Ti ones. On the other hand, in Figure 2B, it's clearly seen that the Ce-O contribution disappears when the distance is beyond the ceria nano particle size, which confirms the phase separation of ceria and titania.

Figure 2. Pair distribution function analysis for CeO_x-TiO₂ samples with different CeO_x content (A): short range and difference after subtracting the TiO₂ standard features to the features for CeO_x-TiO₂ ; (B): long range PDF of pure TiO₂ nanoparticles, three CeO_x-TiO₂ samples and difference after subtracting the TiO₂ standard features.

B. Local Morphology and atomic structure of the CeO_x-TiO₂ systems

Annular dark-field scanning transmission electron microscopy (STEM) micrographs of the three CeO_x-TiO₂ samples are shown in Figure 3. Due to the large difference in atomic weight between cerium ($Z = 58$) and titanium ($Z = 22$), the ceria appears brighter in the STEM images (shown by arrows) than the TiO₂ nanostructured support. On the other hand, light elements like oxygen were not identified due to the weak scattering. It can be seen that the diameter of TiO₂ nanoparticles is ~ 20 nm, which is consistent with the analysis of the XRD results. Figure 3A reveals the well-dispersed CeO_x on the TiO₂ substrate as the bright dots (In supporting information, EELS data was shown as a proof of ceria existence in Figure S1), in which small clusters are less than 1 nm (below the detection limit of XRD). These small nanostructures of CeO_x are similar to the monomers, dimers and chains we have observed previously from CeO_x deposition on TiO₂(110) surfaces.^{37, 49} When the loading of ceria increases to 3 wt%, two dimensional chains and short islands of ceria appear in addition to the small clusters (Figure 3B). The ordered chains are constrained in one or two dimensions (less than 2 nm) while extend to about 8 nm in the other dimension. The growth of trapezoidal nanochains and short islands of ceria is epitaxial with the titania support (as in Figure 3B (020)CeO₂//(1-12)TiO₂, [100]CeO₂//[110]TiO₂). In the last figure, large three dimensional nanoparticles of ceria are observed on TiO₂ in the 6 wt% CeO_x-TiO₂ sample (Figure 3C), together with ceria chains and clusters. Such cubic fluorite CeO_x particles have hemispherical morphology and their radius is about 3 nm. It is important to note that the morphologies of these samples are quite different from those of previous CeO_x-TiO₂ samples where these three types of nanostructures have been observed simultaneously and were distributed heterogeneously on the titania support.³⁵ In this study, various morphologies are isolated and verified in the series of CeO_x-TiO₂ samples. The hierarchical growth progression is

confirmed and extends from 0D clusters to 2D nanochains oriented on the [110] of the TiO_2 support and eventually, to 3D nanoparticles on TiO_2 (112) facet. Also, well ordered anatase titania could be resolved even though there are of some high energy defects, like steps, kinks etc., revealing the well maintained local structure of titania upon addition of ceria. The formation of intermixed $\text{CeO}_x\text{-TiO}_2$ has been previously reported especially in the form of (ie $\text{Ce}_2\text{Ti}_2\text{O}_7$)¹⁷ and Ce^{3+} rich interfacial boundaries^{35, 45} which cannot be ruled out in these materials.

Figure 3. STEM images of (A) 1 wt%, (B) 3 wt% and (C) 6 wt% $\text{CeO}_x\text{-TiO}_2$ samples

C. Electronic structure of the CeO_x-TiO₂ systems

NEXAFS spectra of the Ti L-edge and Ce M-edge of 1 wt%, 3 wt% and 6 wt% CeO_x-TiO₂ samples were collected in both partial electron yield (PEY) and total electron yield (TEY) mode. Bare TiO₂, CeO₂ and as-synthesized Ce(NO₃)₃TiO₂ were also measured for comparison. Soft X-ray (< 1000eV) measurements are intrinsically surface sensitive, and PEY typically provides information from the outermost surface layers with a probing depth of less than 2 nm because of the small effective escape depth of low-energy Auger electrons. In TEY mode, all electrons that emerge from the surface and sub-surface in the range of 5 nm are detected.⁵⁰ As the powder samples are 3D in nature, TEY measurements provide detailed information from the buried interface of the mixed metal oxide (CeO_x-TiO₂) whereas PEY only describes the surface behavior of either CeO_x or TiO₂ nanoparticles.

As depicted in Figure 4, the Ti L-edge spectra clearly prove the tetragonal Ti⁴⁺ structure of anatase TiO₂ in pure TiO₂ and the CeO_x-TiO₂ samples *via* the presence of a characteristic L₂-edge ($2p_{1/2}$) and L₃-edge ($2p_{3/2}$) doublet. The doublet is further split into t_{2g} and e_g sub-bands by the crystal-field effect.⁵¹⁻⁵² While almost no changes are observed in the in PEY (Figure 4(b)) data, there is some perturbation of the TiO₂ electronic structure upon addition of CeO_x evident in the TEY (Figure 4(a)) measurements. The most noticeable difference is the higher relatively intensity ratio of the L₂- t_{2g} and L₂- e_g of 3 wt% CeO_x-TiO₂ sample compared to the other samples. This implies that a 3 wt% CeO_x loading on the TiO₂ surface has imparted an electronic effect to the band structure of TiO₂.

The Ce M-edge measured in PEY and TEY mode are shown in Figure 5. CeO₂ and Ce(NO₃)₃TiO₂ were used as references for the absorption position of Ce⁴⁺ and Ce³⁺ species. It is worth noting that the Ce⁴⁺ state and the partially reduced Ce³⁺ co-exist in all mixed oxides. Both analysis modes exhibit a similar trend of Ce³⁺ / Ce⁴⁺ ratio which markedly decreases with increasing ceria content from 1 to 6 wt%. The Ce⁴⁺ valence state becomes dominant in samples containing higher ceria concentration whereas low loading

content primarily induces trivalent cerium Ce^{3+} . However, the quantitative ratios of the peaks at 884.2 eV (Ce^{3+})/885.4 eV (Ce^{4+}) and at 902.2 eV (Ce^{3+})/903.7 eV (Ce^{4+}) are quite different between PEY (< 1) and TEY (≤ 1) modes in the 3 wt% $\text{CeO}_x\text{-TiO}_2$. PEY detection has a better signal-to-background ratio than TEY, which can probe an average depth of 5 nm. As a consequence, the cation intermixing with larger portion of Ce^{4+} sites exist not only in the sub-surface region (core) but also at the oxide-oxide interface where ceria accumulates on the outermost surface or near the interface region in a reduced state. This result is in concordance with the morphology observed from the aforementioned STEM data. The nano chains in the 3 wt% $\text{CeO}_x\text{-TiO}_2$ sample is constrained to less than 2 nm in the out-of-plane dimension, as thin as only a few atomic layers, which is appropriate to the information depth of the PEY mode of detection. In contrast, the size of the 3D nanoparticles in a hemispherical architecture in the 6 wt% sample are up to 6-8 nm so that the combination of the two analysis modes is useful in discriminating the differences between the outermost surface and sub-surface states.

Figure 4. NEXAFS of Ti L-edge of 1 wt%, 3 wt% and 6 wt% $\text{CeO}_x\text{-TiO}_2$ samples obtained via total electron yield (a) and partial electron yield (b) measurements

Figure 5. NEXAFS of Ce M-edge of 1 wt%, 3 wt% and 6 wt% $\text{CeO}_x\text{-TiO}_2$ samples obtained via total electron yield (a) and partial electron yield (b) measurements

In addition to mapping the density and energy distribution of unoccupied states by soft X-ray absorption, X-ray photoelectron spectroscopy (XPS) was used to characterize the density of occupied states (i.e. valence bands), chemical composition and oxidation state of the $\text{CeO}_x\text{-TiO}_2$ samples. Figure 6 shows the XPS core level spectra for the Ce 3d region. Both reference CeO_2 and $\text{Ce(NO}_3)_3\text{TiO}_2$ spectra are composed of two multiplets, labeled as v and u, corresponding to the spin-orbit coupling $3d_{5/2}$ and $3d_{3/2}$, respectively. Each spin-orbit component of Ce 3d from Ce^{3+} oxides refers to two features, u^0/v^0 and u'/v' ; meanwhile, each component of Ce^{4+} is dominated by three features, u'/v' , u''/v'' and u'''/v''' .^{13, 17, 38, 53} Reduced Ce^{3+} is present together with minor Ce^{4+} in 1 wt% $\text{CeO}_x\text{-TiO}_2$ via a myriad of peaks. The $\text{Ce}^{3+}/\text{Ce}^{4+}$ atomic ratio gradually diminishes with increasing Ce amount. The relative concentrations of Ce^{3+} have been quantitatively obtained through the peak fitting, decreasing from 46 % to 39% and 28% for 1, 3, and 6 wt% $\text{CeO}_x\text{-TiO}_2$ samples, respectively. (Detailed deconvolution of the Ce 3d XPS spectra for the three $\text{CeO}_x\text{-TiO}_2$ samples are shown in the supporting information SI Figure S4) Hence the XPS results are in good agreement with the NEXAFS spectra, confirming the prevailing presence of fully oxidized state Ce^{4+} in the mixed oxide containing higher ceria content. The corresponding Ti 2p XPS spectra (supporting information SI Figure S2) exhibited the Ti $2p_{3/2}$ and Ti $2p_{1/2}$ doublet at 458.7 and 464.2 eV which is indicative of octahedrally coordinated Ti^{4+} .⁵⁴ The shift towards higher binding energy for the $\text{CeO}_x\text{-TiO}_2$ samples in comparison with pure TiO_2 can account for the surface enrichment of ceria inducing the intermixing or the charge transfer between Ti and Ce cations. No reduced titanium state is observed, i.e. Ti^{3+} , Ti^{2+} and Ti^0 , with higher Ce loadings.⁵⁵

Figure 6. XPS core level spectra of Ce 3d of CeO_x-TiO₂ samples with various CeO_x contents and pure standards.

As seen in the valence spectra of Figure S7, the CeO_x-TiO₂ samples exhibit similar features between 3 and 9 eV as bulk TiO₂. All the valence spectra show a main peak located at 7 eV and a smaller peak centered at 5.2 eV, implying the typical O 2s-Ti 3d

structure. However, with increasing ceria up to 6 wt%, a small peak can be distinctly seen at ~1.25 eV which is usually related to oxygen vacancies. This is likely to be the propagation of Ce 4*f* states into the valence band as a consequence of the existence of reduced ceria as discussed above. The low concentration of ceria in the 1wt % and 3 wt% CeO_x-TiO₂ samples makes it a challenge to detect occupied Ce 4*f* states with regular XPS. Nevertheless, the data for 6 wt% CeO_x-TiO₂ clearly shows that the valence electronic states of titania has been modified by the deposition of ceria, consistent with the generation of a unique oxide-oxide interface.³⁵

D. Optical property characterization and photocatalytic activity measurements for CeO_x-TiO₂ and Pt/ CeO_x-TiO₂ systems

The photocatalytic splitting of water was examined on the pure CeO_x-TiO₂ samples and on samples loaded with 0.5 wt% Pt as a co-catalyst. UV-Vis diffusion reflectance spectroscopy was employed to characterize the optical properties of the CeO_x-TiO₂ samples, in comparison to samples loaded with 0.5 wt% Pt, and compared to pure anatase TiO₂ and CeO₂. The spectrum of the reference TiO₂ sample was subtracted from the original spectrum to obtain a difference spectrum (inset). As indicated in Figure 7, the absorption edge of anatase TiO₂ is located at 415 nm is due to the O²⁻ → Ti⁴⁺ charge transfer transition. In contrast, CeO₂ can be easily activated by visible illumination through the onset at > 500 nm. The introduction of ceria significantly alters the optical properties of TiO₂. The absorption tails extend up to 550 nm in the samples containing 1 and 3 wt% loading of cerium. Visible absorption enhancement can be associated with the existence of oxygen vacancies and partially reduced valence states, i.e. Ce³⁺, in CeO_x-TiO₂ samples as determined by the NEXAFS and XPS. Taking into account the electronic configuration of CeO₂, the 4*f* orbital of Ce is unoccupied and the Ce ion is essentially in a tetravalent ground state. The presence of Ce³⁺ and oxygen vacancies induces an occupation of the *f* band. Such partially occupied orbitals are localized and situated above the O 2*p* valence band edge, as shown in Figure S7. This results in the formation of an inter-band transition or intermediate defect energy state between the valence and conduction bands of TiO₂ and therefore, narrows the band gap.^{20, 24}

Negligible difference is recorded with increasing Ce content up to 6%, possibly stemming from the larger portion of low coordination Ce^{4+} ions as well as the morphological transformation from 2D chains to 3D nanoparticles. As indicated in the HR-STEM images, ceria is deposited along the out-of-plane direction to minimize the total increasing strain energy, and thus does not contribute much to the concentration of reduced cerium at the oxide-oxide interface. Interestingly, the loading of Pt metal enhances the absorption of visible light further by forming a metal/semiconductor junction between Pt and TiO_2 . As the Fermi level of Pt is lower than that of TiO_2 , the photo-excited electrons in the CB of TiO_2 can migrate to the Pt to align the two Fermi levels. This shift of the bands is beneficial to the absorption of visible light. The presence of Pt also contributes to the stabilization of Ce^{3+} (NEXAFS spectra of samples with and without Pt are shown in supporting information Figure S3, indicating the more intense Ce^{3+} absorption present after the loading of Pt), thus increasing the occupied Ce 4f states, which results in the further enhancement of visible light absorption.^{45, 56}

Figure 7. A) UV-Vis-DRS spectra of CeO_x-TiO₂ samples, 0.5 wt% Pt/CeO_x-TiO₂ samples, TiO₂ and CeO₂ standards (main view); B) Difference spectra of CeO_x-TiO₂ and 0.5 wt% Pt/CeO_x-TiO₂ samples after subtracting the spectra of pure TiO₂ standard.

Additionally, filled- valence states due to Ce incorporation were studied by valence band photoemission as seen in Figure S7. When a minute amount of Pt was loaded on the samples, features between 0 ~ 3 eV were greatly enhanced; a trend which could be explained invoking a band structure alteration induced by the presence of the noble metal and also could be a consequence of an increase in the Ce^{3+} content (i.e. partially occupied Ce 4f states within the titania band gap).^{45, 57}

Pure $\text{CeO}_x\text{-TiO}_2$ samples were not active for the photocatalytic splitting of water. The photocatalytic water splitting performance over Pt/TiO_2 and $\text{Pt/CeO}_x\text{-TiO}_2$ systems with different CeO_x loading is depicted in Figure 8. The noble metal incorporation not only inhibits the quick backward reaction between O_2 and H_2 but also efficiently improves the separation of charge carriers as an electron trapping site.⁵⁷⁻⁵⁸ Recently, Joo et al.⁵⁹ proposed the alternative role of Pt to promote the recombination of atomic hydrogen, which is in agreement with the fact that the hydrogen production activity is dramatically changed with the addition of Pt for most of the TiO_2 based photocatalysts. Pt/TiO_2 exhibits low photocatalytic activity, producing 43.1 μmol of H_2 in 4 h, due to the rapid recombination between the photoexcited electrons and holes within a few picoseconds upon light excitation. It is obvious that ceria impregnation drastically alters the photocatalytic H_2 generation but the high loading appears to be detrimental to the performance. A smaller amount of H_2 (24.2 μmol) were observed when raising ceria content to 6 wt%. As seen in Figure 8(a), 1CeTi produces 14.1 μmol of H_2 per gram of photocatalyst per hour, much larger than the TiO_2 benchmark and the other samples. However, a further increase of ceria loading causes a reduction in the gas evolution rate to 3.7 and 2.0 $\mu\text{mol/g}\cdot\text{h}$ after illumination for 4 h.

Figure 8. (a) Photocatalytic H_2 evolution rate normalized to mass of photocatalyst over TiO_2 and $\text{CeO}_x\text{-TiO}_2$ (with different ceria contents) suspended (0.5wt% Pt loading co-catalyst, constant temperature at 293 K, 150 W Xenon arc lamp) in aqueous methanol

solution and (b) O₂-production mass normalized turnover rates for TiO₂ and CeO_x-TiO₂ photocatalysts (0.5wt% Pt co-catalyst, 0.01M aqueous AgNO₃ solution, constant temperature at 293 K, 8-h irradiation of a 150 W Xenon arc lamp).

On the other hand, it has been well acknowledged that the oxygen evolution is much more challenging than H₂ production, consuming four positive holes to oxidize water to oxygen. Therefore, water photo-oxidation was also conducted in the present study. Similar behavior is achieved in the case of O₂ evolution in spite of relatively low moles converted as shown in Figure 8(b), where low CeO_x loading (1 wt%) enhances the oxygen production rate, (approximately 1.80 mmol/g·h). The mass normalized turnover rates over CeO_x-TiO₂ are three- or four-fold greater than plain TiO₂ (0.49 mmol/g·h). Identical to the H₂ production rate, the decrease in evolved O₂ amount occurs as ceria increases to 3 and 6 wt%. We can thus conclude that 1 wt% ceria on TiO₂ is the optimal content to increase photocatalytic water splitting performance. Such high reactivity of 1CeTi can be attributed to the presence of well-dispersed, zero-dimensional ultrafine ceria nanoclusters (< 1 nm) on the TiO₂ support. As detected in HR-STEM images, 2D nanochains and 3D hemispherical particles (3 - 8 nm) exist in higher loading samples. The deterioration of the photocatalytic activity when going from 1 wt% to 3 or 6 wt% is most likely a consequence of a decrease in the content of Ce³⁺. Furthermore, the relatively large ceria particles in 6 wt% CeO_x-TiO₂ could prevent the exposure of TiO₂ surface active sites to light irradiation.

In addition, it is known that the photoexcited electron/hole pairs are generated by the light irradiation. Such behavior is additionally elucidated by the transient photocurrent response of TiO₂ and the CeO_x-TiO₂ series illustrated in Figure 9. It is worth noting that 1CeTi exhibits a more rapid and strong signal than the other higher loading samples and pure TiO₂ in which the current density sharply decreases from 50 to 42 μA/cm² in the first on/off cycle and reaches a reversible steady-state of approximately 35 μA/cm² thereafter. The high photocurrent of 1CeTi sample clearly indicates it has the largest

number of photo-generated electrons and the longest photo-generated carrier lifetime, revealing the good separation efficiency and fast transfer of photo-induced charge carriers after harvesting light. The results are consistent with the results obtained from photocatalytic H₂ and O₂ production.

Figure 9. (a) Transient photocurrent response of TiO₂ and CeO_x-TiO₂ during on/off cycles of 150 W Xenon lamp illumination; (b) comparison in surface area normalized turnover rates vs. Ce³⁺ atomic concentration (black dot symbols, calculated from XPS analysis).

Last but not least, the role of partially reduced Ce^{3+} and oxygen vacancies must be taken into consideration in both photovoltaics and photocatalysis. As shown by the NEXAFS and XPS results, increasing the nominal ceria content from 1 to 6 wt% gradually decreased $\text{Ce}^{3+}/\text{Ce}^{4+}$ atomic ratio from 0.46 to 0.28. Figure 9b illustrates the relationship between surface area normalized turnover rate (TORs) of gas evolved and the Ce^{3+} concentration. It is known that normalizing photocatalytic productivity per gram of catalyst per unit time informed about how the effectiveness of a photocatalyst per unit mass may have practical merit, but normalization to photoactive surface sites (i.e. surface area, number of exposed photoactive sites, etc.) allows for the better understanding of bulk and surface structural variations.⁶⁰ TORs values are strongly sensitive to not only the crystallinity of the bulk lattice (photon absorption efficiency and number of trap sites) but also the surface features (surface composition and possible preferential exposure of specific facets possessing unique photocatalytic activity).⁶⁰⁻⁶¹ The N_2 sorption isotherms reveal the porosity of all prepared materials and are shown in the Supporting Information (Figure S8 and Figure S9). Indeed, the highest water splitting reactivity is achieved for 1CeTi which contains highly dispersed clusters, with the largest portion of Ce^{3+} , in particular, 359.7 and 45.88 moles of H_2 and O_2 , respectively, per m^2 of photocatalyst per hour. Trivalent cerium species on the outermost surface or near the oxide-oxide interface act as photocatalytic active sites or hole scavengers, efficiently suppressing the surface charge recombination and extending charge carrier lifetime. Moreover, the formation of inter-band transition or intermediate defect energy state stemming from Ce^{3+} and oxygen vacancies facilitates the interfacial charge transfer and thus, improves the activity. Excess impregnated ceria concentration resulted in larger amount of oxygen vacancies (shown from the valence band photoemission). Such vacancy defects likely become recombination centers, diminishing the photocurrent propagation as well as the photocatalytic performance.

Conclusion

In summary, a series of catalysts consisting of ceria nanoparticles dispersed on anatase TiO_2 has been prepared through wet impregnation methods. Hierarchical growth of ceria nanostructures has been confirmed by HR-STEM from 0-1D clusters, to 2D chains and finally to 3D particles, in samples with increasing ceria loadings ranging from 1, to 3 and 6 wt%. The local morphology, bulk structure, electronic and optical properties have been investigated by XRD, PDF, NEXAFS, XPS, and UV-Vis. The hetero structure interfaces proved to be the likely active sites with the most oxygen vacancies, and the electronic structure shows meaningful perturbation which is believed to be an important contributor to the catalytic performance. Furthermore, photocatalytic tests revealed that the catalyst with small low dimensional ceria clusters with high dispersion gives the best activity for photocatalytic water splitting, despite the lowest ceria concentration. Thus, greatly improved cerium atomic efficiency in the photocatalytic process could be achieved with more precise structural control of the TiO_2 -supported ceria clusters. The understanding of the relationship between morphological, electronic, optical properties and catalytic performance provides significant guidance for the future design of optimized mixed-metal oxide photocatalysts.

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Supporting Information Available: Additional images of catalysts STEM/EELS characterization and spectra of UPS, XPS, NEXAFS of the $\text{CeO}_x\text{-TiO}_2$ catalysts; N_2 sorption isotherms, the revealed pore size and the time course of photocatalytic H_2 production diagrams of Pt loaded $\text{CeO}_x\text{-TiO}_2$ catalysts. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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