On the role of CoO in CoOₓ/TiO₂ for the photocatalytic hydrogen production from water in the presence of glycerol

M.A. Khan, M. Al-Oufi, A. Tossef, Y. Al-Salik, and H. Idriss*

SABIC-Corporate Research and Development (CRD), KAUST, Thuwal, Saudi Arabia

Abstract The photocatalytic water splitting activity of nanocomposite photocatalysts of TiO₂ with CoOₓ was studied under UV and visible light, and the catalysts were characterized by XRD, XPS, and UV–vis techniques. The presence of CoOₓ enhances the hydrogen production activity of TiO₂ by five times at an optimal loading of 2 wt. %. To investigate the role of CoOₓ, the photocatalytic activity was also studied under visible light and with different amounts of sacrificial agent. Our results indicate that the increasing activity was not due to increasing absorption of the visible light but most likely due to the role of CoOₓ nanoparticles as hole scavengers at the interface with TiO₂. XPS Co2p analyses of CoO/TiO₂ showed a considerable decrease in their signal after prolonged reaction time (44 h) when compared to that of the fresh catalyst. Because part of Co²⁺ cations is dissolved in solution, in neutral or acidic pH, the possible increase in the reaction rate upon their addition to TiO₂ under UV excitation was investigated. No change in the reaction rate was observed upon, on purpose, addition Co²⁺ cations to TiO₂ under UV excitation. Thus, one may rule out the reduction of Co²⁺ to Co⁰ with excited electrons within TiO₂. In order to further increase the reaction rate, we have synthesized and tested a hybrid system composed of CoO and Pd nanoparticles (Pd wt. % = 0.1, 0.3, 0.5, and 1 wt. %) where 0.3 wt. % Pd – 2 wt. % CoO/TiO₂ showed the highest rate.

Keywords Photocatalysis, hydrogen production, heterojunction, water splitting, titanium oxide, oxygen evolution

Cite this article M.A. Khan, M. Al-Oufi, A. Tossef, Y. Al-Salik, and H. Idriss: Catal. Struct. React., 2015, 1, 192–200

Introduction

Hydrogen is poised to play an important role in a sustainable energy system because it is storable, transportable, and can be converted into electricity efficiently using fuel cells when necessary. Moreover, it is an essential reactant in chemical industry and making it from renewables will contribute in recycling of carbon dioxide via chemical processes, such as the Fischer–Tropsch, methanol synthesis, and ammonia synthesis reactions. Photocatalytic water splitting using sunlight is considered a promising route to clean and renewable hydrogen production. The current efficiency of the process is still below what is needed for commercialization. The water splitting reaction is an uphill reaction in which the Gibbs free energy increases by 237 kJ mol⁻¹. Water splitting reaction is a multistep process involving (i) light absorption (ii) charge separation and transfer, and (iii) redox reactions on the surface. The water splitting process can be envisaged as two-half reactions: water oxidation and proton reduction to hydrogen fuel. Water oxidation is more challenging than hydrogen ion reductions because the generation of one molecule of gaseous oxygen requires four holes and occurs on a timescale approximately five orders of magnitude slower than that of H₂ evolution.

Various semiconductors such as TiO₂, CdS, ZnO, C₃N₄, and WO₃ have been explored for water splitting. TiO₂ remains the leading semiconductor material for water splitting with its good conversion efficiency (of UV light: ca. 4–5% of the solar spectrum) and stability. Improving the light absorption and charge carrier separation in TiO₂ remains the biggest challenge. In order to improve the oxidation half reaction, semiconductors such as PdS, RuO₂, IrO₂, and CoO have been investigated. Among these, CoO has been reported to be a very efficient oxidation cocatalyst with variety of oxide and...
Oxy-nitride semiconductors. Domen and coworkers reported the use of CoO as an oxygen evolution promoter when used with Ga2ZnInON for photocatalytic water splitting. Recently, Li and coworkers also reported record quantum efficiency electrodes for water oxidation. Using transient absorption water splitting with production of both H2 and O2. Domen and CoOx is higher than that of TiO2.

Upon using a dual cocatalyst system of Pt/CoPi with yttrium-doped BiVO4, the authors were able to achieve overall water splitting with production of both H2 and O2. Domen and coworkers also reported a CoOx-modified LaTiO3N photocatalyst for water oxidation. Under visible light illumination, the O2 evolution dramatically increased from 25 to 736 μmol h−1. Recently, Li and coworkers also reported record quantum efficiency of ~11.3% (when excited with light having a wavelength between 400 and 500 nm) for water oxidation using CoO/Ta N photocatalyst; with Ag2O as an electron scavenger.

Experimental

CoO-TiO2 were prepared by wet impregnation. Anatase TiO2 from Hombikat was used as the support catalyst. Different loadings of Co (0.5, 1, 2 and 4 wt. %) on TiO2 support were prepared by adding known amount of (Co(NO3)2·6H2O salt solution to 500 mg of TiO2 support. Excess water was evaporated under constant stirring with slow heating at 80 °C. The dried photocatalysts was calcined at 400 °C for 5 h. Photocatalysts with dual cocatalysts of Pd and CoOx were prepared by sequential impregnation of Pd on CoO-TiO2, starting from (PdCl).

UV–vis absorbance spectra of the powdered catalysts were collected over the wavelength range of 250–900 nm on a Thermo Fisher Scientific spectrophotometer equipped with prying mantis diffuse reflectance accessory. Absorbance (A) and reflectance (R) of the samples were measured. The reflectance (R) data were used to calculate the band gap of the samples using the Tauc plot (Kubelka–Munk function). XRD spectra were recorded using a Bruker D8 Advance X-ray diffractometer. A 2θ interval between 20 and 90° was used with a step size of 0.010° and a step time of 0.2 s/step. Based on the (1 0 1) diffraction line, the crystallite size is of the order of 8 nm. This was also further confirmed by TEM measurements. XPS was conducted using a Thermo scientific ESCALAB 250 Xi; the base pressure of the chamber was typically in the low 10−10 to high 10−12 mbar range. Charge neutralization was used for all samples (1 eV). Spectra were calibrated with respect to Cls at 285.0 eV. Quantitative analyses were conducted using the following sensitivity factors: Co2p (3.8), Ti2p (1.8), and O1s (0.66). Ar ion bombardment was performed with an EXO6 ion gun at 1 kV beam energy and 10 mA emission current. The sputtered area of 900 × 900 μm2 was larger than the analyzed area: 600 × 600 μm2. Data acquisition and treatment were done using the Avantage software. BET surface areas of catalysts were measured using Quantachrome Autosorb analyzer by N2 adsorption with surface areas of 133 m2 g−1 for pure anatase TiO2 and 131 m2 g−1 for 2 wt. % CoO–TiO2, both calcined at 400 °C.

Photocatalytic reactions were evaluated in a 135-mL-volume Pyrex glass reactor using 4 mg of catalyst. 30 mL of 5 vol. % glycerol aqueous solution or 30 mL of a 0.05 M AgNO3 aqueous solution were used to evaluate the H2 and O2 evolution, respectively. The final slurry was purged with N2 gas to remove any O2 and subjected to constant stirring. The reactor was then exposed to the UV light, a 100 Watt ultraviolet lamp (H-144GC-100, Sylvania par 38) with a flux of ~5 mW cm−2 at a distance of 5 cm. Similarly, to evaluate the UV + visible light activity a Xenon lamp (Asahi spectra MAX-303) with a total flux of 26 mW cm−2 (UV ~ 3.3 mW cm−2 and visible (up to 600 nm) ~ 22.7 mW cm−2) was used. Product analyses were performed by gas chromatography (GC) equipped with thermal conductivity detector (TCD) connected to Porapak Q packed column (2 m) at 45 °C and N2 was used as a carrier gas. O2 analysis was performed by GC equipped with TCD connected to packed molecular sieve (5A) column and He was used as a carrier gas.

Results and discussion

The band gaps and absorption properties of the photocatalysts were studied using diffuse reflectance UV–vis spectroscopy.
The UV–vis spectra of CoOx–TiO2 are recorded in the range of 250–900 nm as shown in Fig. 1(a). Spectra show typical absorption from anatase TiO2 with a band edge around 370–380 nm ($E_g \sim 3.2$ eV) due to the charge transfer from the valence band formed by O2p orbitals to the conduction band formed by 3d $t_2^g$ orbitals of the Ti4+ cations.\textsuperscript{18,19} Spectra of CoOx–TiO2 nano-composite photocatalysts showed absorption in the visible region. One can see, in particular, for the 0.5 and 1 wt. % of Co an absorption peak in the region of 500 nm ($\sim 2.5$ eV) which can be attributed to Co$^{2+} \rightarrow$ Ti$^{4+}$ charge-transfer interaction, as indicated in earlier reports.\textsuperscript{18,19} Another absorption peak near 800 nm ($\sim 1.5$ eV) is caused by the transition of electrons from the occupied Co 3d states below the Fermi level to the unoccupied Co 3d states which form the conduction band of CoOx.\textsuperscript{21,22}

The Kubelka–Munk theory is generally used for the analysis of diffuse reflectance spectra obtained from weakly absorbing samples. It provides a correlation between reflectance and concentration. The concentration of an absorbing species can be determined using the Kubelka–Munk equation:

$$F(R) = \frac{(1 - R)^2}{2R} = \frac{k}{s} = \frac{Ac}{s},$$

where $R$ is reflectance, $k$ is absorption coefficient, $s$ is scattering coefficient, $c$ is concentration of the absorbing species, and $A$ is the absorbance. The optical
Figure 3  (a) H₂ production as a function of time over TiO₂ with different loadings of Co (in wt. %); (b) H₂ production rates (extracted from Figure 3(a)) as function of Co loading. Reaction conditions: 4 mg catalyst, 30 mL H₂O and 5 vol. % glycerol under UV lamp (375 nm) at a flux = 4–5 mW cm⁻²; (c) O₂ evolution from TiO₂ with different loadings of Co (in wt. %) using 0.05 M AgNO₃ solutions and (d) O₂ evolution rates as function of Co loading. Note the 2 to 1 ratio in the hydrogen to oxygen rates (in separate experiments): Figure 3(b) and (d)

Figure 4  (a) H₂ production as a function of time of TiO₂ photocatalysts with different loadings of Co (in wt. %) – excited using a Xe lamp giving both UV and visible light; (b) H₂ production rates as a function of Co loading. Reaction conditions: 4 mg catalyst, 30 mL H₂O and 5 vol. % glycerol under Xenon lamp (250–650 nm) with a total flux of 26 mW cm⁻² (UV ~ 3.3 ± 0.2 mW cm⁻², visible ~ 22.7 mW cm⁻²); (c) H₂ production rates (normalized to UV flux) for UV light vs. (UV + visible) light as a function of Co loading and (d) % drop in activity upon using 1% glycerol as function of Co loading
Figure 5  XPS Co2p of the 4 wt. % CoO/TiO2 before and after photoreaction for 44 h. [Catal.] = 42 mg/80 mL (liquid composed of water and 5 vol. % of glycerol) = 0.53 g L⁻¹; UV flux = ca. 5 mW cm⁻²; total reactor volume = 200 mL; initial solution pH 7.2 and final solution pH < 5. Used catalyst was filtered and dried before XPS measurements.

Figure 6  Electronic diagram of CoO and TiO2 oxide systems; the redox potential of H₂O to H₂ and O₂ is also included.

Figure 7  Photocatalytic hydrogen over TiO₂ (anatase) in the presence of 5 vol. % glycerol under UV lamp (375 nm) at a flux = 4 mW cm⁻². Reactor volume: 135 mL, liquid volume: 30 mL, catalyst concentration = 3 mg/30 mL = 0.1 g L⁻¹; [Co²⁺] = 0.45 mg/30 mL.
In order to further analyze the chemical composition of CoOx and electronic state of the composites, the CoO-loaded TiO2 sample was analyzed by XPS and X-ray valence regions. Fig. 2(c) shows the Co 2p spectra from 1 wt. % CoO–TiO2 samples calcined at 400°C for 5 h. The XPS Co 2p of Co, CoO, and Co3O4 has been studied in some details by many workers. Co2p of Co2+ has its characteristic satellites, reduction of Co2+ leads to Co0 which results in a shift in the binding energy by about 2 eV. The binding energy of Co3+ is very close to that of Co2+ but Co3+ satellites are much more attenuated, and therefore, the presence of strong satellites can gauge the extent of Co2+ contribution. In Fig. 2(c), XPS Co2p before and after Ar ion sputtering is presented. The binding energies for Co 2p3/2 and Co 2p1/2 are at 781.4 eV and 797.1 eV. These positions and the spin orbit splitting of 15.5 eV and satellites presence at about 7 eV above the main peaks (ca. 788 and 804 eV) are consistent with those reported for Co +2 of CoO. Argon ions sputtering results in the preferential removal of oxygen anions and consequently the reduction of metal cations to lower oxidation states. We use to ascertain that our as-prepared sample is mainly composed of Co2+ and not Co0. This can be seen in Fig. 2(c) and (d). In Fig. 2(c), a shoulder at the lower binding energy side is seen at about 778 eV that is attributed to Co0. The appearance of Co0 is associated with the decrease of the signal of Co 2+. In Fig. 2(d), the valence band region is presented for the fresh and Ar ions sputtered surfaces. The appearance of the lines at about 7 eV above the main peaks (ca. 788 and 804 eV) are consistent with those reported for Co2+ of CoO. Tauc plots of our catalysts are shown in Fig. 1(b) (r = 2) which shows a slight decrease in optical bad gap of TiO2 with increasing Co loading.

The effect of Co loading on crystal structure of TiO2 support was studied using XRD. Fig. 2(a) shows the X-ray diffraction patterns of TiO2 with different loadings of Co (in wt. %). The XRD patterns with the characteristic planes of anatase phase at 2θ = 25.5° (1 0 1), 37.7° (0 0 4), and 48.2° (2 0 0) are seen. The XRD pattern does not show any cobalt phase (up to 4 wt. % loading), indicating that cobalt ions are uniformly dispersed on the TiO2 support. This was also indicated by others where at low loadings the CoOx diffraction peaks could not be detected. The XRD peaks positions of anatase TiO2 also do not show any change upon Co loading, confirming there is no change in structure/ crystal phase of TiO2 or doping of Co ions into TiO2. A broadening of the TiO2 diffraction peaks is, however, observed with the addition of Co, larger FWHM. This broadening could be due to either smaller TiO2 crystallites and/or lattice strain on TiO2 due to the presence of CoO nanoparticles. Because BET surface area measurements did not show change upon CoO loading (within experimental errors) loading this change might be due to lattice strain. A table of the diffraction lines of TiO2 (anatase), CoO, and Co3O4 is added, Fig. 2(b).

In order to further analyze the chemical composition of CoOx and electronic state of the composites, the CoO-loaded TiO2 sample was analyzed by XPS and X-ray valence regions. Fig. 2(c) shows the Co 2p spectra from 1 wt. % CoO–TiO2 samples calcined at 400°C for 5 h. The XPS Co 2p of Co, CoO, and Co3O4 has been studied in some details by many workers. Co2p of Co2+ has its characteristic satellites, reduction of Co2+ leads to Co0 which results in a shift in the binding energy by about 2 eV. The binding energy of Co3+ is very close to that of Co2+ but Co3+ satellites are much more attenuated, and therefore, the presence of strong satellites can gauge the extent of Co2+ contribution. Argon ions sputtering results in the preferential removal of oxygen anions and consequently the reduction of metal cations to lower oxidation states. We use to ascertain that our as-prepared sample is mainly composed of Co2+ and not Co0. This can be seen in Fig. 2(c) and (d). In Fig. 2(c), a shoulder at the lower binding energy side is seen at about 778 eV that is attributed to Co0. The appearance of Co0 is associated with the decrease of the signal of Co2+. In Fig. 2(d), the valence band region is presented for the fresh and Ar ions sputtered surfaces. The appearance of the lines at about 7 eV above the main peaks (ca. 788 and 804 eV) are consistent with those reported for Co2+ of CoO. Tauc plots of our catalysts are shown in Fig. 1(b) (r = 2) which shows a slight decrease in optical bad gap of TiO2 with increasing Co loading.

The effect of Co loading on crystal structure of TiO2 support was studied using XRD. Fig. 2(a) shows the X-ray diffraction patterns of TiO2 with different loadings of Co (in wt. %). The XRD patterns with the characteristic planes of anatase phase at 2θ = 25.5° (1 0 1), 37.7° (0 0 4), and 48.2° (2 0 0) are seen. The XRD pattern does not show any cobalt phase (up to 4 wt. % loading), indicating that cobalt ions are uniformly dispersed on the TiO2 support. This was also indicated by others where at low loadings the CoOx diffraction peaks could not be detected. The XRD peaks positions of anatase TiO2 also do not show any change upon Co loading, confirming there is no change in structure/crystal phase of TiO2 or doping of Co ions into TiO2. A broadening of the TiO2 diffraction peaks is, however, observed with the addition of Co, larger FWHM. This broadening could be due to either smaller TiO2 crystallites and/or lattice strain on TiO2 due to the presence of CoO nanoparticles. Because BET surface area measurements did not show change upon CoO loading (within experimental errors) loading this change might be due to lattice strain. A table of the diffraction lines of TiO2 (anatase), CoO, and Co3O4 is added, Fig. 2(b).

In order to further analyze the chemical composition of CoOx and electronic state of the composites, the CoO-loaded TiO2 sample was analyzed by XPS and X-ray valence regions. Fig. 2(c) shows the Co 2p spectra from 1 wt. % CoO–TiO2 samples calcined at 400°C for 5 h. The XPS Co 2p of Co, CoO, and Co3O4 has been studied in some details by many workers. Co2p of Co2+ has its characteristic satellites, reduction of Co2+ leads to Co0 which results in a shift in the binding energy by about 2 eV. The binding energy of Co3+ is very close to that of Co2+ but Co3+ satellites are much more attenuated, and therefore, the presence of strong satellites can gauge the extent of Co2+ contribution. Argon ions sputtering results in the preferential removal of oxygen anions and consequently the reduction of metal cations to lower oxidation states. We use to ascertain that our as-prepared sample is mainly composed of Co2+ and not Co0. This can be seen in Fig. 2(c) and (d). In Fig. 2(c), a shoulder at the lower binding energy side is seen at about 778 eV that is attributed to Co0. The appearance of Co0 is associated with the decrease of the signal of Co2+. In Fig. 2(d), the valence band region is presented for the fresh and Ar ions sputtered surfaces. The appearance of the lines at about 7 eV above the main peaks (ca. 788 and 804 eV) are consistent with those reported for Co2+ of CoO. Tauc plots of our catalysts are shown in Fig. 1(b) (r = 2) which shows a slight decrease in optical bad gap of TiO2 with increasing Co loading.

The effect of Co loading on crystal structure of TiO2 support was studied using XRD. Fig. 2(a) shows the X-ray diffraction patterns of TiO2 with different loadings of Co (in wt. %). The XRD patterns with the characteristic planes of anatase phase at 2θ = 25.5° (1 0 1), 37.7° (0 0 4), and 48.2° (2 0 0) are seen. The XRD pattern does not show any cobalt phase (up to 4 wt. % loading), indicating that cobalt ions are uniformly dispersed on the TiO2 support. This was also indicated by others where at low loadings the CoOx diffraction peaks could not be det ected. The XRD peaks positions of anatase TiO2 also do not show any change upon Co loading, confirming there is no change in structure/crystal phase of TiO2 or doping of Co ions into TiO2. A broadening of the TiO2 diffraction peaks is, however, observed with the addition of Co, larger FWHM. This broadening could be due to either smaller TiO2 crystallites and/or lattice strain on TiO2 due to the presence of CoO nanoparticles. Because BET surface area measurements did not show change upon CoO loading (within experimental errors) loading this change might be due to lattice strain. A table of the diffraction lines of TiO2 (anatase), CoO, and Co3O4 is added, Fig. 2(b).

In order to further analyze the chemical composition of CoOx and electronic state of the composites, the CoO-loaded TiO2 sample was analyzed by XPS and X-ray valence regions. Fig. 2(c) shows the Co 2p spectra from 1 wt. % CoO–TiO2 samples calcined at 400°C for 5 h. The XPS Co 2p of Co, CoO, and Co3O4 has been studied in some details by many workers. Co2p of Co2+ has its characteristic satellites, reduction of Co2+ leads to Co0 which results in a shift in the binding energy by about 2 eV. The binding energy of Co3+ is very close to that of Co2+ but Co3+ satellites are much more attenuated, and therefore, the presence of strong satellites can gauge the extent of Co2+ contribution. Argon ions sputtering results in the preferential removal of oxygen anions and consequently the reduction of metal cations to lower oxidation states. We use to ascertain that our as-prepared sample is mainly composed of Co2+ and not Co0. This can be seen in Fig. 2(c) and (d). In Fig. 2(c), a shoulder at the lower binding energy side is seen at about 778 eV that is attributed to Co0. The appearance of Co0 is associated with the decrease of the signal of Co2+. In Fig. 2(d), the valence band region is presented for the fresh and Ar ions sputtered surfaces. The appearance of the lines at about 1 eV below the Fermi level is indicative of 3d electrons due to both Ti cations in reduced states and metallic Co. The inset in the Fig. presents the Ti3p and O2s for the same samples. The broad structure at the
low binding energy side of the Ti3p is due to the presence of Ti cations in lower oxidation state than +4 due to preferential removal of oxygen anions upon sputtering. Quantitative analyses of the Co2p, Ti2p, O1s indicated that Co is present in about 0.1 at. % on the TiO2 surface.

The H2 and O2 production activities of CoOx–TiO2 photocatalysts under UV excitation are presented in Fig. 3. The photocatalytic activity was evaluated over 24 h and was stable and reproducible. Pure anatase TiO2 calcined at 400 °C showed H2 production rates of ~10 μmol g⁻¹ min⁻¹. The loading of CoOx resulted in improvement in the H2 evolution. The highest H2 production rates of ~47 μmol g⁻¹ min⁻¹ was obtained when the Co metal concentration was 2 wt. % relative to TiO2. The H2 production rates as a function of Co loading is plotted in Fig. 3(b). One can notice that increasing the Co loading above 2 wt. % decreased the photocatalytic activity. The highest photocatalytic activity of 2 wt. % cobalt loaded samples could be due to the optimum dispersion of CoOx particles over TiO2 photocatalyst. This trend is similar to other systems such as CuO/ TiO2, Cu2O/TiO2, and NiO/TiO2 as reported earlier.31–33 Actually, this trend is also seen for noble metals where a maximum efficiency occurs for a narrow range of concentrations depending on the nature of the metal and of the semiconductor.5,34–37 In order to further probe into this trend, we have monitored the O2 evolution activity of the same catalysts under UV excitation and in the same reactor but with 0.05 M AgNO3 solutions to scavenge electrons. While this method has its drawback (such as the possible deposition of the metallic Ag that is reduced on the surface of the catalyst),38,39 it does give a good indication on the potential of the semiconductor for the hole transfer and therefore for comparative reasons the method has its merit.40–42 As shown in Fig. 3(c), the O2 evolution monitored in a separate experiment with AgNO3 as sacrificial agent was linear as a function of time and was observed to be in a stoichiometric ratio of 1:2 to the H2 production indicating considerable O2 evolution.

To further investigate the contribution of CoOx in the enhancement of photocatalytic activity, the reaction was also tested under UV + visible light irradiation under a total flux of ~26 mW cm⁻² (UV ~ 3.3 mW cm⁻², visible ~ 22.7 mW cm⁻²). This is indeed important, as numerous reports have indicated that the addition of CoOx may enhance the reaction due to further electron and hole transfer being comparable. The O2 evolution also showed a similar trend to that before. However, the Co2p/Ti2p ratio decreased from 5 to 1 vol. %. As shown in Fig. 4(d), in pure anatase TiO2, the H2 evolution rate drops by ~45% when glycerol concentration is reduced to 1 vol. %. In contrast, samples with 2 wt. % of CoOx show better activity, a drop of ~10%. This result may indicate that CoOx nanoparticles function similar to the sacrificial agent i.e., as an oxidation cocatalyst/hole trapping agent.

In order to test the possibility of Co⁺ dissolution into the liquid phase, we have conducted long-term photoreaction experiment (44 h) over 4 wt. % CoOx/TiO2 under UV excitation and analyzed the Co content by XPS. We have used a high loading of 4 wt. % CoO in order to decrease the errors associated with computing the total peak area of the Co2p signal. Fig. 5 presents the XPS Co2p region of the fresh and used catalysts. The signal is typical of the Co2p of Co2⁺ cations as indicated in Fig. 2. Qualitatively, the XPS Co2p after reaction is identical to that before. However, the Co2p/Ti2p ratio decreased from 0.16 to 0.04 during the reaction time indicating considerable loss of Co cations.

While the reduction to Co metal (similar to that of Cu2⁺ to Cu0)33 by excited electrons is possible, one may refute it based on the redox potential. The redox potential of Cu is within the band gap of TiO2 (±0.34 V), and therefore, its reduction by conduction band electrons of TiO2 occurs. The redox potential of Co is ~0.28 V, therefore above TiO2 conduction band.44 Still, because the difference between the redox potential of Co2⁺ and that of TiO2 conduction band is very small (within the limits of measurements (Fig. 6), alterations due to changes in dipole moments46 may occur. We have conducted an experiment in which the photoreaction on TiO2 alone was monitored and where Co2⁺ (from Co(NO3)2) cations were introduced during the run. As shown in Fig. 7, no deviation in hydrogen production is seen upon the addition of Co2⁺ cations, indicating that their introduction did not alter the activity of TiO2. This result may exclude the possibility of Co2⁺ reduction by the CB band electrons of TiO2. It is also not possible under the reaction conditions to reduce CoO to Co metal by hydrogen produced.
since thermodynamics indicate that at room temperature the partial pressure of O_2 needs to be equal to 10^{-10} torr.\(^6\)

Fig. 8 presents the events diagram, to complement the electronic diagram of Fig. 6. Upon contact between CoO and TiO\(_2\) and photoexcitation with UV light, electrons are transferred from the VB to the CB of TiO\(_2\) (leaving holes in the VB) – step 1. Electrons can then be transferred from the VB of CoO to the empty states of the VB of TiO\(_2\) – step 2. This results in increasing the likelihood of electrons in the CB of TiO\(_2\) to reduce H\(_2\)O to \(\frac{1}{2}\) H\(_2\) – step 3. At the same time, O\(_2\) anions of OH (a) (surface hydroxyls) donate electrons to the VB of CoO – step 4. Based on the work’s results (in particular, the absence of enhancement of the rate when visible light is added), the rate of reaction can be explained without invoking visible light excitation of CoO, in the presence of UV light equivalent to that provided from the sun. It is worth mentioning that because no change in the reaction rate is seen between excitation under UV and excitation under UV + vis. light, in addition to the absence of hydrogen production under vis. light alone, electron excitation from the VB of CoO to its CB does not contribute into the reaction. Within this context, electron transfer from CoO CB to TiO\(_2\) CB, as often invoked in many work, may have no physical meaning. This is simply because under UV excitation, the TiO\(_2\) CB is populated by excited electrons and therefore less poised to receive excited electrons from the CoO CB.

The role of dual cocatalysts i.e., oxidation and reduction cocatalysts has been investigated by many workers including those reported in Refs.\(^1\)\(^4\)\(^6\)\(^7\). To investigate the role of another cocatalyst, we loaded Pd metal as the reduction cocatalyst on top of 2 wt. % Co-TiO\(_2\) which showed the best activity. In order to assess the activity, we also changed the concentration of Pd on top of the catalyst. The H\(_2\) production activity of 2 wt. % CoO\(_2\)-TiO\(_2\) photocatalysts impregnated with Pd metal is shown in Fig. 9(a). Further improvement of the H\(_2\) evolution reaction was observed. The highest H\(_2\) production rates were achieved when the Pd concentration was 0.3 wt. % as seen in Fig. 9(b), with H\(_2\) production rates of ~180 \(\mu\)mol g\(^{-1}\) min\(^{-1}\). Thus it seems that a system where a dual semiconductor-based cocatalyst i.e., CoO as an oxidation cocatalyst and Pd as reduction cocatalyst can function and is stable. The best performing Pd/Co ratio is ca. 0.1.

It is worth extracting a few points from this study. The optimum amount of CoO on top of TiO\(_2\) is found to be 2 wt. %. Because we do not see a change in the slope of hydrogen production and because the reduction potential is above the CB of TiO\(_2\), the chemical state of the cobalt oxide(s) is plausibly maintained as CoO. The BET surface area of TiO\(_2\) is \(133 \text{ m}^2/\text{g}_{\text{CoO}}\). We have calculated the expected surface area of a 2 wt. % of CoO, as an example. It is equal to \(3 \times 10^{-4} \text{ mole/g}_{\text{CoO}} = 16 \text{ m}^2\) assuming monolayer dispersion (as an upper limit). This would cover a small fraction of the surface; agglomeration would decrease it further. Therefore, the finding of an optimal reaction rate so narrowly dependent on the fraction of CoO may not be linked to a geometric effect (blocking of available sites) but most likely to an electronic effect where electrons transfer are optimized at the interface TiO\(_2\) and CoO.

Conclusions

 Nanocomposite photocatalysts by impregnating anatase TiO\(_2\) with different amounts of Co salt solutions were prepared, characterized, and tested. The presence of CoO enhances the activity of TiO\(_2\) with optimal loading determined to be ca. 2 wt. %, and the rate of hydrogen evolution was about five times higher than that of TiO\(_2\) alone. The increase in activity was not due to Co\(^2+\) reduction by TiO\(_2\) CB electrons. The increase in activity was also not due to increasing absorption of the visible light. It is most likely due to the role of CoO nanoparticles as hole scavengers at the interface with TiO\(_2\). The addition of Pd (as hydrogen ion reduction sites) further improved the reaction rate ca. 4 times compared to that of the composite system, to 180 \(\mu\)mol g\(^{-1}\) min\(^{-1}\). No catalytic deactivation was seen for prolonged reaction time (up to ca. 24 h). A schematic description of the events is given in which electron transfer occur from the VB of CoO to that of TiO\(_2\) (upon photoexcitation), this results in increasing water oxidation upon electron transfer from hydroxyl oxygen anions to the VB of CoO.

References

1. A. Kudo and Y. Miseki: *Chem. Soc. Rev.*, 2009, **38**, 253–278.
2. S. J. A. Moniz, S. A. Shevelin, D. J. Martin, Z.-X. Guo and J. Tang: *Energ. Environ. Sci.*, 2015, **8**, 731–759.
3. T. Hisatomi, J. Kubota and K. Domen: *Chem. Soc. Rev.*, 2014, **43**, 7520–7535.
4. A. J. Cowan, C. J. Barnett, S. R. Pendlebury, M. Barroso, K. Sivula, M. Grätzel, J. R. Durrant and D. R. Klug: *J. Am. Chem. Soc.*, 2011, **133**, 10134–10140.
5. J. Tang, J. R. Durrant and D. R. Klug: *J. Am. Chem. Soc.*, 2008, **130**, 13885–13891.
6. J. Yang, D. Wang, H. Han and C. Li: *Acc. Chem. Res.*, 2013, **46**, 1900–1909.
7. L. Yang, H. Zhou, T. Fan and D. Zhang: *Phys. Chem. Chem. Phys.*, 2014, **16**, 6810–6826.
8. S. Bashir, A. K. Wahab and H. Idriss: *Catal. Today*, 2015, **240**, (Part B), 242–247.
9. V. Jovic, W.-T. Chen, D. Sun-Waterhouse, M. G. Blackford and H. Idriss, G. J. N. Waterhouse: *J. Catal.*, 2013, **305**, 307–317.
10. M. Murdoch, G. I. N. Waterhouse, M. A. Nadeem, J. B. Metson, M. A. Keane, R. F. Howe, J. Llorca and H. Idriss: *Nat. Chem.*, 2011, **3**, 489–492.
11. R. Su, R. Tiruvalam, A. J. Logsdail, Q. He, E. A. Downing, M. T. Jensen, N. Dimitratos, L. Kesanav, P. W. Pells, R. Bechtstein, H. H. Jensen, S. Wondt, C. R. A. Catlow, C. J. Kiey, G. J. Hutchings and F. Besenbacher: *ACS Nano*, 2014, **8**, 3490–3497.
12. Z. Zhang, A. Li, S.-W. Cao, M. Bosman, S. Li and C. Xue: *Nanoscale*, 2015, **6**, 5217–5222.
13. K. Kamata, K. Maeda, D. Lu, Y. Kako and K. Domen: *Chem. Phys. Lett.*, 2009, **470**, 90–94.
14. M. Barroso, A. J. Cowan, S. R. Pendlebury, M. Grätzel, D. R. Klug and J. R. Durrant: *J. Am. Chem. Soc.*, 2011, **133**, 14868–14871.
15. D. Wang, R. Li, J. Zhu, J. Shi, J. Han, X. Zeng and C. Li: *J. Phys. Chem. C*, 2012, **116**, 5082–5089.
16. F. Zhang, A. Yamakata, K. Maeda, Y. Moriya, T. Takata, J. Kubota, K. Teshima and S. Oishi, K. Domen: *J. Am. Chem. Soc.*, 2012, **134**, 8348–8351.
17. S. Chen, S. Shen, G. Liu, Y. Qi, F. Zhang and C. Li: *Angew. Chem.*, 2015, **127**, 3090–3094.
18. G. Sadanandam, K. Lalitha, V. D. Kurnari, M. V. Shankar and M. Subrahmanyan: *Int. J. Hydrogen Energ.*, 2013, **38**, 9655–9664.
19. Z. Yan, H. Wu, A. Han and X. Yu, P. Du: *Int. J. Hydrogen Energ.*, 2014, **39**, 13353–13360.
20. X. He, X. Song, W. Qiao, Z. Li, X. Zhang, S. Yan, W. Zhong and Y. Du: *J. Phys. Chem. C*, 2015, **119**, 9550–9559.
21. K. Deori and S. Deka: *CryssEngcomm*, 2013, **15**, 8465–8474.
22. L. Liao, Q. Zhang, Z. Su, Z. Zhao, Y. Wang, Y. Li, X. Lu, D. Wei, G. Feng, Q. Yu, X. Cai, J. Zhao, Z. Ren, H. Fang, F. Robles-Hernandez, S. Baldey and J. Bao: *Nat. Nanotechnol.*, 2014, **9**, 69–73.
23. P. Jiang, W. Xiang, J. Kuang, W. Liu and W. Cao: *Solid State Sci.*, 2015, **46**, 27–32.
24. L. Samet: Mater. Charact., 2013, 85, 1–12.
25. S. C. Petitt, E. M. Marsh, G. A. Carson and M. A. Langell: J. Mol. Catal. A: Chem., 2008, 281, 49–58.
26. H. Idriss, C. Diagne, J. P. Hindermann, A. Kiennemann and M. A. Barateau: J. Catal., 1995, 155, 219–237.
27. H. Idriss and M. A. Barateau: Catal. Lett., 1994, 26, 123–139.
28. H. Idriss, V. S. Lusvardi and M. A. Barateau: Surf. Sci., 1996, 348, 39–48.
29. M. C. Biesinger, L. W. M. Lau, A. R. Gerson and R. S. C. Smart: Appl. Surf. Sci., 2010, 257, 887–898.
30. R. Riva, H. Miessner, R. Vitali and G. Del Piero: Appl. Catal. A: Gen., 2000, 196, 111–123.
31. W.-T. Chen, A. Chan, D. Sun-Waterhouse, T. Morija, H. Idriss and G. I. N. Waterhouse: J. Catal., 2015, 326, 43–53.
32. W.-T. Chen, V. Jovic, D. Sun-Waterhouse, H. Idriss and G. I. N. Waterhouse: Int. J. Hydrogen Energ., 2013, 38, 15036–15048.
33. L. Sinatra, A. P. LaGrow, W. Peng, A. R. Kirmani, A. Amassian, H. Idriss and O. M. Bakr: J. Catal., 2015, 322, 109–117.
34. G. R. Bamwenda, S. Tsubota, T. Nakamura and M. Haruta: J. Photochem. Photobiol., A: Chem., 1995, 89, 177–189.
35. M. Bowker, L. Millard, J. Greaves, D. James and J. Soares: Gold Bull., 2004, 37, 170–173.
36. Z. H. N. Al-Azri, W.-T. Chen, A. Chan, V. Jovic, T. Ina, H. Idriss and G. I. N. Waterhouse: J. Catal., 2015, 329, 355–367.
37. V. Jovic, Z. N. Al-Azri, W.-T. Chen, D. Sun-Waterhouse, H. Idriss and G. N. Waterhouse: Top. Catal., 2013, 56, 1139–1151.
38. A. Bhardwaj, N. V. Burbure, A. Gamalski and G. S. Rohrer: Chem. Mater., 2010, 22, 3527–3534.
39. J. Giocondi, P. Salvador and G. Rohrer: Top. Catal., 2007, 44, 529–533.
40. R. M. Navarro Yerga, M. C. Álvarez Galván, F. del Valle, J. A. Villoria de la Mano and J. L. G. Fierro: ChemSusChem, 2009, 2, 471–485.
41. E. M. Sabio, R. L. Chamousis, N. D. Browning and F. E. Osterloh: J. Phys. Chem. C, 2012, 116, 3161–3170.
42. R. Li, Y. Weng, X. Zhou, X. Wang, Y. Mi, R. Chong, H. Han and C. Li: Energ. Environ. Sci., 2015, 8, 2377–2382.
43. Y.-F. Wang, M.-C. Hsieh, J.-F. Lee and C.-M. Yang: Appl. Catal. B: Environ., 2013, 142–143, 626–632.
44. M. T. Greiner, M. G. Helander, W.-M. Tang, Z.-B. Wang, J. Qiu and Z.-H. Lu: Nat. Mater., 2012, 11, 76–81.
45. http://www.chemeddl.org/services/moodle/media/QBank/GenChem/Tables/EStandardTable.htm.
46. D. Zhang, M. Yang and S. Dong: J. Phys. Chem. C, 2015, 119, 1451–1456.
47. M. Ivill, S. J. Pearton, S. Rawal, L. Leu, P. Sadik, R. Das, A. P. Hebard, M. Chisholm, J. D. Budai and D. P. Norton: New J. Phys., 2008, 10, 065002.
48. K. Maeda, D. Lu, K. Teramura and K. Domen: Energy. Environ. Sci., 2010, 3, 470–477.
49. K. Maeda and K. Domen: J. Phys. Chem. Lett., 2010, 1, 2655–2661.