Visible Light-Driven Gas-Phase Artificial Photosynthesis Reactions over Ruthenium Metal Nanoparticles Modified with Anatase TiO₂

Eduardo Morais, Colin O’Modhrain, K. Ravindranathan Thampi, and James A. Sullivan

1UCD School of Chemistry, University College Dublin, Belfield, Dublin 4, Ireland
2UCD School of Chemical and Bioprocess Engineering, University College Dublin, Belfield Dublin 4, Ireland

Correspondence should be addressed to K. Ravindranathan Thampi; ravindranathan.thampi@ucd.ie and James A. Sullivan; james.sullivan@ucd.ie

Received 31 January 2019; Accepted 5 March 2019; Published 30 April 2019

Guest Editor: Wei Wei

Copyright © 2019 Eduardo Morais et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

1. Introduction

Increasing concentrations of atmospheric CO₂ have drawn considerable attention in the scientific sphere driving researchers to seek strategies to reduce current levels and curtail overall emissions [1, 2]. CO₂ utilisation is a desirable strategy as it can potentially lead to decreased levels of atmospheric CO₂ and the generation of products that aid energy and raw material demand. Thus, with an appropriate process, from an undesired waste, CO₂ becomes a valuable and cheap feedstock [3, 4].

Reduction of CO₂ using H₂O involves the breaking of strong C=O and O-H bonds and thus requires energy input [5, 6]. The photoconversion of CO₂ is performed by nature through photosynthesis [7]. Artificial photosynthesis (AP) involves the reduction of CO₂ using H₂O and solar energy in a nonbiological system. However, C=O and O–H bonds are optically inert in the range of near-UV and visible light (200–900 nm) making the use of a photocatalyst a requirement [1, 7, 8]. The photochemical reduction of CO₂ is a multiple electron transfer process leading to the formation of many different products ranging between CO and CH₄ and including all semireduced C₁ and C₂ species [8, 9]. Following over 40 years of research on this reaction, the scientific community is still a long way from producing efficient and viable devices for promoting artificial photosynthesis and there are many unresolved questions surrounding the reaction mechanisms and other parametric effects [9, 10].

Nanocrystals of noble metals have been used in various applications including electronics, optics, magnetics, and catalysis and exhibit unique electronic, photonic, and catalytic properties compared to their bulk counterparts [11]. Ruthenium (Ru) is a widely used catalyst for the promotion of active and selective CO₂ and organic reactions [12, 13]. Despite being an important element in catalysis, the application of Ru nanoparticles in the AP reaction, to our knowledge, has not been reported. This study describes a facile
solvothermal approach to fabricate nanoparticles of ruthenium (in the presence and absence of TiO$_2$) from an ethanol solvent.

Three catalysts were prepared. The materials were characterised, and their catalytic activity was investigated in the AP reaction under batch reaction conditions. The described results show the first example of the use of metallic nanoparticles in an artificial photosynthetic reaction without the aid of a semiconductor component. It is also the first example of plasmon-promoted photocatalysis over Ru nanoparticles and of plasmon excitation transfer from Ru to TiO$_2$.

2. Experiment

2.1. Preparation of the Photocatalysts. The ruthenium-based photocatalysts were prepared using a solvothermal route. At room temperature, RuCl$_3$·3H$_2$O (Sigma-Aldrich, 100 mg, 0.5 mmol) was left to equilibrate overnight in absolute ethanol (Fischer, 12 mL). The resulting solution was then transferred to a 20 mL Teflon-lined, stainless-steel autoclave (Parr) and heated at 160°C for 12 hours. The resulting solid was centrifuged, washed with distilled water and acetone several times, and dried at 60°C overnight. This procedure was repeated adding TiCl$_3$ (Acros, 20% in ethanol) to the RuCl$_3$ solution after the equilibration. The addition of TiCl$_3$ was carried out dropwise at two Ru:Ti molar ratios: 10:1 and 1:10. Thus, three different Ru$_x$Ti$_y$ samples were prepared (Ru$_x$Ti$_y$, Ru$_x$(Ti$_y$)$_1$, and Ru$_y$(Ti$_x$)$_1$), where x and y are the respective Ru:Ti molar ratios. These are designated as 100%Ru, 10%TiO$_2$/Ru, and 10%Ru/TiO$_2$ in the text.

2.2. Characterisation Methods. X-ray powder diffraction analysis was carried out on a Siemens D500 Kristalloflex diffractometer using Cu Kα radiation (λ = 1.54056 Å). The voltage and the current were set to 40 kV and 30 mA, respectively, and the scan was conducted in 20 mode, an angular range of 10°–90°, 0.01 step per degree, and 5 seconds per step.

UV-visible spectra were recorded on a Jasco V-650 instrument equipped with an integrating sphere (ISV-722). Absorbance was recorded in the range of 190–900 nm in baseline correction mode, with background spectra being collected prior to the experiments.

A Quantachrome NovaWin2 instrument was used to obtain N$_2$ adsorption/desorption isotherms at 77.3 K. The BET-specific surface area ($S_{BET}$) was calculated from the linear fit of the data in the N$_2$ adsorption/desorption isotherms over the relative pressure range ($P/P_0$) of 0.05–0.30 using the Brunauer-Emmett-Teller (BET) equation.

Samples for TEM (Transmission Electron Microscopy) analysis were dispersed in isopropanol and sonicated for 15 minutes. 10 µL of the suspension was then dropped onto holey carbon films supported by copper TEM meshes. The solvent was evaporated prior to analysis. Images were recorded on a FEI Tecnai G220 TWIN microscope operated at 200 kV.

XPS (X-ray Photoelectron Spectroscopy) analysis was performed on a Kratos Axis Ultra DLD instrument. Samples for XPS were pressed into pellets using a hydraulic press prior to analysis.

TPD (Temperature Programmed Desorption) experiments were carried out using both H$_2$O and CO$_2$ as probe molecules. For CO$_2$ TPD, samples were loaded into a quartz tubular reactor and held in place using quartz wool plugs. While the solid was kept under a flow of Ar (100 mL min$^{-1}$), the reactor was housed in a furnace and heated at 110°C for 30 minutes to remove any physisorbed species from the surface. This system was then allowed to cool at 5°C C, and the CO$_2$ signal at this stage was recorded as a calibration factor, before CO$_2$ was removed from the stream and replaced by an equivalent flow of Ar, retaining the overall flow (100 mL min$^{-1}$). The temperature was lowered to 20°C, and the CO$_2$ signal (as measured using an online mass spectrometer—Prolab) returned to background levels. The catalyst was then heated from 20°C to 700°C at a ramp rate of 10°C min$^{-1}$ while a portion of the exhaust gas was continuously monitored on the Prolab instrument. For H$_2$O TPD experiments, a mixture H$_2$O/Ar was produced by flowing Ar (50 mL min$^{-1}$) through a bubbler containing 500 mL of H$_2$O immersed in a water bath kept at 60°C. Considering the bubbler as an isolated system and the relative vapour pressure of H$_2$O at 60°C

![Figure 1: pXRD patterns of the RuTi series compared with the standards Ru$^0$, RuO$_2$, and TiO$_2$.](image)

Table 1: BET surface areas and weight percentages (as derived from pXRD) of the phases in the RuTi series.

<table>
<thead>
<tr>
<th>Samples</th>
<th>SSA (m$^2$ g$^{-1}$)</th>
<th>Ru (wt%)</th>
<th>RuO$_2$ (wt%)</th>
<th>TiO$_2$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100%Ru</td>
<td>195</td>
<td>96</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>10%TiO$_2$/Ru</td>
<td>177</td>
<td>86</td>
<td>6</td>
<td>8</td>
</tr>
<tr>
<td>10%Ru/TiO$_2$</td>
<td>68</td>
<td>6</td>
<td>4</td>
<td>90</td>
</tr>
</tbody>
</table>
as 0.1961 atm \[5\], the resulting mixture was 7.2% \(\text{H}_2\text{O} (v/v)\). This was used to dose the catalyst at 50°C with 3.9% \(\text{H}_2\text{O}\) in a flow of \(\text{Ar} (96.1 \text{ mL min}^{-1})\) until saturation was reached (~1 h). The \(\text{H}_2\text{O}\) signal at this stage was recorded as a calibration factor, before \(\text{H}_2\text{O}\) was removed from the stream and replaced by an equivalent flow of \(\text{Ar}\), retaining the overall flow (100 mL min\(^{-1}\)). The temperature was lowered to 20°C, and the \(\text{H}_2\text{O}\) signal returned to background levels. The catalyst was then heated from 20°C to 700°C at a ramp rate of 10°C min\(^{-1}\) while a portion of the exhaust gas was continuously monitored using an online ProLab mass spectrometer.

2.3. Catalytic Activity Measurements. The catalytic evolution of gaseous products was investigated with a top irradiation photoreactor vessel under batch conditions. In a typical experiment, the catalyst (20 mg) was loaded into the reactor (73.5 cm\(^3\)) and initially the system was held under a flow of \(\text{Ar} (100 \text{ mL min}^{-1})\) while the temperature was increased to 110°C for 30 minutes in order to ensure that any species attached to the surface by physisorption had been removed. The temperature was then lowered to 50°C, and a mixture of \(\text{H}_2\text{O}\), \(\text{CO}_2\), and \(\text{Ar} (100 \text{ mL min}^{-1})\) was switched into the stream. The catalyst in the reactor was held under a flow of \(\text{CO}_2\) and \(\text{H}_2\text{O}\) for 1 hour with a \(\text{CO}_2 : \text{H}_2\text{O}\) ratio of 1 : 14. After 1 hour, the reactor was cooled at 25°C, sealed, and placed into the chamber of an Atlas Suntest™ CPS+ instrument and externally irradiated by a 300 W Xe lamp (Figure SI 1) that only emits visible light. During the reaction, the system was cooled to ensure that the temperature was kept constant at 25°C. The reactor was equipped with a septum which allowed sample extraction for analysis. The extraction of gaseous aliquots for GC analysis was carried out periodically using a 500 \(\mu\)L Swagelok™ gastight syringe. The GC was Varian

---

**Figure 2:** (a, b, c) TEM images of 100%Ru, 10%\(\text{TiO}_2\)/Ru, and 10%Ru/\(\text{TiO}_2\), respectively. Insets show Ru particle size histograms.
GC-450 equipped with CARBOWAX and Hayesep C packed columns, a methaniser, and detectors TCD and FID. The injector, the FID, and the TCD were held at 200°C, while the methaniser was held at 400°C. Ar was the carrier gas with an overall flow of 50 mL min⁻¹, and the pressure on the column was set to 30 psi. For the analysis, the initial temperature of the column was set to 50°C, and the column was then ramped at a rate of 20°C min⁻¹ to 120°C and held at the final temperature for 2 minutes.

3. Results and Discussion

The XRD patterns of the RuTi series and reference XRD patterns are shown in Figure 1. Hexagonal ruthenium metal with a space group P63/mmc and lattice constants of \( a = 2.704 (7) \) Å and \( c = 2.958 (4) \) Å was observed in all samples via the presence of (100), (002), and (101) diffraction peaks at \( 2\theta = 38.7, 42.2, \) and 44.2°. A small fraction of tetragonal rutile-phase RuO₂ \((a = b = 4.593 (7) \) Å, \( c = 2.958 (7) \) Å; weight percentages shown in Table 1) was also observed in all samples, detected via the presence of (110) and (101) diffraction peaks at \( 2\theta = 27.8, \) and 35.1°. With regard to Ti phases, only anatase TiO₂ was detected in the 10%TiO₂/Ru and 10%Ru/TiO₂ samples via the presence of (101), (103), and (200) diffraction peaks at \( 2\theta = 25.7, 37.8, \) and 48.4°. The anatase TiO₂ was obtained in the tetragonal crystalline system with a space group I41/amd and lattice constants of \( a = b = 3.793 (1) \) Å and \( c = 9.510 (4) \) Å. No other diffraction features associated with ruthenium- or titanium-related species were found regardless of the Ru:Ti molar ratio used in the preparation.

A small negative shift of 0.06° and 0.10° in the (110) and (101) peaks of the RuO₂ phase was observed in the profiles of the 10%TiO₂/Ru and 10%Ru/TiO₂ samples, respectively (when compared to the reference peaks of RuO₂). Such a shift, which can be correlated with expansive residual strain, defects, or change in electronic configuration or atomic structure, was not detectable in the pattern of the 100%Ru sample. The shift is ascribed to the inclusion of Ti into the RuO₂ matrix in these samples. This observation obeys Vegard’s law [14, 15] where the lattice of metallic substitutional solid solution is compressed with increasing solute concentration as the atomic radius of solute atoms (Ti, 176 pm) is smaller than that of the solvent atoms (Ru, 178 pm).

TEM images of the solids are presented in Figures 2(a), 2(b) and 2(c). In all cases, the morphology of the ruthenium metal particles is spherical. This morphology can also be observed in the SEM images (Figure SI 2). The inset plot on each image displays the corresponding particle size distribution histogram of the ruthenium metal nanoparticles in the catalysts. The particle sizes ranged between 2 and 10 nm—with an average diameter of 5 nm across the three samples. Neither the morphology nor the size of the Ru particles was affected by the introduction of anatase TiO₂. This is clear in Figure 2(c) in which the ruthenium nanoparticles can be observed on the larger TiO₂ particles. As for the anatase TiO₂ particles in 10%Ru/TiO₂, these are approximately spherical with an average size of 0.5–0.7 μm.

It is also noteworthy that the extent of aggregation of the Ru nanoparticles differs across the three prepared samples. In the 10%TiO₂/Ru, the Ru nanoparticles appear more aggregated than those in the 100%Ru sample and in the 10%Ru/TiO₂ sample, and the aggregation is found to be the least. The aggregation of Ru nanostructures into larger spherical features may decrease the surface area of the final material and affect the nature of the plasmon resonance, which is
known to be size dependent on these nanoparticles [16, 17]. In turn, these characteristics may impact the catalytic properties. However, the UV-visible spectra, which analyse the plasmons, do not show any conclusive difference in the plasmon band across the three samples.

3.1. Surface and Optical Properties. These materials showed appreciable BET surface areas (Table 1). The multipoint BET analysis plots are shown in Figure SI 3. The two Ru-abundant samples—100%Ru and 10%TiO$_2$/Ru—have much higher BET surface areas than the Ti-abundant sample—10%Ru/TiO$_2$. This can be attributed to the different sizes of the particles (see above).

Figure 3(a) shows TPDs of CO$_2$ from the catalyst series. The 100%Ru and 10%TiO$_2$/Ru materials show two desorption events in each profile, confirming the presence of two CO$_2$ accessible adsorption sites. These are well separated peaking at $T_1 = 195^\circ$C and $T_2 = 270^\circ$C in the profile from the 100%Ru catalyst, while for 10%TiO$_2$/Ru, there is a main peak at $T_2 = 270^\circ$C with a lower temperature shoulder at $T_1 = 220^\circ$C. The incorporation of 10%Ti strengthens the interaction between CO$_2$ and the surface (as seen by the change in desorption temperatures) and reverses the relative concentrations of the adsorption sites. The 10%TiO$_2$/Ru catalyst contains the highest concentration of CO$_2$ desorption sites with 645.6 μmol g$^{-1}$ of CO$_2$ desorbing from the saturated catalyst, compared to 439.6 and 212.5 μmol g$^{-1}$ from 100%Ru and 10%Ru/TiO$_2$, respectively.

Upon increasing the Ti loading to ~90%, the CO$_2$ adsorption/desorption characteristics were altered substantially.

Figure 4: High-resolution XPS core-level spectra of (a) 100%Ru (Ru 3d), (b) 10%TiO$_2$/Ru (Ru 3d), (c) 10%TiO$_2$/Ru (Ti 2p), and (d) 10%TiO$_2$/Ru (O 1s).
The extent of desorption was much lower, and it occurred at higher temperatures (300–500°C), indicating the formation of stronger adsorption sites on the (mostly) TiO₂ surface. These new (presumably TiO₂-based) sites are more stable than those on the 100%Ru and 10%TiO₂/Ru materials; however, they are less stable than the typical CO₂ adsorption sites on anatase TiO₂ [18]. Mao et al. have studied CO₂ desorption from various anatase TiO₂ samples and reported that the main desorption events occur in the 500–600°C range. This shift in the CO₂ peaks to lower temperatures suggests that the presence of Ru has weakened the CO₂–TiO₂ interactions. These catalysts are also capable of adsorbing and desorbing H₂O (see the H₂O-TPD profiles in Figure 3(b)). These profiles show that the presence of TiO₂ decreases the H₂O adsorption/desorption capacities of the materials. The Ru sample without TiO₂ shows a large peak at 225°C with a secondary peak at 300°C, while when TiO₂ is added to the material the water desorption is singly (relatively broad feature) peaking at 250°C from the 10%TiO₂/Ru sample and at ~350°C from the 10%Ru/TiO₂ material. These results confirm that the samples can adsorb (and desorb) both reactants required for the AP reaction.

XPS measurements shed light on the nature of the surface of these catalysts. Figure 2(a) shows the Ru 3d spectrum of the 100%Ru sample. The two peaks observed in the Ru 3d region are related to electron emission from Ru 3d⁵/₂ and Ru 3d⁷/₂ levels (with binding energies at 280.7 and 276.2 eV, respectively). These peaks correspond mainly to emission from hexagonal Ru⁰ with a coordination number of 12 and a spin-orbit splitting Δ of 4.5 eV [19]. Upon deconvolution of this spectrum, emission from small amounts of Ru⁴⁺ (at higher energies relative to those from Ru⁰) was also detected, confirming the presence of RuO₂.

The Ru 3d spectrum of the 10%TiO₂/Ru material shows signals related to Ru⁰ and Ru⁴⁺ (as above) but also signals related to emission from Ru⁵⁺ (Figure 4(b) and Figure SI 4). The existence of Ru⁵⁺ (0 < n < 4) species in this catalyst must be ascribed to the added Ti and its effect on the electronic structure of Ru. Kim and Winograd considered that the substitution of metal ions into the RuO₂ lattice is most likely responsible for the formation of Ru⁵⁺ (0 < n < 4) ions via electron transfer from Ti to Ru⁴⁺ ions [20].

Such observations are in good agreement with the XRD results which show dissolution of Ti into the RuO₂ lattice. Furthermore, Rodriguez et al. reported the creation of interstitial M⁵⁺ species in solid solutions of (Ti–Ru)O₂, such as Ru⁵⁺, which may lead to undercoordinated oxygen species (oxygen vacancies) preserving the electrostatic balance [21].

The Ti 2p spectrum of the 10%TiO₂/Ru catalyst was also recorded (Figure 4(c)). Emission from the Ti 2p1/2 and 2p3/2 levels with binding energies at 458.5 and 464.4 eV is related to emission from octahedrally coordinated Ti⁴⁺. However, a second, less intense peak at lower energy, related to Ti⁵⁺, was also detected in the Ti 2p region. This peak may be related to incorporation of Ti into the RuO₂ lattice. The O 1s spectrum of this catalyst shows the presence of both lattice and surface hydroxyl O atoms.

Figure 5 shows the UV-Vis spectra of the catalysts. The absorption feature in the range of 250-358 nm observed in the Ti-containing samples is associated with the O 2p–Ti 3d (band gap) transition of TiO₂. The absorption beyond 358 nm towards the visible and near-infrared range (λ = 400–800 nm) is significantly pronounced in the spectra of all catalysts. This has previously been attributed to interband transitions and localised surface plasmonic resonance (LSPR), i.e., surface electron oscillation under continuous electromagnetic stimuli [22–24] on Ru particles.

3.2. Photocatalytic Activity. The photocatalysis results are shown in Figure 6. Regarding photoreactivity, it should be noted that no products resulted from reactions that were carried out (a) in the dark or (b) in the absence of catalyst. Neither was there any detection of products when P25 TiO₂ was used as a photocatalyst in the presence or absence of light.

Consumption of CO₂ and production of either gaseous CO or CH₄ were only observed when both Ru-containing catalysts and light were present. The reaction was carried out in the presence of CO₂ and H₂O (with no hole scavenger agents), and evolution of O₂ at a larger rate in comparison to evolution of the carbon-containing products was observed in all cases (see Figure 6(a)). The levels of CH₄ and CO produced as a function of reaction time for the different catalysts are shown in Figure 6(b). While CH₄ was the sole product observed when using the 100%Ru catalyst, CO was formed alongside CH₄ over the Ti-containing catalysts. In the case of the 10%TiO₂/Ru catalyst, CO only arose as a minor by-product; however, over the 10%Ru/TiO₂ catalyst, CO was produced in comparable amounts to CH₄. Thus, as the quantities of CO involved increase with the concentration of TiO₂ in the catalyst, the generation of CO appears to be related to the levels of TiO₂ (anatase) in the material.

No carbon balance was achieved in these reactions. Attainment of one is difficult for several reasons. Firstly, at the beginning of the reaction, the reactor contains both...
gaseous and adsorbed CO$_2$. It is possible to measure the former and estimate the latter from CO$_2$-TPD once an equilibrium is attained without any reactions involved. However, this is not the case here. This adsorbed CO$_2$ desorbs during the course of the reaction depending upon the partial pressure of gaseous CO$_2$ remaining to be reacted, and the attainment of this adsorption-desorption equilibrium is not instantaneous.

Following the experiments, we measured the gas phase concentrations of reactants and products. This data is presented in Table 2 from the reaction over the 10%TiO$_2$/Ru catalyst and shows a discrepancy of ~10% in the C balance. This is not large when considering the dynamics of the reaction.

**Figure 6:** Evolution of (a) O$_2$ and (b) CH$_4$ and CO with time over P25 and the three Ru-containing catalysts and (c) rate of CO$_2$ conversion over each of the Ru-containing catalysts.

**Table 2:** Carbon balance from the artificial photosynthesis reaction carried out over the 10%TiO$_2$/Ru catalyst.

<table>
<thead>
<tr>
<th></th>
<th>Before reaction (mmol g$^{-1}$)</th>
<th>Following reaction (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In the reactor</td>
<td>3.54</td>
<td>3.78</td>
</tr>
<tr>
<td>Adsorbed</td>
<td>0.65</td>
<td>?</td>
</tr>
<tr>
<td>Products</td>
<td>0</td>
<td>0.03</td>
</tr>
<tr>
<td>Total</td>
<td>4.19</td>
<td>3.81</td>
</tr>
</tbody>
</table>
and the factors affecting the attainment of adsorption-desorption and reaction equilibria.

The formation and adsorption of gaseous products, e.g., CH₃OH and CH₂O, also need to be considered when trying to establish a mass balance. The FTIR spectrum of the 10%TiO₂/Ru catalyst following reaction shows alkyl, carbonyl, and C–O vibrations (Figure 7).

The most reactive catalyst within the series was 10%TiO₂/Ru, converting approximately 1.2 μmol of CO₂ g⁻¹ h⁻¹ (with an apparent quantum efficiency (AQE) of ~0.07%), compared to conversions of 0.4 and 0.43 μmol g⁻¹ h⁻¹ over the 100%Ru and 10%Ru/TiO₂ catalysts, respectively (Figure 6(c)).

This photocatalyst is robust, maintaining a product evolution rate of 1.2 μmol of product g⁻¹ h⁻¹ for three reaction cycles (Figure 8(a)). Moreover, the pXRD pattern (Figure 8(b)) and the XPS spectra (Figure 8(c)) of the 10%TiO₂/Ru catalyst also remained unchanged after three reaction cycles, confirming the stability of this photocatalyst.

The photocatalytic activity of metallic Ru nanoparticles is surprising and may be ascribed to a number of factors. Firstly, as reported by Kim et al., upon chemisorption onto the surface of Ru nanoparticles, CO₂ molecules experience a pronounced narrowing in the energy gap between their HOMO (5τ bonding) and LUMO (2π antibonding) levels. They report a decrease from 8.5 eV (free CO₂) to 2.4 eV (Ru-bound CO₂ species) [25]. The new energy gap of Ru–CO₂ molecules falls within the visible region; hence, adsorbed CO₂ molecules can absorb the incident irradiation and this can promote the dissociation reaction.

Secondly, the effect of localised surface plasmon resonance (LSPR) must be considered. It is widely known that “free electrons” on the surface of noble metals can absorb light in the visible range to trigger a collective oscillatory wave (plasmon) which gives rise to creation of hot electrons, electron transfer, and catalytic activity [26]. Also, as reported by Christopher et al., the photocatalysis observed is likely due to polarisation of the Ru nanoparticles’ surface into electron/hole-rich regions, ultimately generating “metallic electrons and holes” [24].

Furthermore, the photocatalysis over pure Ru nanoparticles may be partially attributed to thermal promotion, since light absorption in the range of the LSPR band will lead to a slight temperature rise within the nanoparticles [27]. The combination of thermal and photoenergies to initiate catalytic processes of CO₂ conversion is deemed beneficial firstly by Thampi et al. [13] and recently by Kim et al. [25]. In their case, heat was purposefully used alongside light to carry out the hydrogenation of CO₂ over Ru nanoparticles, yielding better overall catalytic performance when both heat and light were used. Therefore, we conclude that the generation of hot electrons from the metallic nanoparticles, the reduced gap between the HOMO and LUMO levels in the adsorbed CO₂ molecules, and the photoinduced thermal energy all work in tandem to promote the CO₂ photoreduction [23–25, 28].

To our knowledge, this is the first example of Ru nanoparticles catalysing the AP reaction. Furthermore, the absorbance of light by the Ru particle generates plasmons (and these plasmons yield the photocatalytic activity). This is the first example of such plasmonic reactivity seen with Ru catalysts.

Also, this result shows that anatase TiO₂ has a role in the photocatalytic process. Coupling Ru nanoparticles to anatase TiO₂ led to higher photocatalytic activity in the case of 10%TiO₂/Ru, possibly owing to the combined effect of LSPR on Ru nanoparticles and charge separation at the semiconductor [26]. However, such improvements were not observed over the 10%Ru/TiO₂ catalyst (suggesting that there is an optimum loading of Ti for this promotion). Moreover, the activity improvement cannot be assigned to enhanced absorption of visible light as all catalysts’ absorption of visible light (Figure 5) is comparable.

The addition of TiO₂ changes the reaction selectivity (increasing the proportion of CO in the product mixture) indicating that TiO₂ plays a role in the catalysis. However, it must be noted that TiO₂ itself cannot be photoexcited under these conditions. Given this, the reaction on TiO₂ must involve the transfer of excitons generated on Ru to TiO₂ before they are used in the reaction. Plasmon-induced photocatalysis in TiO₂ has previously only been seen in Au/TiO₂ systems [26].

4. Conclusions

We have shown the preparation of ruthenium metal nanoparticles using a facile one-pot solvothermal method without the use of templates or of structure-directing agents. The materials formed are nanoparticles with a narrow size distribution and relatively high surface areas and are capable of adsorbing and desorbing CO₂ and H₂O. The Ru particles absorb visible light and are active in the promotion of the CO₂+H₂O reaction under this light via a plasmonic excited state. Incorporation of Ti-containing precursors into the preparation mixture (forming anatase TiO₂ in the final materials) changes the light absorption properties, the photocatalytic activity, and CH₃/O selectivity of the
catalysts. The effects of TiO₂ appear to be derived from the transfer of plasmon-induced excitons in the Ru to the TiO₂ material.

Data Availability

The data used to support the findings of this study are available from the corresponding authors upon request.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Acknowledgments

EM is funded by Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (CAPES) through the “Science without Borders (SwB) scheme” supported by the Ministry of Education, Brazil. The publication cost of this paper is provided jointly by the University College Dublin (UCD) Output-Based Research Support Scheme (OBRSS) and UCD College of Engineering & Architecture internal fund.

Supplementary Materials

Figure SI 1: UV-visible emission spectrum of the Xe lamp radiation (recorded inside the solar simulator). Figure SI 2: (a, b, c) SEM images of 100%Ru, 10%TiO₂/Ru, and
References


[18] J. Mao, L. Ye, K. Li et al., “Pt-loading reverses the photocatalytic activity order of anatase TiO$_2$ [0 0 1] and [0 1 0] facets for photoreduction of CO$_2$ to CH$_4$,” *Applied Catalysis B: Environmental*, vol. 144, pp. 855–862, 2014.


