The Effect of Methanol on the Photodeposition of Pt Nanoparticles on Tungsten Oxide

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Formation of platinum nanoparticles on tungsten oxide by photodeposition from acidic $[PtCl_6]^{2-}$ solutions in the absence or presence of methanol is studied in detail. Without methanol, $[PtCl_6]^{2-}$-ions adsorbed on the WO_3 surface are converted to highly dispersed $PtO/Pt(OH)_2$ particles upon illumination, the maximum achievable amount being limited to 10–30% of $[PtCl_6]^{2-}$ present in solution. Inclusion of methanol not only promotes adsorption of $[PtCl_6]^{2-}$ ions, but upon illumination results in a deposited Pt quantity close to 100% of $[PtCl_6]^{2-}$. The obtained Pt particles are in the metallic state, large, and often clustered. The limited loading and presence of $PtO/Pt(OH)_2$ in the absence of methanol is explained by reduction of WO_3-surface sites, accompanied by water oxidation catalyzed by $PtO/Pt(OH)_2$ deposits. The extensive reduction of Pt in methanol solutions is likely induced by methoxy-radicals, oxidatively formed by reaction of methanol with photogenerated holes. This study provides guidelines for optimization of synthesis procedures of Pt/WO_3 (photo)catalysts.

1. Introduction

Photocatalysis is a promising technology for water splitting,[1] air purification,[2] and water decontamination.[3] To enhance activity, catalytic nanoparticles are often loaded on light-responsive semiconductor crystals.[1c,4] Techniques to realize this include impregnation,[5] chemical reduction,[6] deposition-precipitation,[5c] physical mixing,[5c] sputtering,[7] and electro-deposition.[8] In 1978, Kraeutler and Bard demonstrated that cocatalytic nanoparticles can also be deposited on semiconductor surfaces using a photodeposition method.[9] Since then, photodeposition has become a very popular technique.[5c,10] In the procedure, photoexcited states (electrons and holes) either reduce or oxidize metal ions in solution to form respectively metallic or metal oxide nanoparticles.[11] For deposition of metal nanoparticles, a sacrificial agent such as methanol,[4a,b,5a,c]

ethanol,[12] isopropanol,[13] or acetate[9,14] is often used, added either initially, or during photodeposition in aqueous conditions.[4b,15] Generally, the presence of a sacrificial agent favors the formation of metallic nanoparticles.

WO_3 has a relatively small bandgap of 2.6 eV, and has been successfully applied in photocatalytic applications, such as water oxidation[16] or water purification.[15a,17] Abe et al. have demonstrated that the addition of Pt to WO_3 can result in a dramatic increase in photocatalytic activity.[4b] Despite the large amount of research describing applications of Pt/WO_3 prepared by photodeposition,[4a,b,15a,c,18] the effect of sacrificial agents on the oxidation state and particle size distribution of as-deposited platinum nanoparticles received relatively little attention.[10c,14,19]

Here, we describe the photodeposition of Pt nanoparticles on WO_3 in detail, focusing on the effect of methanol on the rate of photodeposition, and the obtained dispersion, morphology, and oxidation state of the as-deposited Pt particles, respectively.

2. Results and Discussion

2.1. Kinetics of Photodeposition

Figure 1a depicts Pt consumption from a 62 mL H_2PtCl_6 solution (168 mg L^{-1}, pH = 3), containing 12 mL of methanol, 50 mL of water, and 200 mg of WO_3. Before illumination, an equivalent of 0.53 wt% of Pt is removed from solution, likely by adsorption of the anionic platinum complex ($[PtCl_6]^{2-}$) on the WO_3 surface.[20] When illumination is initiated, after a quick, but small rise, the consumed Pt amount is constant, up to about 11 min. Then, a quick increase in Pt consumption is evident. Within 15 min, almost all Pt to the equivalent of 2 wt% is deposited on the surface of WO_3. The kinetics of the photodeposition process can be divided into four intervals, including (I) adsorption of $[PtCl_6]^{2-}$ in darkness, (II) an additional small quantity deposited during the first 11 min of illumination, (III) a sharp increase to almost complete photodeposition within ≈4 min, and (IV) completion of photodeposition in the last 45 min.

Photodeposition phenomena are completely different in the absence of methanol (Figure 1b). First, in darkness, the amount of Pt consumed from solution is lower than when MeOH is

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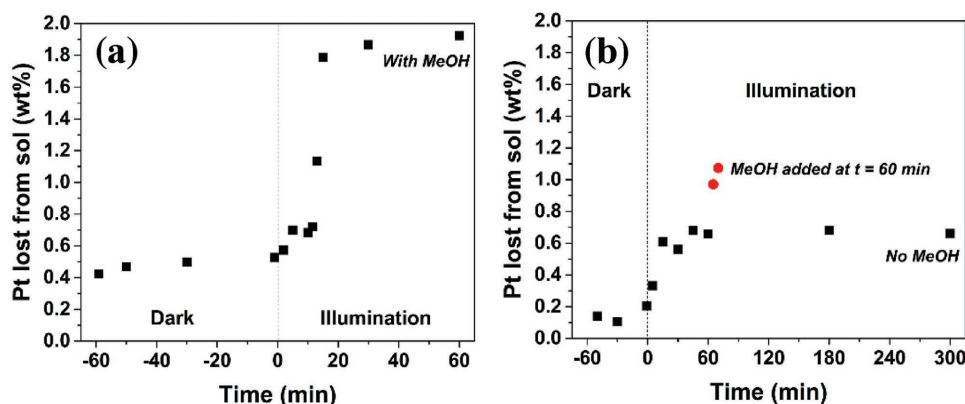www.particle-journal.com

Figure 1. Amounts of Pt lost from the H_2PtCl_6 solution in wt% after a) photodeposition in the presence of methanol and b) photodeposition in the absence of methanol (or MeOH added after 60 min of illumination).

present (the equivalent of 0.20 wt% vs 0.53 wt%). Apparently, MeOH favors the adsorption equilibrium. Upon illumination, the Pt consumption increases to the equivalent of 0.60 wt%, and then stabilizes with little change for 300 min. To validate incomplete Pt consumption, deposition was also evaluated for a larger concentration of H_2PtCl_6 (in solution to the equivalent of 10 wt% of Pt on the WO_3 surface): again Pt deposition was far from complete (≈10% of Pt present in solution), even after 300 min of illumination. Figure 1b also demonstrates that when methanol is introduced to the photodeposition mixture after 60 min of illumination, the rate of Pt deposition increases rapidly, further demonstrating the strong influence of methanol on the photodeposition rate. The last three intervals are summarized in **Table 1**.

2.2. Oxidation State of Pt after Photodeposition

Figure 2 provides an overview of Pt4f X-ray photoelectron spectroscopy (XPS) of Pt/WO_3 obtained after different time intervals of photodeposition, both in the absence or presence of methanol. When methanol was used (Figure 2a), XPS peaks of Pt species formed prior to and just after the start of illumination (5 min), are observed at 72.6 and 76.0 eV, corresponding to the Pt4f doublet of Pt in oxidized states. **Table 2** summarizes the amounts of Pt and Cl^- detected by XPS. Less residual chloride than expected is present, which might be a result of the following reaction [12,19,21]

$$\left[Pt(OH)_n Cl_{6-n}\right]^{2-} + OH^-$$
$$\leftrightarrow \left[Pt(OH)_{n+1} Cl_{5-n}\right]^{2-} + Cl^- \quad (n = 0..5) \quad (1)$$
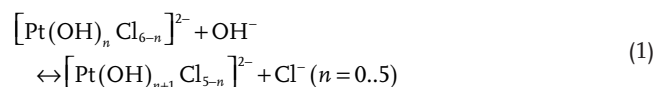
The Pt4f peaks shift to 71.5 and 74.7 eV after illumination for 15 min, demonstrating formation of metallic Pt^0.[19,21] The additional signal apparent in the XPS spectra at around 79 eV is assigned to W5s, corresponding to W^{VI}, which remains at constant position before and after illumination.

Figure 2b shows that in the absence of methanol, after adsorption the Pt4f doublet is found at 72.7 and 75.9 eV, again corresponding to oxidized Pt species. However, extensive periods of illumination do not result in reduction of these Pt species, and likely particles remain present as $Pt(OH)_2$ or PtO. Remarkably, the W5s signal now shifts to lower energies, which suggests some reduction of W^{VI} to W^V has occurred, which will be discussed later.

(Semi-)quantification of the XPS spectra suggests that the amount of Pt on the surface is relatively low when MeOH was used during the photodeposition procedure, contrary to the inductively coupled plasma (ICP)-based results shown in Figure 1. We will demonstrate on the basis of TEM analysis that the Pt dispersion obtained in the absence of methanol is much larger than in methanol-assisted Pt deposition, Pt in the presence of methanol being deposited as large clusters on the surface of WO_3. Large clusters significantly lower relative XPS intensities of Pt as compared to the "support" WO_3, and particle dispersion largely affects quantification by XPS.

For the Pt/WO_3 sample, which was obtained (in the absence of methanol) from a solution containing Pt to the equivalent to 10 wt%, XPS analysis (shown in **Figure 3**, spectrum (a)) reveals that Pt is again exclusively present in oxidized states ($Pt(OH)_2$ or PtO), while again the W5s signal has shifted to lower energies than 79 eV, implying (fractional) surface reduction to W^V.

To corroborate the assignment of the XPS spectra, and to determine the reducibility of the oxidized Pt species, hydrogen treatment of samples containing oxidized Pt species was performed. Of the XPS spectra shown in Figure 3, spectrum (b) clearly demonstrates PtO/$Pt(OH)_2$ is reduced by hydrogen treatment at 500 °C, evidenced by the presence of peaks at 74.7 and 71.4 eV. Remarkably, the W5s signal can now be found at

Table 1. Definition of intervals during photodeposition using MeOH.

Interval	Start [min]	wt%	Stop [min]	wt%	Δwt%	Δwt% min⁻¹
1	−1	0.53	11.5	0.72	0.19	0.017[a]
2	11.5	0.72	15	1.79	1.07	0.31
3	15	1.79	60	1.92	0.13	0.0029

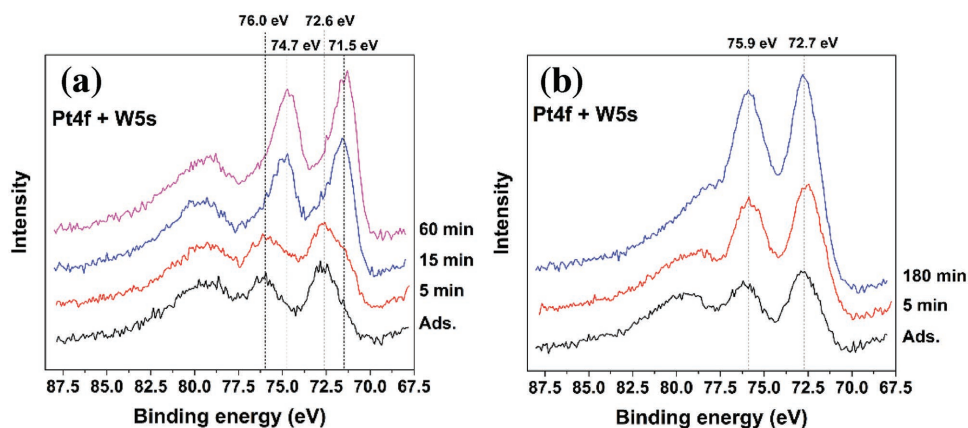[a]Over 11.5 min. It is assumed that at 0 min the same amount of wt% was present as at −1 min.

Figure 2. XPS spectra recorded of various samples obtained at different photodeposition times a) with usage of methanol and b) without usage of methanol. Spectra were recorded in the Pt4f + W5s region. Measurements labeled as "Ads.," which is an abbreviation for adsorption, are measurements on samples recovered 1 min prior to photodeposition. The peaks around 79 eV correspond to the W5s singlet.

79 eV, apparently shifted to higher energies. A similar shift to higher binding energies (of W4f peaks) was also observed by Liu et al., and assigned to the formation of a H_xWO_3 phase.[22]

2.3. Additional Photodeposition Experiments

To further study the redox chemistry of oxidized and metallic Pt particles, as well as of the surface of the applied WO_3, we performed photodeposition of Pt on the hydrogenated Pt/WO_3 sample, both in the presence and absence of methanol, and evaluated the oxidation states by XPS. The XPS spectra and the corresponding percentages of Pt and Cl on the surface are shown in **Figure 4** and **Table 3**, respectively. When additional photodeposition is performed in the presence of MeOH, as expected additional Pt is deposited in the Pt^0 state, and the W5s peak position does not significantly change. However, when additional photodeposition is performed in the absence of methanol, a complex XPS spectrum is obtained, containing significant features at 75.7 and 72.5 eV, suggesting that additional Pt species are predominantly present in oxidized form, and excluding extensive progressive growth of existing Pt nanoparticles. The W5s signal is of apparent lower intensity after reaction, and appears shifted to lower energies (compare spectra (a) and (c)), now likely signaling conversion of H_xWO_3 to $WO_{(3-x)}$.

Table 2. XPS studies of different as-obtained Pt/WO_3 samples, demonstrating the at% of Pt and Cl present on the surface.

MeOH/No MeOH	Reaction time [min]	At% Pt	At% Cl
MeOH	Ads.	0.80	0.14
	5	1.09	0.23
	15	1.30	0.00
	60	1.57	0.10
No MeOH	Ads.	0.94	0.16
	5	1.41	0.36
	180	2.26	0.61

2.4. Illumination of Pt/WO₃ in Water without Dissolved H₂PtCl₆

To investigate the photochemical stability of WO_3 containing oxidized or metallic Pt nanoparticles, we performed additional illumination in H_2SO_4 (pH 2) and in situ monitored the amount of oxygen formed. The trends are depicted in **Figure 5**. For WO_3 containing PtO/Pt(OH)$_2$, initially O_2 is formed showing an exponential decay in rate, while H_2 was not formed, which is expected, as the conduction band edge of WO_3 is less negative than the reduction potential of H^+. On the contrary, neither O_2 nor H_2 was formed upon illumination of Pt/WO_3, suggesting stability of the metallic Pt^0 particles. XPS spectra of the PtO/Pt(OH)$_2$ containing WO_3 before and after reaction are shown in **Figure 6**. The shoulder induced by W^V in the W5s peak has significantly reduced in intensity, and shifted to higher binding
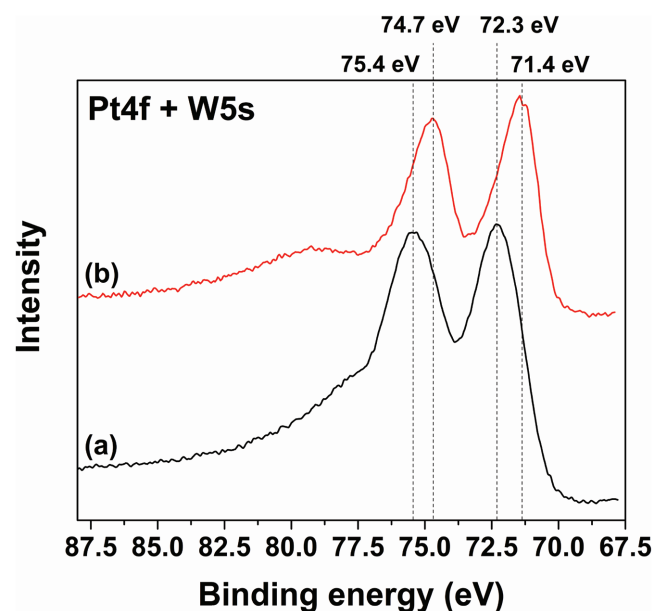

Figure 3. XPS spectra of Pt/WO_3 obtained through 5 h of photodeposition without MeOH and a solution amount equivalent to 10 wt% Pt; a) before and b) after hydrogenation.
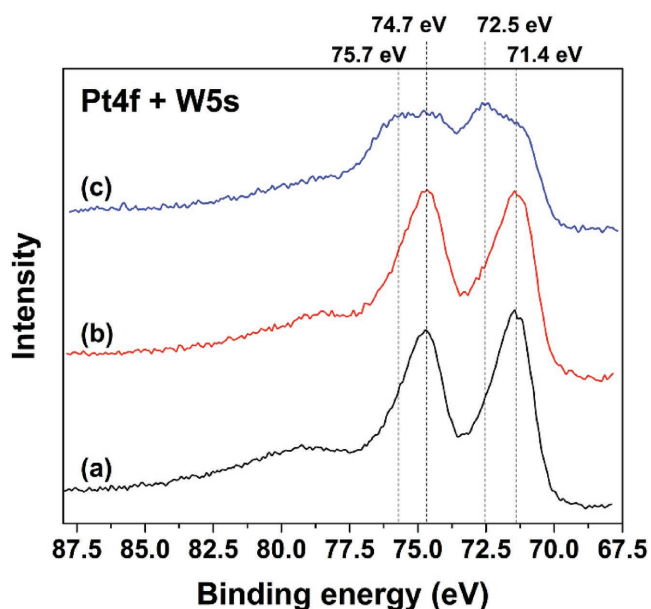
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Figure 4. XPS spectra of hydrogenated Pt/WO$_3$ a) before, b) after an additional photodeposition experiment in the presence of methanol and c) after an additional photodeposition experiment in the absence of methanol.

Table 3. XPS studies of hydrogenated Pt/WO$_3$ samples, demonstrating the at% of Pt and Cl present on the surface.

Sample	At% Pt	At% Cl
Before additional photodeposition	1.75	N.A.[a]
After additional photodeposition with MeOH	2.29	0.14
After additional photodeposition without MeOH	1.86	0.12

[a]N.A. = Not available.

energy, suggesting increasing surface reduction of WO$_3$, possibly to H$_x$WO$_3$. Although the Pt4f signature also appears to have shifted to higher binding energy, we believe this is mainly due to the lower intensity of the W5s peak. Likely the oxidation state of Pt^{II} hardly changes. The similarity in XPS spectra of the hydrogenated Pt/WO$_3$ sample before and after treatment in illuminated acidified water suggests that metallic Pt^0 particles have not oxidized.

2.5. HR-TEM Studies

Figure 7 displays high-resolution transmission electron microscopy (HR-TEM) images of (a) Pt/WO$_3$ obtained after 60 min of photodeposition (aim: 2 wt% Pt) using methanol as a hole scavenger, (b) Pt/WO$_3$ obtained after 300 min of photodeposition without MeOH (aim: 2 wt% Pt), and (c) Pt/WO$_3$ obtained after 300 min of photodeposition without MeOH (aim: 10 wt% Pt). Energy-dispersive X-ray spectroscopy (EDX) studies confirm that in all cases platinum is present on the surface. When photodeposition is performed in the presence of methanol (compare Figure 1), large clusters of metallic Pt nanoparticles (particles of 2–4 nm ranging up to clusters of even 55 nm) are deposited on the WO$_3$ particles. In the absence of MeOH, photodeposition results in very disperse, small platinum (oxide) particles (in the order of roughly 1–3 nm). A higher concentration of platinum in solution does not result in an obvious change in size (Figure 7c): only an apparent higher loading of particles is observed.

After hydrogen treatment of highly dispersed PtO/Pt(OH)$_2$ species at 500 °C, HR-TEM images reveal that the Pt particles have increased in size, ranging from roughly 3 to 11 nm (**Figure 8**a). It should be noted that also the morphology of

the surface of WO$_3$ is altered by the H$_2$ treatment, containing an amorphous surface layer, likely related to surface reduced WO$_3$ and/or the H$_x$WO$_3$ phase. The TEM images obtained after additional illumination of the sample in Pt-precursor solution without methanol, show additional photodeposition leads to platinum forming domains of small particles (1–4 nm) (Figure 8b). The presence of these small (oxidized) Pt particles is in agreement with the higher XPS intensities obtained for this sample. When methanol is present during the additional photodeposition, more Pt particles are observed at the surface of the WO$_3$ (Figure 8c), comparable in sizes to those present after hydrogen treatment. This is also in agreement with the XPS results in Table 3. In summary, the presence of H$_2$-reduced Pt particles on (H$_x$)WO$_3$ has very little effect on the Pt morphologies obtained by photodeposition in the presence, as well as in the absence of methanol.

2.6. Discussion on the Photodeposition Mechanism of Pt on WO$_3$

In the following, we will explain the observed phenomena (liquid concentration profiles, XPS spectra, and TEM images) on the basis of two main assumptions/observations: i) the surface of the applied WO$_3$ is susceptible toward reduction upon
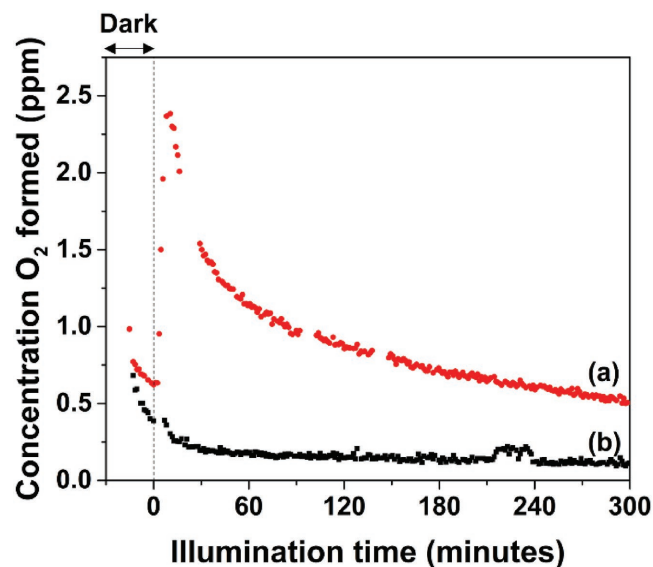

Figure 5. O$_2$ evolution during additional illumination of Pt/WO$_3$ (obtained without 5 h illumination, no MeOH and an aim of 10 wt% Pt) in H$_2$SO$_4$; a) without hydrogenation and b) with hydrogenation at 500 °C.
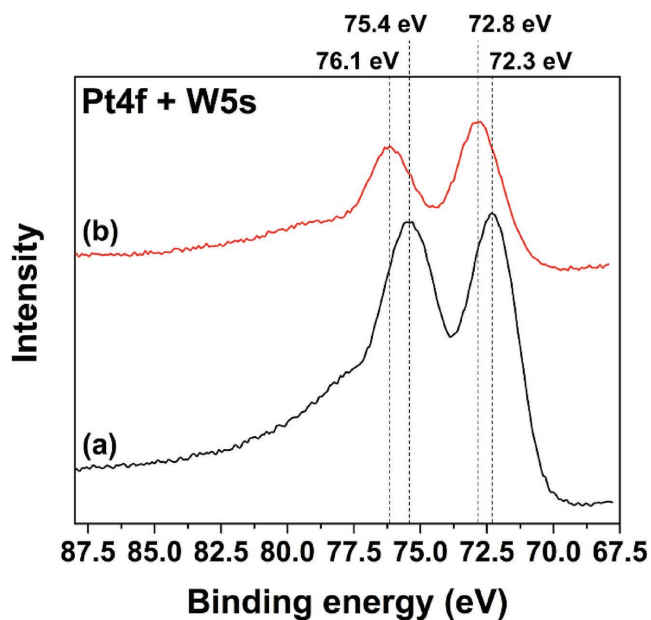
Figure 6. XPS spectra of Pt/WO$_3$ obtained through 5 h of photodeposition without MeOH and an aim of 10 wt% Pt; a) before and b) after additional illumination in H$_2$SO$_4$.
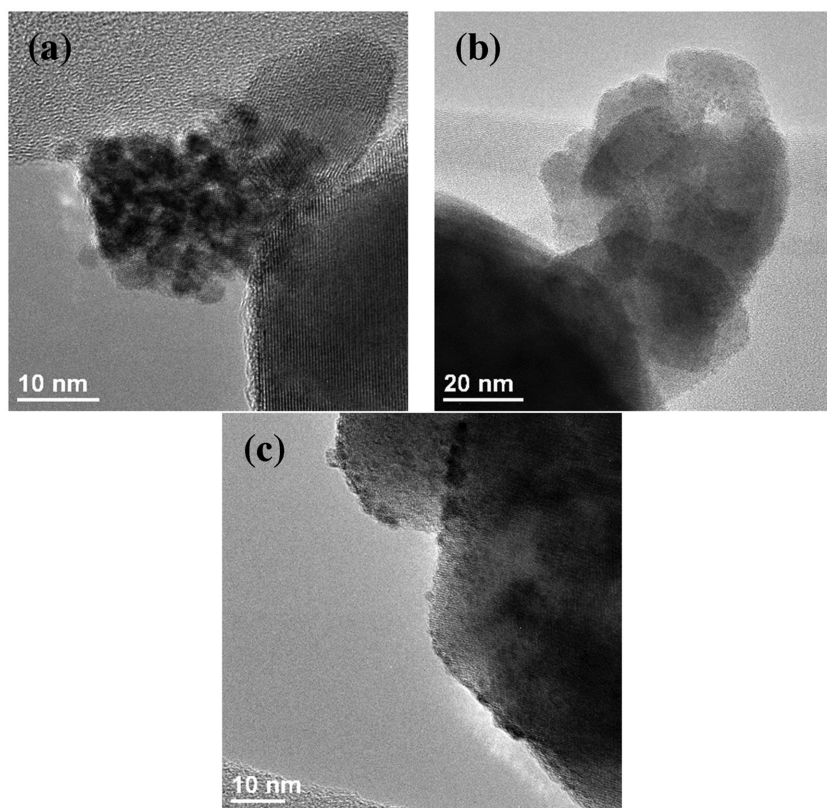

Figure 7. HR-TEM images of Pt/WO$_3$ obtained through a) 1 h of photodeposition using MeOH (aim: 2 wt% Pt), b) 5 h of photodeposition using no MeOH (aim: 2 wt% Pt), and c) 5 h of photodeposition using no MeOH (aim: 10 wt% Pt).

illumination in the absence of methanol, including the formation of H$_x$WO$_3$ during treatment of PtO$_x$/WO$_3$ in illuminated, acidified water, and ii) reduction of Pt^{II}O/Pt^{II}(OH)$_2$ is induced by methoxy-radicals created by hole-induced oxidation of methanol. The observations are illustrated in **Figure 9**, in the absence (left) and presence of methanol (right).

2.6.1. Absence of Methanol

The first step in the functionalization of the surface is the adsorption of the Pt precursor on the surface of WO$_3$. This is likely to occur without significant reduction. Upon illumination, these adsorbed species are reduced to form Pt^{II}O/Pt^{II}(OH)$_2$, according to reactions (2) and (3)

$$WO_3 \xrightarrow{h\nu} WO_3\left(e^- + h^+\right) \tag{2}$$

$$Pt^{IV}(s,l) + 2H_2O + 2e^- \rightarrow Pt^{II}(OH)_2(s) + 2H^+ \tag{3}$$

For a corresponding oxidation reaction complementing reaction (3), several possibilities arise, which involve the re-oxidation of Pt^{II}(OH)$_2$, or water oxidation

$$Pt^{II}(OH)_2(s) + 2H^+ + 2h^+ \rightarrow Pt^{IV}(s,l) + 2H_2O \tag{4}$$

$$2H_2O + 4h^+ \rightarrow O_2 + 4H^+ \tag{5}$$
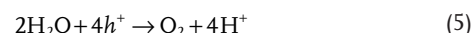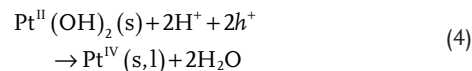
We propose reaction (5) is most likely, assuming that this reaction is catalyzed by PtO/Pt(OH)$_2$. This is in agreement with the extensive oxygen evolution observed in Figure 5. Interestingly, even in the absence of Pt^{IV} in solution, hydrogen evolution or significant reduction of the PtO/Pt(OH)$_2$ species did not accompany oxygen evolution, as evidenced from the XPS analysis of samples illuminated in the absence of methanol.

We therefore assume the following reduction reactions of the WO$_3$ surface to occur

$$WO_3 + 2xH^+ + 2xe^- \rightarrow xH_2O + WO_{3-x} \tag{6}$$

$$WO_3 + H^+ + e^- \rightarrow HWO_3 \tag{7}$$
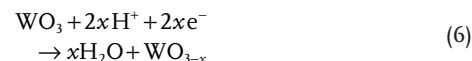
These surface reduction reactions are corroborated by the apparent shifts in the W5s signal in all XPS spectra of illuminated WO$_3$ in the absence of methanol. We therefore also propose reactions (6) and (7) to compete with reduction of the adsorbed PtO/Pt(OH)$_2$ to Pt^0
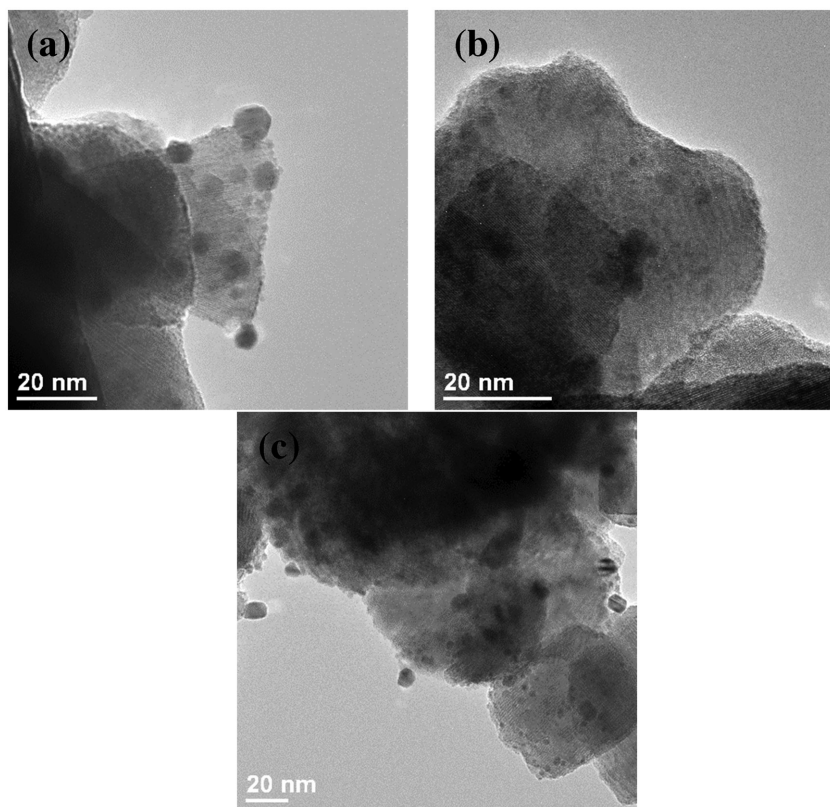
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Figure 8. HR-TEM images of a) hydrogen treated Pt/WO$_3$. The Pt/WO$_3$ was obtained using 5 h of photodeposition in the absence of MeOH with a Pt quantity in solution equivalent to 10 wt% Pt. b) Sample A after 5 h of additional photodeposition in the absence of MeOH with a Pt quantity in solution equivalent to 2 wt% Pt. c) Sample A after 1 h of additional photodeposition using MeOH with a Pt quantity in solution equivalent to 2 wt% Pt.

(explaining lack of Pt^0 formation), and reaction (3), explaining the limited Pt quantity after photodeposition.

2.6.2. Role of Methanol

Clearly methanol changes the surface properties of WO$_3$, enhancing the quantity of adsorbed Pt^{IV} precursor. Upon

illumination, an initiation period of ≈11 min is observed, before extensive photodeposition occurs (Figure 1). We believe, initially, oxidation of methanol complements reductive Pt deposition (reaction 3), according to reaction (8)

$$CH_3OH + h^+ \rightarrow CH_2OH \cdot + H^+ \tag{8}$$
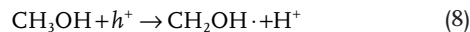
Once sufficient quantities of methoxy-radicals are formed, Pt^{IV} and Pt^{II}(OH)$_2$ can now be further reduced to metallic Pt^0 by reactions (9) and (10), as advocated by Lee and Choi,[10c] and evidenced by the XPS analysis shown in Figure 2a

$$2CH_2OH \cdot + Pt^{IV}(aq) + 2H_2O \\ \rightarrow Pt^{II}(OH)_2(s) + 2CH_2O + 4H^+ \tag{9}$$

$$2CH_2OH \cdot + Pt^{II}(OH)_2(s) \\ \rightarrow Pt^0(s) + 2CH_2O + 2H_2O \tag{10}$$

Methoxy radicals are indeed very strong reducing agents. We propose reactions (9) and (10) might be catalyzed by Pt^0 particles in statu nascendi, explaining the very high rate of photodeposition (Figure 1a) and cluster formation (Figure 7a). We also believe the catalytic properties of Pt^0, and favorable transfer of photoexcited electrons from WO$_3$ to Pt, prevent surface reduction reactions of WO$_3$, as evidenced by the absence of shifts in the W5s XPS spectra recorded for samples containing Pt^0.

Future studies in our laboratory focus on the analysis of products formed from sacrificial agents during photodeposition (formaldehyde, CO, and CO$_2$ by conversion of methanol), using on-line mass spectrometry (MS), to obtain conclusive evidence for the occurrence of Equations (9) and (10).

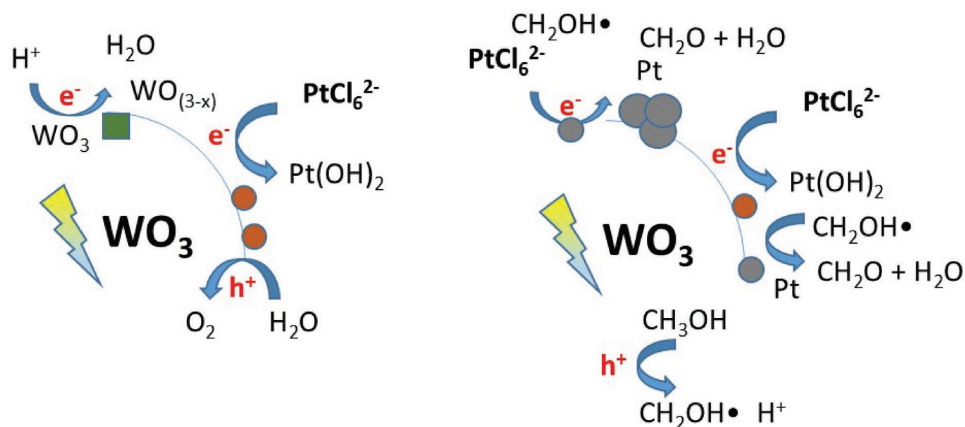Furthermore, we plan to apply the as-prepared catalysts in photocatalytic applications such as water and air purification,
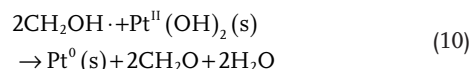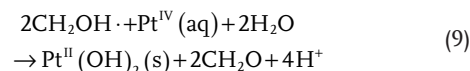

Figure 9. Processes occurring on the surface of photoexcited WO$_3$ when illuminated in the absence (left) or presence of methanol (right).

to compare the performance of $PtO/Pt(OH)_2-$ modified, to Pt-modified WO_3.

3. Conclusions

In this manuscript, we demonstrate methanol has a large impact on the kinetics of photodeposition of Pt on WO_3 from H_2PtCl_6 solutions, as well as on the obtained morphology and oxidation state of the obtained particles. In the absence of methanol, deposition of Pt is limited to 10–30% of the theoretical amount present in solution, while particles are small and predominantly oxidized (likely $Pt^{II}O$ or $Pt^{II}(OH)_2$ is formed). We propose photoreduction to metallic platinum is incomplete as a result of competing reduction of the W^{VI}-oxide surface to W^V-oxide and/or H_xWO_3.

In the presence of methanol, after an initial phase, photodeposition of Pt is fast and complete, and yields predominantly metallic nanoparticles, which are clustered. The extensive reduction of Pt in methanol solutions is likely induced by i) methoxy-radicals, oxidatively formed by reaction of methanol with holes, and ii) catalyzed by Pt^0 once a certain concentration of these particles has been obtained.

4. Experimental Section

Photodeposition: In a typical photodeposition experiment, a 50 mL aqueous solution containing 168 mg L^{-1} H_2PtCl_6 (the equivalent of 2 wt% Pt, pH = 3), 12 mL of MeOH, and 200 mg of WO_3 was prepared inside a quartz container. This container was covered by a quartz plate to prevent evaporation of the solution. Then, it was placed inside a black box reactor as described by Romão et al.[23] Aluminum foil was used to cover the sides of the beaker glass to make sure that the solution was only top-illuminated. First, the suspension was stirred at 450 rpm to obtain adsorption/desorption equilibrium. Afterward, all lamps were switched on inside the box, and reaction took place for t min, where t = 2, 5, 10, 11.5, 13, 15, 30, or 60 min. Solid and solution were subsequently separated by centrifugation for 30 min at 8500 rpm. The supernatant solution was stored, whereas the precipitate was washed two times with Millipore water and afterward dried overnight at 80 °C. To verify whether Pt adsorbs very strongly on the WO_3 surface, we repeated these experiments in the dark using different stirring times. These were labelled as t = −59, −50, −30, and −1 min, which corresponded to 1, 10, 30, and 59 min of stirring the suspension in darkness.

When methanol was not used as a sacrificial agent, a 50 mL aqueous solution containing 168 mg L^{-1} H_2PtCl_6 and 200 mg WO_3 was prepared. Photodeposition took place as described above, but with different time intervals: t = −50, −30, −1, 5, 15, 30, 45, 60, 180, or 300 min (the negative values corresponding with t + 60 min stirring time in the dark). Again, centrifugation as described above was used to separate powder and solution and to wash the precipitate.

Furthermore, photodeposition experiments in the absence of methanol were performed for 1 h after which 12 mL of methanol were added to the suspension. Then t = 5 or 10 min of additional illumination took place after which powder and solution were separated by using a centrifuge.

In a variation of the photodeposition experiment without MeOH described above, illumination took place for 300 min with a 50 mL aqueous solution containing 840 mg L^{-1} H_2PtCl_6 and 200 mg WO_3, corresponding to ≈10 wt% Pt (compared to WO_3). The obtained powder was hydrogenated in a tube-furnace for 14 h at 500 °C (heating rate of 10 K min^{-1}) under a gas flow of 4.76 vol% H_2 in nitrogen. The hydrogenated powder was exposed to additional photodeposition in two different experiments. In the first case, a 50 mL aqueous solution

containing 8.4 mg L^{-1} H_2PtCl_6, 0.6 mL of methanol, and 10 mg of H_2 treated Pt/WO_3 was inserted in a quartz beaker glass covered by a quartz plate on top and aluminum foil on the sides. Photodeposition took place for 1 h in the box reactor as described above. In a variation of this experiment a 50 mL aqueous solution containing 21 mg L^{-1} H_2PtCl_6 and 25 mg of H_2 treated Pt/WO_3 was prepared and illuminated for 5 h in the box reactor as described above.

Additional Illumination Studies: Additional illumination of both the untreated and the H_2 treated Pt/WO_3 took place in a reactor as described by Zoontjes.[24] 25 mL of aqueous solution containing 25 mg of Pt/WO_3 or H_2 treated Pt/WO_3 and 0.01 M H_2SO_4 (corresponding to a pH of 2) was illuminated for a minimum period of 5 h. Prior to light exposure, purging of the reactor took place with helium to remove most of the oxygen and nitrogen inside the solution. The amounts of oxygen formed during illumination were monitored on a micro-gaschromatograph, using a very sensitive Pulsed Discharge Detector.[25]

Characterization: To determine how much Pt had been deposited on the various samples, the supernatant solutions after centrifugation were analyzed using inductively coupled plasma atomic emission spectroscopy (ICP-AES) (Varian Liberty II, Sequential ICP-AES). In the case of the samples where methanol was used, the supernatant solutions were diluted with water, lowering the concentration of Pt in solution by a factor of 6, before being measured by ICP-AES. Further characterization of some of the as-obtained powders took place using XPS (Quantera SXM from Physical Electronics) to determine the oxidation state of Pt, and HR-TEM (FEI Instruments) to study the dispersion and morphology of as-deposited Pt.

Conflict of Interest

The authors declare no conflict of interest.

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