



Self-assembled monolayers enhance the efficiency of Pt single atom co-catalysts in photocatalytic H₂ generation

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ABSTRACT

Single atom (SA) catalysis, over the last 10 years, has become a forefront in heterogeneous catalysis, electrocatalysis, and most recently also in photocatalysis. Pt SAs on titania have been reported to be a highly effective co-catalyst in photocatalytic H₂ generation. Most recently, for the synthesis of SA loading on titania surfaces, some simple immersion techniques have been described. Here we introduce a so far unexplored but evidently very effective approach to enhance the effectivity of Pt SA co-catalysts on anodic TiO₂ layers. For this, we first decorate TiO₂ surfaces with a partial coverage of headgroups of silane self-assembled monolayers (SAMs) and then deposit Pt SAs on this SAM modified surface. We observe a significantly enhanced photocatalytic activity for H₂ generation using this sensitization of the surface with a modified SAM.

1. Introduction

Single atom (SA) catalysis, over the recent years, has become a highly investigated topic in heterogeneous catalysis [1–6], and supported single atom catalysts have been explored for a wide range of “classic” heterogeneous catalysis reactions of high economic relevance, such as CO oxidation [2,3,7–9], oxidation of alcohols, aldehydes, methane or benzene [10–14], for various hydrogenation reactions [13,15,16], or for water–gas-shift and reforming reactions [6,17–19].

Also in electrocatalysis, the high significance of SA catalysts has increasingly become clear [20,21], including findings that point out entirely novel reaction pathways that become possible using SAs [22]. More recently also in photocatalysis SAs gained increasing attention – this particularly in view of using noble metal SAs as co-catalyst for some key reactions.

In general, in photocatalytic reactions mobile charge carriers are generated in a semiconductor and after migration to the surface react with a red-ox species in the environment. This type of charge transfer reactions are often rate determining and noble metals are very widely used as co-catalysts, to promote the kinetics of such reaction steps. A prime example is photocatalytic H₂ generation, where the hydrogen evolution reaction (HER) needs to be catalyzed – typically by Pt – to

reach reasonable efficiencies [23,24].

For the benchmark photocatalyst, TiO₂, the decoration with a noble metal co-catalyst, namely Pt, has been widely investigated [25–29]. In virtually all classic attempts that use TiO₂ for photocatalytic H₂ generation, Pt nanoparticles are decorated onto the titania substrate. However, in 2013, in a pioneering paper Yang et al. showed that Pt in the form of single atoms can be decorated on anatase powders using impregnation/annealing techniques [30]. More recently we showed that SAs can be attached on TiO₂ surfaces by trapping at substrate defects that are either naturally present or that can be introduced by defect engineering [25,29,31]. Such a decoration may be able to achieve a remarkable photocatalytic H₂ evolution using only minimum amounts of Pt [32].

Here we explore the influence of the presence of a self-assembled monolayer on the titania surface for Pt SA attachment and reactivity. For this we use an approach that is based on the self-assembly of a silane monolayer (SAM) followed by photoinduced chain scission as previously reported in literature [33]. We show that this modified SAM surface after decoration with Pt SAs shows a strongly enhanced photocatalytic activity compared with non-SAM engineered SA-decorated surfaces.

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2. Experimental

2.1. Materials and preparation

First anodic TiO₂ layers were formed on titanium foils (99.6% pure, 0.125 mm thick, ADVENT) cut into 1.5 × 1.5 cm² pieces as substrates. The foils were cleaned by ultrasonication in acetone, ethanol and deionized (DI) water for 15 min, and then dried with N₂ stream.

The foils were then anodized at 20 V for 30 min in a 1 M sulfuric acid aqueous solution. This leads to an approx. 50 nm thick oxide layer [34]. After anodization, the foils were washed with water and dried in a N₂ stream. Then the anodic layers were annealed in air at 450 °C for 1 h with heating and cooling rates of 0.5 °C/min using rapid thermal annealer (RTA, Jipelec Jetfirst 100) to convert the layers to anatase [35]. After that, the samples were exposed to an LED with a wavelength of 365 nm for 1 h for surface cleaning.

To attach the SAMs, samples were immersed in 10 mL of toluene solution containing 5 mM octadecylsilane (C₁₈H₃₇SiH₃) for 48 h at room temperature in the dark. After immersion, the samples were washed with toluene, acetone and deionized water respectively, then dried at 70 °C overnight in an oven.

To photocatalytically cut off the hydrocarbon chains from the SAMs, UV light experiments were performed using a 200 mW He–Cd laser (Kimmon, Japan) with a wavelength of 325 nm for 30 min, as described in our previous work [33].

For single atom deposition, samples were immersed in 10 mL MeOH (50 vol%) solution containing 2 mM H₂PtCl₆ (Metakem) solution in a quartz cell for 24 h in dark. Prior to sealing, the solution was purged with Ar for 20 min to remove remaining oxygen from the solution. After keeping in dark for 24 h, the TiO₂ layers were then soaked in EtOH and DI water for 15 min each. Subsequently, the samples were dried in a N₂ stream and further investigated using various characterization tools.

2.2. Characterization

High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) was carried out by a high-resolution transmission electron microscope (HRTEM, FEI Titan G2 60–300). The morphology of the samples was investigated by field-emission scanning electron microscope (FESEM, S-4800, Hitachi, Japan). Chemical composition of the samples and oxidation states of the SAs was studied by X-ray photoelectron spectroscopy (XPS, PHI 5600) and all XPS spectra were calibrated with the Ti2p peak to 458.5 eV. Peak deconvolution was carried out by MultiPak software.

In order to evaluate the photocatalytic H₂ generation performance, the different samples were irradiated with a 365 nm LED (power intensity: 65 mW cm^{−2}) in a 10 mL 50 vol% MeOH solution in a sealed quartz reactor. Evolved H₂ was determined by a gas chromatograph (GCMS-QO2010SE, SHIMADZU) with a thermal conductivity detector (TCD). Water contact angle measurements were performed under equilibrium conditions. Optical images were acquired by a CCD camera interfaced to a computer.

3. Results and discussion

In order to verify SA deposition by the treatment described in the experimental section, using our simple immersion (“dark deposition”) technique [31], we acquired HAADF-TEM on thin film titania layers – as described in our previous work [25]. Fig. 1a shows a HAADF-TEM image taken from such an anatase TiO₂ thin layer on a TEM grid (inset of Fig. 1a). In this case, the anatase TiO₂ layer was exposed to a 2 mM H₂PtCl₆ solution for 24 h. After rinsing and drying, the thin anatase layer is decorated with single atoms of Pt at a density of 2.38 × 10⁵/μm², determined by direct counting individual Pt atoms within a defined area in the HAADF-TEM image.

As expected, in the high-resolution SEM images of this layer

(Fig. 1b), no distinct particles can be seen (this is of course expected, as for uniform SA deposition, non-aggregated SAs are below the resolution of a high-resolution SEM). An additional feature of such a single atom deposited surface is apparent in XPS. It should be noted that for the deconvolution of Pt4f XPS spectra, notably in low loading cases, one has to consider the contribution of the Ti3s satellite peak [36]. The XPS spectrum of the Pt4f region (Fig. 1c) shows a clear Pt peak at a position of 72.3 eV. This is typical for SA Pt coordinated to an oxide surface [25] – the peak position corresponds to a formal charge (δ⁺) on Pt of δ⁺ ≈ 2. This charge stems from SAs that are co-coordinated with the TiO₂ surface (rather than Pt in a Pt⁰ nanoparticle).

If this is compared to SEM and XPS of a surface decorated by classic photodeposition [37] (Fig. 1d, e), clear differences are evident. Using photodeposition leads to nanoparticles of a size of ≈ 2 nm and these Pt nanoparticles show an XPS Pt peak at 70.5 eV which corresponds to metallic Pt⁰ (well in line with literature [38]). Please note that the surface loading of Pt for the SA case (0.37 at%) and the particle case (0.35 at%) are in the same range. Therefore, the combination of SEM (no identifiable particles) with XPS (characteristic peak position) can be used to indirectly gain evidence for the presence of SAs on titania surfaces that are non-TEM transparent.

Fig. 1f and g show SEM and XPS for an anodic TiO₂ layer prepared as described in the experimental section after annealing to anatase and after the layer was exposed to the same “dark deposition” treatment from a 2 mM H₂PtCl₆ solution. In analogy to the anatase surface on the TEM grid, no distinct Pt nanoparticle decoration can be detected by SEM but again an XPS Pt signal at 72.3 eV (Pt δ⁺) is clearly evident. This is therefore indicative of the loading of the layer with single atom Pt. The surface concentration of Pt from XPS results as 0.40 at%.

In a next step, we modified the anodized and annealed TiO₂ layer with an organic monolayer using silane as described in the experimental section and in literature [33]. This renders the titania surface hydrophobic as evident from the changes in contact angle shown in Fig. 2a. The drawback is that this prevents access of the aqueous Pt precursor solution to the surface. Therefore, we applied a previously reported photocatalytic chain scission treatment to the surface [33]. That is, the monolayer decorated anatase layer was exposed in water to UV light (325 nm). This leads to silane head groups remaining on the titania surface as evident from XPS. Fig. 2b, c, d show XPS spectra for the C1s, Si2p and Ti2p region for the anodic TiO₂ layer after it was modified by silane, then after photocatalytic chain scission and after Pt decoration. After monolayer attachment, a strong C1s signal is apparent due to the hydrocarbon chains of the silane monolayer, as well as a clear Si-signal due to the Si-headgroup attached to the titania. After photocatalytic action, the C1s peak significantly decreases and the Si peak slightly increases in its intensity. At the same time, after monolayer attachment, the Ti peak from TiO₂ becomes weaker, and after cutting more intense. These findings confirm the successful removal of the hydrocarbon chain, while leaving the Si head group on the surface. This is further supported by contact angle measurements using a water droplet placed on the silane decorated TiO₂ layer (Fig. 2a) where clearly after illumination (and cutting the hydrocarbon tails) the surface changes from highly hydrophobic to hydrophilic.

If the hydrophobic surface is exposed to the H₂PtCl₆ precursor solution, one finds no clear deposition of Pt, i.e. the precursor solution seems not to sufficiently reach the TiO₂ surface to successfully anchor SA Pt. In contrast, once the surface has turned hydrophilic, after cutting the hydrocarbon tail, a treatment in 2 mM H₂PtCl₆ solution leads to a Pt XPS signal as shown in Fig. 2f at a position of 72.0 eV. Evidently, Pt is present as SA with a charge δ⁺ ≈ 2 with 0.32 at%. Again, a high-resolution SEM image (Fig. 2e) does not show the deposition of any Pt nanoparticles.

From the differently treated surfaces, we then evaluated the photocatalytic H₂ generation efficiency (Fig. 3). For this we used illumination with an LED of 365 nm and a detection of the evolved H₂ using a GC-TDC setup as described in the experimental section. Clearly, all Pt treated surfaces show a significant enhancement of the photocatalytic H₂

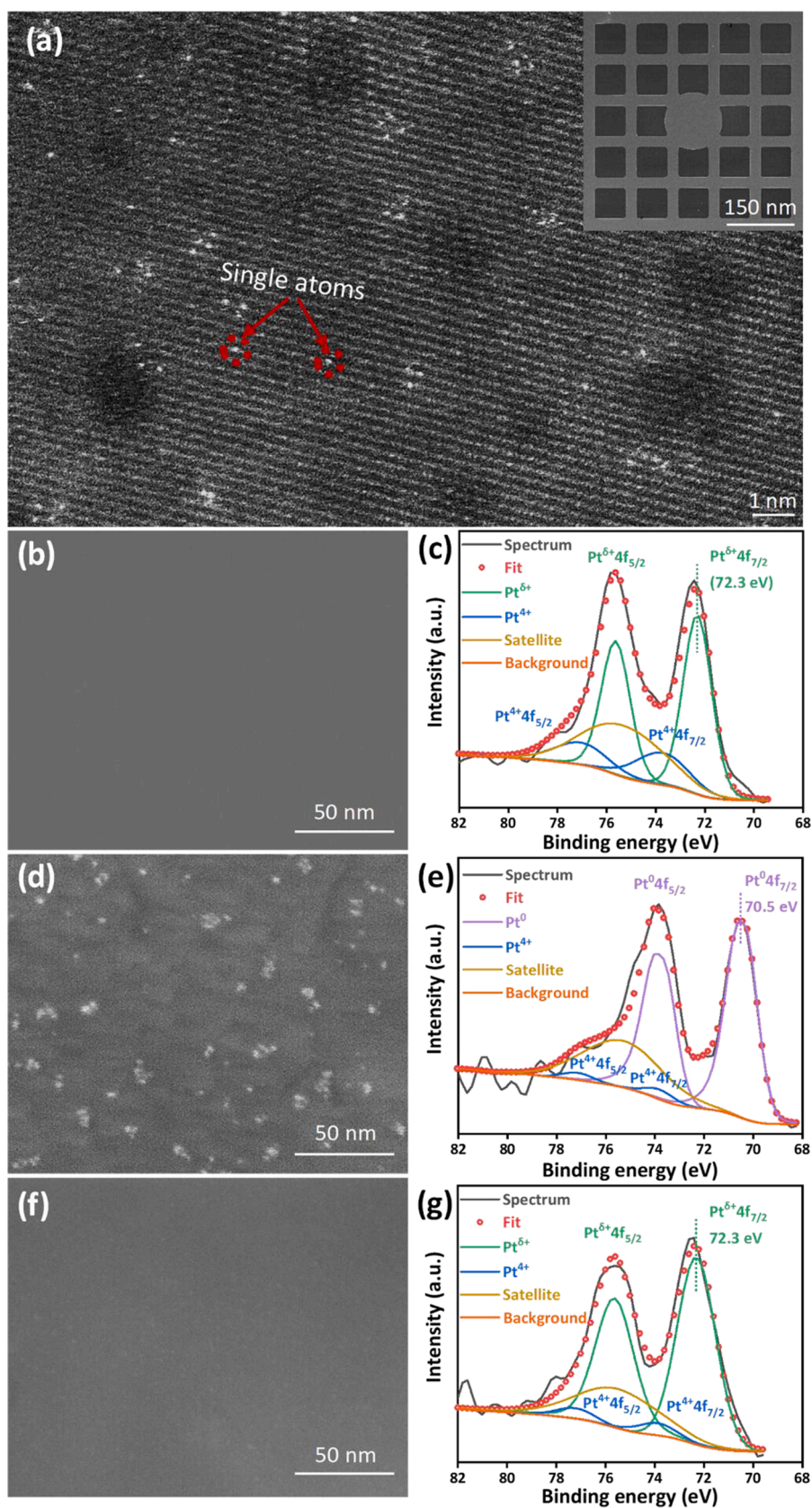


Fig. 1. a) HAADF-TEM image of TiO₂ anatase layer decorated with Pt single atoms. The inset shows top-surface SEM image of the TiO₂ layer deposited on a SiO₂-Si TEM grid. b) SEM image and c) XPS Pt4f spectra of TiO₂ anatase layer decorated with Pt single atoms. d) SEM image and e) XPS Pt4f spectra of TiO₂ anatase layer with photodeposited Pt nanoparticles (as in d). f) SEM image and g) XPS Pt4f spectra of TiO₂ anatase layer with Pt dark deposition.

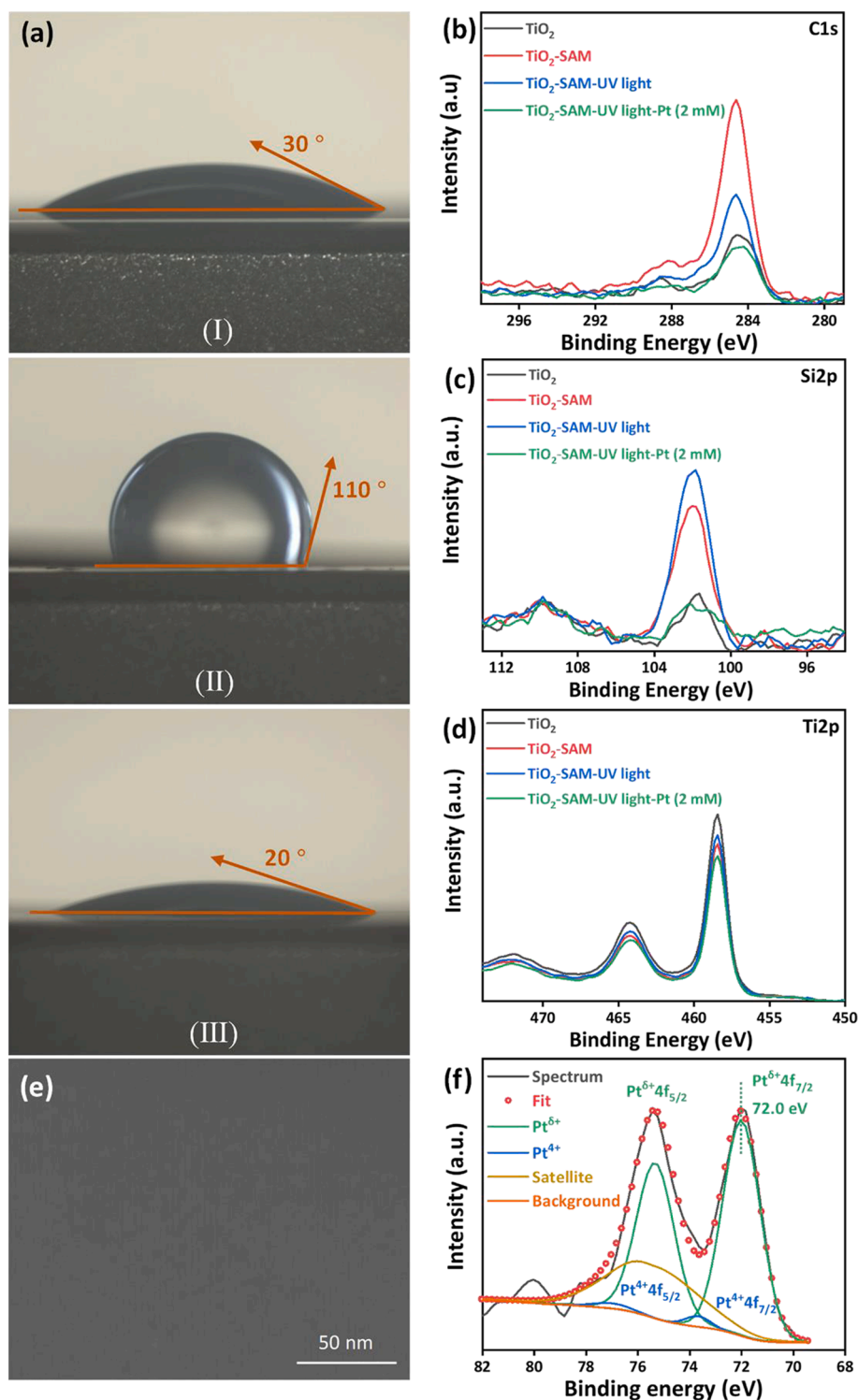


Fig. 2. a) Optical images of contact angle changes (a I) before SAM covered anodic TiO₂ layer, (a II) after of a silane-SAM attachment and (a III) after chain scission respectively. XPS spectra of b) C1s, c) Si2p and d) Ti2p for the whole sequence (the anodic TiO₂ layer was covered with silane-SAM, subjected to photocatalytic chain scission, followed by Pt dark deposition). e) SEM image and f) Pt4f XPS spectra of silane modified TiO₂ surface after UV light treatment and 2 mM Pt dark deposition.

generation compared with the non-decorated anatase surface. From the result in Fig. 3, it is evident that decoration of the titania surface with a hydrophobic monolayer is detrimental for the photocatalytic hydrogen evolution. As the surface is hydrophobic, not only the Pt precursor cannot reach the surface but likely also the reactant (H₂O) is prevented from reaching the surface during photocatalytic H₂ generation. Most important, however, is the finding that a surface decorated with silane

head groups is highly beneficial for Pt co-catalyzed photocatalytic H₂ generation. Compared with the neat anatase surface decorated with SA Pt, the silane modified surface shows a H₂ evolution rate that is more than 3 times higher (11.88 μl/h).

Notably, from XPS the Pt loading of the TiO₂ surface without SAM treatment is similar. It is noteworthy that the surface deposition of Pt SAs to a large extent displaces the Si-remnants on the TiO₂ surface. The

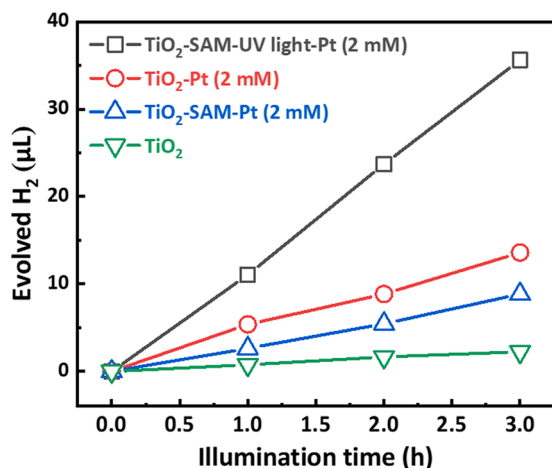


Fig. 3. Photocatalytic H₂ evolution of non-decorated TiO₂ surface and silane modified TiO₂ surface (both with and without UV light treatment).

results therefore show that the use of these silane stumps to mediate the SA deposition leads to a highly beneficial effect on co-catalytic activity in photocatalytic H₂ generation. It should also be mentioned, that electronic interactions with the Si-remnants may further affect the electron transfer reaction and could be additionally beneficial for electron transfer [39].

4. Conclusion

The present work shows that mediation of Pt SA deposition on a TiO₂ surface with a modified SAM can lead to a significantly more active co-catalytic effect of the Pt SA decorated TiO₂ surface than a non-modified Pt SA decorated surface. In fact, we achieve a 3 times higher photocatalytic H₂ production rate from the SAM modified surface for the same Pt loading. We believe that such SAM modification combined with SA decoration provides wide opportunities in the development of the next generation of photocatalysts.

CRediT authorship contribution statement

Yue Wang: Investigation, Visualization, Writing – original draft. **Imgon Hwang:** Investigation, Visualization. **Zhenni Wu:** Investigation, Formal analysis. **Patrik Schmuki:** Writing – review & editing, Methodology, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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