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Effect of TiO$_2$ Film Thickness on the Stability of Au$_9$ Clusters with a CrO$_x$ Layer

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1. Introduction

Titanium dioxide (TiO$_2$) is a semiconductor widely used for a large range of photocatalytic applications and is also an ideal model system for various types of studies [1,2]. There are various techniques to prepare TiO$_2$ films, such as sol-gel [3], evaporation [4], chemical vapour deposition [5], atomic layer deposition [6] and radio frequency (RF) magnetron sputtering [7]. Each of these methods has advantages and disadvantages in regard to fabrication costs, uniformity of the film morphology, thermal stability, purity and preparation time. Therefore, the best method of choice for TiO$_2$ film preparation depends on which application the film will be used in.

Amongst the above-named methods, RF magnetron sputtering is known to produce high-purity TiO$_2$ films with uniform thickness, ease of use and strong film adhesion to the substrate [8]. The properties of these films are significantly impacted by the sputtering
conditions, such as RF power, gas pressure, substrate type, substrate temperature and target-to-substrate distance [9–14]. For instance, it has been reported that control of TiO$_2$ film thickness is possible by modulating the deposition time and the gas sputtering pressure [15].

TiO$_2$ films prepared with the RF magnetron sputtering method can be amorphous or have a rutile, anatase, or brookite crystal structure. It is well known that the physical properties of TiO$_2$ films depend highly on the post-deposition treatment, including heat treatment conditions [16–18]. Çörekçi et al. reported that a correlation between heating treatment and surface morphology with different TiO$_2$ film thicknesses. It was observed that an increase in surface roughness and grain sizes occurred during heating depending on TiO$_2$ film thicknesses, which also increased with film thickness. This is because increasing temperatures transform TiO$_2$ from amorphous to anatase and then to rutile [17], and these phase transitions affect the surface morphology of the TiO$_2$ film, which includes the roughness and crystallinity of the surface [19].

The aim of this study is to investigate the influence of heat treatment on the surface morphology of RF sputter-deposited TiO$_2$ films with two different thicknesses, and the effect this has on size-specific Au clusters deposited on the surface. TiO$_2$ films have attracted interest as substrates for investigating the role of Au clusters as cocatalysts in photocatalysis [20,21]. In these studies, TiO$_2$ films had been heated as part of the sample preparation procedure. The change in morphology, including surface mobility, upon heating, can lead to agglomeration of the Au clusters. Understanding the change in surface morphology upon heating, thus, is important when using TiO$_2$ as a substrate for investigating the cocatalyst properties. In the present work, phosphine-protected Au$_9$ clusters covered by a photodeposited CrO$_x$ layer were used as probes for the TiO$_2$ mobility during the change of morphology upon heating. Scanning electron microscopy (SEM), X-ray diffraction (XRD), laser scanning confocal microscope (LSCM) and X-ray photoelectron spectroscopy (XPS), have been applied to characterise the thickness, crystal structure, surface morphology and chemical composition and size of the Au cluster. The importance of the present work is to show that morphology changes in RF sputter-deposited TiO$_2$ depend on the thickness of the TiO$_2$ layer, and that Au$_9$ clusters can be used to probe morphology changes in the surface.

2. Experimental Methods and Techniques

2.1. Material and Sample Preparation

2.1.1. Preparation of TiO$_2$ Films

The RF magnetron sputtering method was used to prepare TiO$_2$ films on a silicon wafer under high vacuum conditions (HHV/Edwards TF500 sputter coater) [22]. Before the deposition, the silicon wafer was cleaned with ethanol and acetone and then dried in a stream of dry nitrogen. The TiO$_2$ film was deposited onto a p-type silicon wafer substrate by sputtering a 99.9% pure TiO$_2$ ceramic target with 500 W sputtering power using Ar$^+$ (flow rate of 5 sccm) for 50 min. The sputter coating chamber was held under vacuum at $2 \times 10^{-5}$ mbar. This process resulted in TiO$_2$ films formed on the silicon wafer with a native oxide layer of TiO$_2$.

TiO$_2$ films with two different thickness were fabricated applying the above-described procedure. The TiO$_2$ films had different colours based on light interference [23]: a TiO$_2$/Si wafer with a purple colour and a TiO$_2$/Si wafer with a gold-like colour (see Figure S1). The difference in colour of the films is related to the difference in light interference patterns within the films due to their difference in film thickness [24]. The thickness of TiO$_2$P is $\sim$400 nm, while TiO$_2$G is $\sim$1100 nm (vide infra). The TiO$_2$ wafers were cut into 1 cm $\times$ 1 cm pieces and used without further treatment. The two TiO$_2$ wafers are hereafter referred to as (i) TiO$_2$P and (ii) TiO$_2$G.

2.1.2. Deposition of Au$_9$ Clusters

The deposition procedure of Au$_9$(PPh$_3$)$_9$(NO$_3$)$_3$ (Au$_9$) was identical for both the TiO$_2$P and TiO$_2$G samples. Phosphine-protected Au$_9$ clusters were synthesised as reported.
previously [25]. A UV-Vis spectrum of the Au_{9} cluster is shown in Figure S2. The TiO_{2} films were immersed in Au_{9} methanol solutions (2 mL) for 30 min at concentrations of 0.006, 0.06 and 0.6 mM. The TiO_{2} samples were rinsed by quickly dipping them into pure methanol and then dried in a stream of dry nitrogen. These samples are hereafter referred to as (i) TiO_{2}P-Au_{9} and (ii) TiO_{2}G-Au_{9}.

2.1.3. Photodeposition of CrO\textsubscript{x} Layer

Photodeposition of the CrO\textsubscript{x} layer was the same for both TiO\textsubscript{2}-Au\textsubscript{9} samples (TiO\textsubscript{2}P-Au\textsubscript{9} and TiO\textsubscript{2}G-Au\textsubscript{9}). A 0.5 mM potassium chromate solution was prepared by dissolving K\textsubscript{2}CrO\textsubscript{4} (≥99%, Sigma-Aldrich) in deionised water. The TiO\textsubscript{2}-Au\textsubscript{9} samples were immersed into the K\textsubscript{2}CrO\textsubscript{4} solution (1 mL) and irradiated for 1 h using a UV LED (Vishay, VLMU3510-365-130) with ~1 cm between the sample and the irradiation source. The UV LED had a radiant power of 690 mW at 365 nm wavelength. After photodeposition, the samples were washed by dipping them into deionised water and dried in a stream of dry nitrogen [26]. These samples are hereafter referred to as (i) TiO\textsubscript{2}P-Au\textsubscript{9}-CrO\textsubscript{x} and (ii) TiO\textsubscript{2}G-Au\textsubscript{9}-CrO\textsubscript{x}.

2.1.4. Heat Treatment

To remove the phosphine ligands from Au\textsubscript{9} clusters, all samples were treated with heating at 200 °C for 10 min under ultra-high vacuum (1 × 10\textsuperscript{-8} mbar) in the XPS chamber.

2.2. Characterization Methods

2.2.1. Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDAX)

The thickness of TiO\textsubscript{2} films (TiO\textsubscript{2}P and TiO\textsubscript{2}G) was determined by combining SEM imaging and SEM-EDAX (FEI Inspect F50 microscope) scans on cross-sections of the TiO\textsubscript{2} samples. Cross-sectional images were recorded at a magnification of up to 100 k with 15 keV electron energy.

2.2.2. X-ray Diffraction (XRD)

The crystal and phase structure of the TiO\textsubscript{2} films (TiO\textsubscript{2}P and TiO\textsubscript{2}G) before and after heating were analysed using XRD. A Bruker D8 Advance apparatus was used to record the XRD patterns with an irradiation source of Co-K\textsubscript{α} (λ = 1.789 Å) operating at 35 kV and 28 mA.

2.2.3. Laser Scanning Confocal Microscope (LSCM)

The surface morphology of TiO\textsubscript{2} films (TiO\textsubscript{2}P and TiO\textsubscript{2}G) was measured using a LSCM (Olympus LEXT OLS5000-SAF 3D LSCM) with 100x/0.80NA and 50x/0.60NA LEXT objective lenses. The Olympus Data Analysis software was used to calculate the arithmetic mean deviation (Ra) and root mean square deviation (Rq) values.

2.2.4. X-ray Photoelectron Spectroscopy (XPS)

XPS analysis was performed using an X-ray source with Mg K\textsubscript{α} line (hv = 1253.6 eV). A detailed description of the equipment has been given previously [27]. Survey spectrum scans were performed with a pass energy of 40 eV using a SPECS PHOIBOS-HSA 3500 hemispherical analyser. High-resolution XPS spectra were recorded for C, O, P, Si, Ti, Cr and Au with a pass energy of 10 eV. All XPS binding energy scales were normalised using the C 1 s peak at 285 eV. The peaks were fitted to calculate relative intensities considering atomic sensitivity factors. XPS was recorded immediately after sample preparation and heating, thus, reducing the number of atmospheric exposures.

3. Results and Discussion

3.1. Influence of the Thickness of the TiO\textsubscript{2} Films

The influence of the thickness of the RF sputter-deposited TiO\textsubscript{2} on the change in film morphology upon heating is investigated. First, we will determine the thickness of the TiO\textsubscript{2} films for TiO\textsubscript{2}P and TiO\textsubscript{2}G and describe the crystallinity and morphology of both samples before and after heating. Then, the XPS results will be reported for both TiO\textsubscript{2}P and
TiO$_2$G. Subsequently, the agglomeration of Au$_9$ clusters beneath a Cr$_2$O$_3$ overlayer upon heating of the two films is determined and discussed.

3.2. Determination of the TiO$_2$ Film Thickness

Figure 1 shows cross-section SEM images of TiO$_2$P and TiO$_2$G with line measurements of the thickness of the TiO$_2$ films. These SEM images clearly show that the thickness of the film for the TiO$_2$P and TiO$_2$G samples is ~400 nm and ~1100 nm, respectively; the film thickness of TiO$_2$G is more than two times greater than for TiO$_2$P. To confirm the film thickness, EDAX was further processed at the same image spots as SEM. Cross-section SEM-EDAX elemental maps of Ti, O and Si of TiO$_2$P and TiO$_2$G are shown in Figure S3. The EDAX elemental maps confirm that the thickness of the TiO$_2$ film for TiO$_2$G is larger than for TiO$_2$P.

![Figure 1](image)

**Figure 1.** Cross-section SEM images of the (A) TiO$_2$P [28] and (B) TiO$_2$G layer.

3.3. Crystal Structure of the TiO$_2$P and TiO$_2$G before and after Heating

To assess the crystal structure of the TiO$_2$ film for TiO$_2$P and TiO$_2$G, XRD was conducted (Figure 2). There are no observable anatase, rutile or brookite crystal phase peaks [29], indicating that the films have an amorphous crystal structure. The crystallographic state of the TiO$_2$ is known to be transformed upon heating. The XRD patterns of TiO$_2$ films (TiO$_2$P and TiO$_2$G) after heating at 200 °C for 10 min are shown in Figure 2. Both spectra show an anatase peak at 29.8°, which confirms that the crystal structure of TiO$_2$P and TiO$_2$G has changed to the anatase phase after heating. The intensity of the anatase diffraction peak for TiO$_2$G is more than two times higher than for TiO$_2$P, which is due to the difference in the total amount of TiO$_2$ in each film. The TiO$_2$G layer is more than two times thicker than TiO$_2$P, so we also expect that there is more than twice as much anatase in the TiO$_2$G film. Thus, the percentage change in crystal structure in the films is comparable. The formation of the anatase phase strongly suggests the TiO$_2$ film could be mobile during the heating process, which could influence the morphology of the TiO$_2$ films, as will be discussed below.

3.4. Morphology of the TiO$_2$P and TiO$_2$G Layer before and after Heating

LSCM was conducted on both TiO$_2$ films before and after heating to compare their morphology. Figure 3 shows the surface morphology of TiO$_2$P and TiO$_2$G before and after heating over an area of 16 × 16 μm and the determined Ra and Rq values. The 3D profiles of the same spots are displayed in Figure S4. Before heating, the Ra (and Rq) values of the TiO$_2$P and TiO$_2$G are 0.6 nm (0.8 nm) and 1.0 nm (1.3 nm), respectively. However, after heating, the values become 1.0 nm (1.2 nm) and 12.7 nm (14.7 nm), respectively. The change in Ra (and Rq) for TiO$_2$P is small after heating, especially in comparison to TiO$_2$G, which is 12 times higher after heating. The Ra (and Rq) values were also calculated over a much larger area of 595 × 595 μm and show a similar change (Figure S5). The change in the Ra
(and Rq) values indicates that both the TiO₂P and TiO₂G increase in surface roughness after heating. The XRD results show that the TiO₂G and TiO₂P have the same fraction of anatase after heating, so the total amount of anatase in TiO₂G is larger compared to TiO₂P (vide supra). Çörekçi et al. noted a similar finding in their study of different thicknesses of TiO₂ films heated at different temperatures [19]. The authors reported that the surface roughness of the thicker TiO₂ film (300 nm) increased more compared to thinner films (220 and 260 nm) upon heating. In our study, a large change in the surface roughness was observed clearly with the thicker film (more than two times thicker) by a factor of six. Çörekçi et al. assumed that the increase in surface roughness was due to increases in the grain sizes with increasing film thickness and the recrystallization in the TiO₂ films during heating. A number of studies have reported comparable findings that the surface morphology of the TiO₂ films changes upon heating [17,30]. Thus, we conclude that the thicker TiO₂G film is more mobile during heating in comparison to the thinner film in the TiO₂P sample.

![XRD patterns of Si wafer, TiO₂P, TiO₂P Heated, TiO₂G, and TiO₂G Heated](image)

**Figure 2.** XRD patterns of the Si wafer, TiO₂P and TiO₂P after heating, TiO₂G and TiO₂G after heating to 200 °C. The positions of the diffraction peaks for anatase, rutile and brookite, as well as Si, are indicated using the standard XRD patterns (anatase PDF 01-075-1537, rutile PDF 01-071-4809, brookite PDF 04-007-0758 and Si PDF 00-013-0542).

### 3.5. Au₉ Clusters on TiO₂P and TiO₂G; a Probe for Mobility during Heating

In order to provide insight into the mobility of the TiO₂ during the recrystallisation process, Au₉ clusters were deposited onto the TiO₂ films and analysed with XPS. XPS was used to investigate the size of phosphine-protected Au₉ clusters deposited onto TiO₂P and TiO₂G. In addition, the effect of the CrO₃ overlayer on the Au₉ clusters was investigated, also with XPS. Figures 4 and 5 show the peak positions and relative intensities of Au 4f½ peaks in the XP spectra of three different concentrations (0.006, 0.06 and 0.6 mM) of TiO₂P-Au₉, TiO₂G-Au₉, TiO₂P-Au₉-CrO₃ and TiO₂G-Au₉-CrO₃ before and after heating. Tables S1 and S2 show a summary of all the Au 4f½ peak positions and full-width-half-maximum (FWHM). Note that all the Au 4f spectra for both substrates (TiO₂P and TiO₂G) are shown in Figures S6 and S7. The TiO₂P XPS results will be first presented, followed by the TiO₂G results.
Figure 3. Surface morphology with the Ra and Rq values of (A) TiO$_2$P before heating and (B) TiO$_2$P after heating, (C) TiO$_2$G before heating and (D) TiO$_2$G after heating (area 16 × 16 μm). Note that the scale bars are different.

Figure 4. XPS results of TiO$_2$P-Au$_9$ for three different Au$_9$ concentrations: (A) position of Au 4f$_{7/2}$ and (B) relative intensity of Au before and after heating. TiO$_2$P-Au$_9$-CrO$_x$, (C) position of Au 4f$_{7/2}$ and (D) relative intensity of Au before and after photodeposition of the CrO$_x$ layer and after heating. Note that the vertical scales of (B,D) are different and that the samples in (A,C) are different but are prepared in the same manner.
Photodeposition of CrO$_x$ concentration (mM)

After heating

B

Relative intensity of Au %

Deposition of Au$_9$

Relative intensity of Au %

Deposition of Au$_9$

Photodeposition of CrO$_x$

Photodeposition of CrO$_x$

D

Relative intensity of Au %

Deposition of Au$_9$

After heating

Without the CrO$_x$ layer and before heating, the Au 4f$_{7/2}$ peaks appeared at 85.1–85.4 eV with an FWHM of 1.7–1.8 eV (Figure 4A), whereas after heating, the Au 4f$_{7/2}$ peaks shifted to slightly lower binding energies (84.7–84.8 eV) and FWHM (1.5–1.6 eV), and also showed a decrease in relative Au intensity across all Au$_9$ concentrations (Figure 4B). The results of the samples covered with a CrO$_x$ layer are shown in Figure 4C,D. The Au 4f$_{7/2}$ peak positions of TiO$_2$P-Au$_9$ after CrO$_x$ deposition but before heating were observed at 85.3 eV and an FWHM of 1.6 eV for all three concentrations. Note that the Au relative intensities decrease after the photodeposition of the CrO$_x$ layer, confirming the coverage of Au clusters with the CrO$_x$ layer (Figure 4D). After heating, the XPS peak position decreases slightly to 85.0 eV with no significant change in FWHM. The relative Au intensities also remained unchanged upon heating. XPS has been shown previously to be a reliable indicator of the size of phosphine-protected Au$_9$ clusters through the final state effect [21,28,31–36]. Generally, non-agglomerated Au$_9$ clusters on TiO$_2$ appear at a high binding peak (HBP) between 85.0–85.4 eV with an FWHM of 1.7 ± 0.2 eV, and agglomerated Au$_9$ clusters shift toward a low binding peak (LBP) at 84 eV with a decreasing FWHM that corresponds to bulk Au [28,31–35]. This XPS interpretation has been confirmed by correlating the XPS results with other techniques, such as HRTEM [33,34]. Here, the Au 4f$_{7/2}$ peak positions of TiO$_2$P-Au$_9$ without the CrO$_x$ layer after heating indicate a small degree of agglomeration of the Au$_9$ clusters for all concentrations. This is further confirmed by a small decrease in Au intensity after heating, indicating that some of the gold is attenuated due to some larger, agglomerated particles. Electrons emitted from the part of the clusters facing toward the substrate are attenuated when leaving the sample, which decreases the overall Au intensity [31,32]. Therefore, the same total amount of gold...
deposited on the surface will have a lower intensity for large gold particles than that of small gold clusters. In contrast to the CrO$_x$ layer of the Au 4f$_{7/2}$ peaks, positions are unchanged after heating and there is no further decrease in the Au relative intensities, indicating that Au clusters remain non-agglomerated clusters with CrO$_x$ coverage (see Scheme 1A). It is important to note that there is a decrease in Au intensity after photodeposition of the CrO$_x$ layer due to the coverage of Au$_9$ clusters (Figure 4D). These results are in agreement with our previous report showing that CrO$_x$ overlayers inhibit the agglomeration of Au clusters [28].

Scheme 1. Schematic illustration of the experimental procedure for preparing (A) TiO$_2$P-Au$_9$-CrO$_x$ and (B) TiO$_2$G-Au$_9$-CrO$_x$.

The P 2p spectra of TiO$_2$P-Au$_9$ without and with the CrO$_x$ layer before and after heating are shown in Figure S8 and the peak positions are discussed in the Supplementary Section. The Cr 2p spectra for TiO$_2$P-Au$_9$-CrO$_x$ before and after heating at the three different concentrations are shown in Figure S9. A summary of all the Cr 2p$_{3/2}$ peak positions is shown in Table S3 and the peak positions are discussed in the supplementary section.

3.7. XPS of TiO$_2$G Sample

For the thicker film, TiO$_2$G-Au$_9$, the Au 4f$_{7/2}$ peak positions before heating for all three different concentrations appeared at the HBP at 85.3 ± 0.1 eV (Figure 5A) and an FWHM of 1.8 ± 0.2 eV, corresponding to non-agglomerated Au clusters. However, after heating, the Au 4f$_{7/2}$ shifted toward lower energy (84.6–84.9 eV) and an FWHM of 1.5–1.7 eV with a decrease in Au intensity (Figure 5B), indicating that Au clusters are partially agglomerated. With the CrO$_x$ layer deposited before heating, the Au 4f$_{7/2}$ peak positions are observed at the HBP position at 85.3–85.5 eV (Figure 5C), with a decrease in Au 4f$_{7/2}$ intensity due to the coverage of the CrO$_x$ layer on Au$_9$ clusters (Figure 5D). There is a slight increase in the binding energy of the Au 4f peak after the photodeposition of CrO$_x$ and we do not know if this is a significant change or not. However, the position found can be used as an indication of the presence of non-agglomerated Au clusters. With the CrO$_x$ layer after heating, the Au 4f$_{7/2}$ peak positions have further shifted to lower energy (84.3–84.8 eV) positions and an FWHM of 1.3–1.8 eV with a decrease in Au intensity, which is attributed to further agglomeration of the Au clusters based on the final state effect (see Scheme 1B). The degree of agglomeration increases with increasing Au$_9$ concentration for both cases (without and with the CrO$_x$ layer). Note here the difference; Au clusters on the surface of TiO$_2$G undergo increased agglomeration after heating, even in the presence of the CrO$_x$ layer. This is different to the TiO$_2$P, where Au clusters are less likely to agglomerate under the CrO$_x$ layer after heating. This difference will be further discussed below.

The chemical state of the phosphorous ligands of TiO$_2$G-Au$_9$ without and with the CrO$_x$ layer, both before and after heating, was determined using the P 2p region (see Figure S10 for more information and accompanying text). Figure S11 shows the Cr 2p spectra for TiO$_2$G-Au$_9$-CrO$_x$ before and after heating of the three different concentrations. All the Cr
2p3/2 peak positions are given in Table S4 and the peak positions are discussed in the Supplementary Section.

3.8. Effect of the TiO2 Film Thickness

The protective effect of the CrOx layer on the agglomeration of Au9 clusters is not the same for both the TiO2P and TiO2G substrates. The agglomeration of Au9 clusters is inhibited on TiO2P with the CrOx overlayer but not on TiO2G, which shows a higher degree of agglomeration. The coverage of the CrOx layer on Au9 clusters for both substrates is demonstrated by the decrease in the Au-XPS intensities. After heating, it is observed that the relative amount of CrOx decreases for both films (Table S5). Our previous studies on a similar system revealed that the CrOx layer diffuses into a TiO2 film after heating to 600 °C due to the differences in surface energy between TiO2 and CrOx [26]. In this study, both films were heated to only 200 °C, however, CrOx on TiO2G experienced more diffusion of CrOx into the film compared to TiO2P. One possibility for the higher degree of Au9 agglomeration and CrOx diffusion is the mobility of the TiO2 film. Cluster agglomeration can be due to either (i) growth of the clusters over the surface or (ii) mobility of the substrate. In the case of (i), the cluster growth and agglomeration on a substrate can be ascribed to either Smoluchowski ripening or Ostwald ripening mechanisms. For Smoluchowski ripening, the agglomeration of clusters is caused by the collision and coalescence of entire clusters to larger particles [37]. For Ostwald ripening, the growth of larger particles takes place by the detachment of single atoms, which diffuse onto a nearby cluster or nanoparticle [38].

In the case of (ii), a section of the substrate to which a cluster is adsorbed moves closer to another section of the substrate, which has another adsorbed cluster. The significant change in the surface morphology of TiO2G after heating (Ra: 11.7 nm and Rq: 13.4 nm) compared to TiO2P (Ra: 0.4 nm and Rq: 0.5 nm) strongly suggests that the agglomeration of the Au9 clusters with different concentrations on TiO2G after heating is due to the high distortion of the surface upon heating. A higher mobility of the TiO2 substrate during heating means that the local surface beneath an Au cluster moves larger distances compared to a substrate which exhibits lower mobility during heating (see Scheme 2). The high mobility of the thick film is assumed to be due to the recrystallisation during heating, which is in agreement with previous studies [17,19,30]. With increasing mobility, the likelihood of close contact between two or more Au clusters increases, and thus the likelihood of agglomeration is also increased. Furthermore, the degree of agglomeration of the Au clusters is larger for the thicker TiO2G substrate compared to the thinner TiO2P substrate.

Scheme 2. Schematic illustration showing the agglomeration mechanism of Au9 clusters on the TiO2G film during heating.

4. Conclusions

In summary, the change in surface morphology of two different film thicknesses of RF sputter-deposited TiO2 (~400 nm and ~1100 nm) was examined and compared upon heating. After heating, the thick TiO2 film showed a larger change in surface morphology, which is associated with higher mobility during heating compared to the thin TiO2 film. The difference in mobility is attributed to the differences in the total amount of amorphous
TiO$_2$ transformed to anatase in each of the films, which then results in differences in the morphology of the surface upon heating. Au$_{49}$ clusters were used as a probe for TiO$_2$ mobility. Au$_{49}$ clusters were deposited onto the two different TiO$_2$ films, followed by photodeposition of the CrO$_x$ layer. After heating, the Au clusters on the thicker film showed a larger degree of agglomeration compared to the thinner film. The higher mobility of the thick film during heating increased the probability of close encounters of Au clusters, which resulted in agglomeration of the Au$_{49}$ clusters even in the presence of a CrO$_x$ overlayer. In contrast, the lower mobility of the thin film resulted in less agglomeration of the Au$_{49}$ clusters after heating.

**Supplementary Materials:** The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12183218/s1. The supporting information shows the EDAX-SEM elemental mapping of the TiO$_2$P and TiO$_2$G cross-section images, the details of the XP spectra, their fitting, and quantification. Figure S1: A photo of the TiO$_2$P (left) and TiO$_2$G (right) films. Figure S2: UV-Vis spectrum of Au$_4$(PPh$_3$)$_3$(NO$_3$)$_3$ in Methanol. Figure S3: Cross-section SEM-EDAX elemental maps of Ti, O and Si of TiO$_2$P and TiO$_2$G. Note that the scale bars are different. Figure S4: 3D Profile of (A) TiO$_2$P before heating, (B) TiO$_2$P after heating, (C) before heating, TiO$_2$G and (D) TiO$_2$G after heating (area 16 × 16 µm). Figure S5: Surface morphology with the average of Ra and Rq values of (A) TiO$_2$P before heating, (B) TiO$_2$P after heating, (C) before heating, TiO$_2$G and (D) TiO$_2$G after heating. (area 595 × 595 µm). It is important to know that the scale bars are different. Figure S6: XP spectra of Au 4f of (A) TiO$_2$P-Au$_{49}$: after Au$_{49}$ deposition (blue) and after heating (grey) (B) TiO$_2$P-Au$_{49}$-CrO$_x$: after Au$_{49}$ deposition (blue), after CrO$_x$ layer photodeposited (orange) and after heating (grey). Figure S7: XP spectra of Au 4f of (A) TiO$_2$G-Au$_{49}$: after Au$_{49}$ deposition (blue) and after heating (grey) (B) TiO$_2$G-Au$_{49}$-CrO$_x$: after Au$_{49}$ deposition (blue), after CrO$_x$ layer photodeposited (orange) and after heating (grey). Figure S8: XP spectra of P 2p of (A) TiO$_2$P-Au$_{49}$: after Au$_{49}$ deposition (blue) and after heating (grey) (B) TiO$_2$P-Au$_{49}$-CrO$_x$: after Au$_{49}$ deposition (blue), after CrO$_x$ layer photodeposited (orange), and after heating (grey). Figure S9: XP spectra of Cr 2p of the TiO$_2$P-Au$_{49}$-CrO$_x$ sample of (A) 0.006mM sample, (B) 0.06mM sample and (C) 0.6mM sample: after CrO$_x$ layer photodeposited (orange) and after heating (grey). Figure S10: XP spectra of P 2p of (A) TiO$_2$G-Au$_{49}$: after Au$_{49}$ deposition (blue) and after heating (grey) (B) TiO$_2$G-Au$_{49}$-CrO$_x$: after Au$_{49}$ deposition (blue), after CrO$_x$ layer photodeposited (orange), and after heating (grey). Figure S11: XP spectra of Cr 2p of the TiO$_2$G-Au$_{49}$-CrO$_x$ sample of (A) 0.006mM sample, (B) 0.06mM sample and (C) 0.6mM sample: after CrO$_x$ layer photodeposited (orange) and after heating (grey).

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References
1. Daghir, R.; Drogui, P.; Robert, D. Modified TiO2 For Environmental Photocatalytic Applications: A Review. Ind. Eng. Chem. Res. 2013, 52, 3581–3599. [CrossRef]
2. Linsebigler, A.L.; Lu, G.; Yates, J.T. Photocatalysis on TiO2 Surfaces: Principles, Mechanisms, and Selected Results. Chem. Rev. 1995, 95, 735–758. [CrossRef]
3. Brinker, C.J.; Harrington, M.S. Sol-gel Derived Antireflective Coatings for Silicon. Sol. Energy Mater. 1991, 26, 195–204. [CrossRef]
4. Lottiaux, M.; Boulesteix, C.; Nihoul, G.; Varnier, F.; Flory, F.; Galindo, R.; Pelletier, E. Morphology and Structure of TiO2 Thin Layers vs. Thickness and Substrate Temperature. Thin Solid Films. 1989, 170, 107–126. [CrossRef]
5. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
6. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
7. Brinker, C.J.; Linsebigler, A.L. Sol-Gel Synthesis of Silica and Other Glass Materials. J. Mater. Chem. 1990, 3, 939–947. [CrossRef]
8. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
9. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
10. Wang, T.M.; Zheng, S.K.; Hao, W.C.; Wang, C. Studies on photocatalytic activity and transmittance spectra of TiO2 films prepared by rf magnetron sputtering. Surf. Coat. Technol. 2002, 155, 141–145. [CrossRef]
11. Ye, Q.; Liu, P.Y.; Tang, Z.F.; Zhai, L. Hydrophilic properties of nano-TiO2 thin films deposited by RF magnetron sputtering. Vacuum 2007, 81, 527–531. [CrossRef]
12. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
13. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
14. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
15. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
16. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
17. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
18. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
19. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
20. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
21. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
22. Aarik, J.; Aidla, A.; Uustare, T.; Kukli, K.; Sammelselg, V.; Ritala, M.; Leskelä, M. Atomic Layer Deposition of TiO2 and other oxides for applications in electronics. J. Vac. Sci. Technol. A 2007, 25, 1–6. [CrossRef]
23. Yeung, K.S.; Lam, Y.W. A Simple Chemical Vapour Deposition Method for Depositing Thin TiO2 Films. Thin Solid Films. 1983, 109, 169–178. [CrossRef]
23. Yuan, X.; Ye, Y.; Lian, M.; Wei, Q. Structural Coloration of Polyester Fabrics Coated with Al/TiO$_2$ Composite Films and Their Anti-Ultraviolet Properties. *Materials* **2018**, *11*, 1011. [CrossRef] [PubMed]

24. Diamanti, M.V.; Del Curto, B.; Pedeperri, M. Interference Colors of Thin Oxide Layers on Titanium. *Color Res. Appl.* **2008**, *33*, 221–228. [CrossRef]

25. Wen, F.; Englert, U.; Gutthörl, B.; Simon, U. Crystal Structure, Electrochemical and Optical Properties of [Au(PPh$_3$)$_8$](NO$_3$)$_3$. *Eur. J. Inorg. Chem.* **2008**, *2008*, 106–111. [CrossRef]

26. Alotabi, A.S.; Gibson, C.T.; Metha, G.F.; Andersson, G.G. Investigation of the Diffusion of Cr$_2$O$_3$ into Different Phases of TiO$_2$ upon Annealing. *ACS Appl. Energy Mater.* **2021**, *4*, 322–330. [CrossRef]

27. Acres, R.G.; Ellis, A.V.; Alvino, J.; Lenahan, C.E.; Khodakov, D.A.; Metha, G.F.; Andersson, G.G. Molecular Structure of 3-Aminopropyltriethoxysilane Layers Formed on Silanol-Terminated Silicon Surfaces. *J. Phys. Chem. C* **2012**, *116*, 6289–6297. [CrossRef]

28. Alotabi, A.S.; Yin, Y.; Redaa, A.; Tesana, S.; Metha, G.F.; Andersson, G.G. Cr$_2$O$_3$ layer inhibits agglomeration of phosphine-protected Au$_9$ clusters on TiO$_2$ films. *J. Chem. Phys.* **2021**, *155*, 164702. [CrossRef]

29. Ali, S.; Granbohm, H.; Lahtinen, J.; Hannula, S.-P. Titania Nanotubes Prepared by Rapid Breakdown Anodization for Photocatalytic Decolorization of Organic Dyes under UV and Natural Solar Light. *Nanoscale Res. Lett.* **2018**, *13*, 179. [CrossRef]

30. Chandra Sekhar, M.; Kondaiah, P.; Jagadeesh Chandra, S.; Mohan Rao, G.; Uthanna, S. Substrate temperature influenced physical properties of silicon MOS devices with TiO$_2$ gate dielectric. *Surf. Interface Anal.* **2012**, *44*, 1299–1304. [CrossRef]

31. Anderson, D.P.; Alvino, J.F.; Gentleman, A.; Al Qahtani, H.; Thomsen, L.; Polson, M.I.; Metha, G.F.; Golovko, V.B.; Andersson, G.G. Chemically-Synthesised, Atomically-Precise Gold Clusters Deposited and Activated on Titania. *Phys. Chem. Chem. Phys.* **2013**, *15*, 3917–3929. [CrossRef] [PubMed]

32. Anderson, D.P.; Adnan, R.H.; Alvino, J.F.; Shipper, O.; Donoева, B.; Ruzicka, J.-Y.; Al Qahtani, H.; Harris, H.H.; Cowie, B.; Aitken, J.B. Chemically Synthesised Atomically Precise Gold Clusters Deposited and Activated on Titania. Part II. *Phys. Chem. Chem. Phys.* **2013**, *15*, 14806–14813. [CrossRef] [PubMed]

33. Al Qahtani, H.S.; Kimoto, K.; Bennett, T.; Alvino, J.F.; Andersson, G.G.; Metha, G.F.; Golovko, V.B.; Sasaki, T.; Nakayama, T. Atomically resolved structure of ligand-protected Au$_9$ clusters on TiO$_2$ nanosheets using aberration-corrected STEM. *J. Chem. Phys.* **2016**, *144*, 114703. [CrossRef] [PubMed]

34. Al Qahtani, H.S.; Metha, G.F.; Walsh, R.B.; Golovko, V.B.; Andersson, G.G.; Nakayama, T. Aggregation Behavior of Ligand-Protected Au$_9$ Clusters on Sputtered Atomic Layer Deposition TiO$_2$. *J. Phys. Chem. C* **2017**, *121*, 10781–10789. [CrossRef]

35. Howard-Fabretto, L.; Metha, G.F.; Andersson, G.G.; Metha, G.F.; Golovko, V.B.; Andersson, G.G. Suppression of phosphine-protected Au$_9$ cluster agglomeration on SrTiO$_3$ particles using a chromium hydroxide layer. *Nanoscale Res. Lett.* **2018**, *13*, 28007–28016. [CrossRef]

36. Smoluchowski, M.V. Drei vortrage uber diffusion, brownsche bewegung und koagulation von kolloidteilchen. Z. Far Phys. **1916**, *17*, 557–585.

37. Ostwald, W. Blocking of Ostwald ripening allowing long-term stabilization. *Phys. Chem.* **1901**, *37*, 385.

38. Wilcoxon, J.P.; Provencio, P. Etching and Aging Effects in Nanosize Au Clusters Investigated Using High-Resolution Size-Exclusion Chromatography. *J. Phys. Chem. B* **2003**, *107*, 12949. [CrossRef]

39. Biesinger, M.C.; Brown, C.; Mycroft, J.R.; Davidson, R.D.; McIntyre, N.S. X-ray photoelectron spectroscopy studies of chromium compounds. *Surf. Interface Anal.* **2004**, *36*, 1550–1563. [CrossRef]

40. Kawakami, T.; Kataoka, Y.; Hirata, M.; Akinaga, Y.; Takahata, R.; Wakamatsu, K.; Fujiki, Y.; Kataoka, M.; Kikkawa, S.; Alotabi, A.S.; et al. Creation of High-Performance Heterogeneous Photocatalysts by Controlling Ligand Desorption and Particle Size of Gold Nanocluster. *Angew. Chem. Int. Ed.* **2021**, *60*, 21340–21350. [CrossRef] [PubMed]

41. Madridejos, J.M.L.; Harada, T.; Falcinella, A.J.; Small, T.D.; Golovko, V.B.; Andersson, G.G.; Metha, G.F.; Kee, T.W. Optical Properties of the Atomically Precise C4 Core [Au(9(PPh$_3$)$_8$)]$_2^+$ Cluster Probed by Transient Absorption Spectroscopy and Time-Dependent Density Functional Theory. *J. Phys. Chem. C* **2021**, *125*, 2033–2044. [CrossRef]

42. Krishnan, G.; Al Qahtani, H.S.; Li, J.; Yin, Y.; Eom, N.; Golovko, V.B.; Metha, G.F.; Andersson, G.G. Investigation of Ligand-Stabilized Gold Clusters on Defect-Rich Titania. *J. Phys. Chem. C* **2017**, *121*, 28007–28016. [CrossRef]