Size- and density-controlled photodeposition of metallic platinum nanoparticles on titanium dioxide for photocatalytic applications: Supplementary Information

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1. Image processing

Particle size distributions and nearest neighbor distances were analyzed from SEM images (S1) with ImageJ: the built-in bandpass filter increases the contrast between the TiO_2 surface and the metal nanoparticles. The image is then made binary, as seen in Figure S2, with the particles showing as black and the substrate surface as white.



Figure S1 Examples of SEM micrographs of the platinum deposited samples.

ImageJ is used to analyze the particle size and the nearest neighbor distance from the coordinates of each particle. The strategy applied to avoid the detection of false particle is the assessment of the circularity of the analyzed particles, and a visual assessment of the crystal edges. The data obtained by ImageJ are then processed to verify the size distribution, the density and the nearest neighbor distance distribution on all samples. The sizes present a log-normal distribution, as expected from a random growth process¹, as shown in figure S3, while the nearest neighbor distances fit into a Poisson distribution, as figure S4 depicts.

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(a) SEM micrograph before image processing

Figure S2 Image processing via ImageJ.



(b) SEM micrograph after image processing



Figure S3 Particle size distribution for the platinum-deposited samples: histograms of the data are shown as bar graphs, while the line is the log-normal distribution fit for the data.



Figure S4 Particle nearest neighbor distribution for the platinum samples: histograms of the data are shown as bar graphs, while the line is the Poisson distribution for the number of particles observed in the examined area.

2. Statistical analysis

Following the sampling method developed by G. Taguchi², eight samples were fabricated, to evaluate the influence of seven parameters, each with two levels. The parameter sets were chosen so that the binary vectors representing the parameter choices for each sample were mutually orthogonal. Therefore, these parameter sets can be represented by an orthogonal array, as Figure 1(b) shows in the main article. The orthogonality ensures that all subgroups of samples with fixed value of any single parameter will have all the other parameters appear with both values in equal amounts. An example is shown in table S1. This allows to separate the effects of the different parameters during the statistical analysis.

H ₂ treatment	1	1	1	1	2	2	2	2
CH ₃ OH	1	1	2	2	1	1	2	2
Illumination P	2	2	1	1	1	1	2	2
Deposition time	2	1	2	1	2	1	2	1
Precursor C	1	2	1	2	2	1	2	1
N ₂ purge time	2	1	1	2	2	1	1	2
H_2SO_4 addition	2	1	1	2	1	2	2	1

Table S1 The orthogonal array separated into two groups based on the illumination intensity. All other parameters have both values appear twice in both groups, so any difference measured between these two groups is explained by the changed illumination intensity.

The results from the image analysis (diameter of particles, density and nearest neighbor distances) are evaluated by computing the averages of the results for values 1 and 2 of the process parameters and using a 7-way analysis of variance (ANOVA) to extract the sums of squares for every different treatment with respect for the total mean. In this step the ratio (F-ratio) between the variance between the sample groups with different process parameter values and the variance within the same group results infinite. This is because a model with N-1 parameters will always perfectly fit the data. As the error term only contains the variance not explained by the model, it is in this case zero (as visible in table S2 for the particle density).

The next step is to apply a reduced ANOVA by pooling the groups that have less than 5% contribution to the total sum of squares into the error group, thus obtaining meaningful F-ratios and p-values, as tables S3 (particle size) and S5 (particle density) show. The low sum of squares indicates that the parameters are unlikely to have any effect on the measured results, so the results are treated as if these negligible parameters were not controlled in the first place.

Parameters	Sum of squares	DoF	F	P value
H ₂ thermal treatment	1.320	1	Inf	NaN
CH ₃ OH concentration	3.014	1	Inf	NaN
Illumination power	1.044	1	Inf	NaN
Deposition time	0.063	1	Inf	NaN
Precursor concentration	0.078	1	Inf	NaN
N ₂ purge time	0.633	1	Inf	NaN
H ₂ SO ₄ addition	0.154	1	Inf	NaN
Error	0	0		
Total	6.306	7		

Table S2 7-way ANOVA of the effect of the photodeposition parameters on the size of the particles. From the sum of squares values it is evident that the deposition time, the H_2SO_4 addition, and the precursor concentration are the parameters that least influence the experimental results, and thus they can be removed from the following step in the analysis of variance.

Variable	Sum of squares	DoF	F	P value
H ₂ thermal treatment	1.320	1	13.425	0.035
CH ₃ OH concentration	3.014	1	30.642	0.012
Illumination power	1.044	1	10.616	0.047
N ₂ purge time	0.633	1	6.435	0.085
Error	0.295	3		
Total	6.306	7		

Table S3 4-way ANOVA of the effect of the photodeposition parameters on the size of the particles. The p-values indicate that the H_2 treatment, the methanol concentration and the illumination power have a statistically significant effect on particle size.

Parameters	Sum of squares	DoF	F	P value
H ₂ thermal treatment	8374176	1	Inf	NaN
CH ₃ OH concentration	232927	1	Inf	NaN
Illumination power	820180	1	Inf	NaN
Deposition time	2461792	1	Inf	NaN
Precursor concentration	9774898	1	Inf	NaN
N ₂ purge time	150863	1	Inf	NaN
H ₂ SO ₄ addition	2354396	1	Inf	NaN
Error	0	0		
Total	24169230	7		

Table S4 7-way ANOVA of the effect of the photodeposition parameters on the density of the particles. From the sum of squares values it is evident that the parameters that belong in the error group are the purge time, the illumination power and the methanol concentration.

Parameters	Sum of squares	DoF	F	P value
H ₂ thermal treatment	8374176	1	20.866	0.020
Deposition time	2461792	1	6.134	0.090
Precursor concentration	9774897	1	24.357	0.016
H ₂ SO ₄ addition	2354396	1	5.867	0.094
Error	1203969	3		
Total	24169230	7		

Table S5 4-way ANOVA of the effect of the photodeposition parameters on the density of the particles. The p-values indicate that the H₂ treatment and the precursor concentration have a statistically significant effect on particle density.

3. Formation of platinum oxides

The photodeposition of platinum after the addition of H_2SO_4 resulted in two distinctly different phases, which are the metallic and oxidized phase. X-ray photoelectron spectroscopy reveals that the oxidized phase is indeed a mixture of platinum oxide and platinum hydroxide.



(a) Sample 1 in an area where metallic platinum formed.



(b) Sample 1 in an area where platinum oxdides have formed.

Figure S5 Comparison of SEM micrographs of the same sample in areas where different phases of platinum.

Similar results have been previously reported $^{3-6}$. The oxidized phase resembled mycelia that covered wide areas in the illuminated spot (figure S5b.2, while the metallic phase contained separate platinum particles (Figure S5a). According to earlier studies, the platinum oxide formed at pH 5-7 is primarily in the form of PtO, while the oxides formed in the 7-9 pH range form a mixed phase of PtO and PtO₂⁴. As the precursor solution used in this paper was acidic due to the acidic precursor salt, the pH of the final mixture was below pH 7, making PtO the most likely oxide. Oxide formation was observed on every platinum sample that was prepared with the solution containing H₂SO₄. The formation of platinum oxides decreased the accuracy of the platinum analysis significantly. In order to conduct the analysis for the samples, the oxidized platinum samples and metallic platinum samples were processed as if they were identical. This is justified, since previous studies have proven that the oxidized samples also contain metallic platinum⁴. The particle size analysis

was conducted on areas without any obvious oxidized platinum. However, there was no way to determine whether the platinum nanoparticles in the analyzed area were actually metallic that had a high degree of certainty. Attempts at characterizing the particles by detecting the oxygen bonded to the platinum was limited by the small size of the particles, and surface-active methods such as EDS would have difficulty distinguishing between the oxide peaks generated from the oxygen bonded to platinum and the oxygen bonded to the titanium dioxide substrate. Based on both our work and previous studies, platinum oxide growth can be inhibited by performing the photodeposition below pH 5. While using methanol as a sacrificial donor does aid in the reduction of platinum oxides into metallic platinum and is necessary to promote the deposition of metallic Pt, it is not sufficient in and of itself to prevent platinum oxide growth.

XPS results appear in figure S6, confirming the presence of metallic platinum and oxides on most samples; a more precise estimate is reported in the main article. The platinum is in majority metallic on samples 1, 3, 4 and 7, and hydroxide on samples 5 and 6. Samples number 2 and 8 are uncertain, due to the low signal-to-noise ratio preventing the decomposition from being reliable. The X-ray photoelectron spectroscopy (XPS) measurements were made using Kratos Axis Ultra system, equipped with a monochromatic Al Kls X-ray source. The spectra were measured with 20 eV/40 eV pass energy and 0.1 eV energy step. The energy scale was calibrated to give 284.8 eV binding energy for the C1s peak corresponding to adventitious carbon.

The metallic Pt peaks were fitted with a doublet of asymmetric peaks (in CasaXPS LA(1.2,85,70) and the other Pt components with symmetric Gauss-Lorenz peaks (GL30). The PtOH was fixed 1.6 eV above the metallic component and the oxide components were allowed to move but their mutual separation was 0.9 eV. The peak widths of all metallic components and non-metallic components were set equal. The binding energy difference in the Pt 4f7/2 - 4f5/2 splitting was fixed to 3.35 eV for all components.



Figure S6 X-ray photoelectron spectroscopy results from the eight platinum-deposited samples: the regions where there are the binding energies for the different platinum components are highlighted.

4. Photodeposition of gold

Figure S7 shows SEM micrographs of the gold-deposited samples. The images are acquired with a JEOL JSM-6335F scanning electron microscope, and then they underwent the same ImageJ treatment and statistical analysis as the platinum micrographs, to infer the distributions for the size (figure S8) of the particles, and for the nearest neighbor distance (figure S9). The only process difference between the gold and the platinum photodeposition is in the deposition time, which is 15 and 30 minutes for gold; this is due to the faster reaction kinetics for gold photodeposition. The mean diameter for the particles lays between 10 and 20 nm, with the exception of sample 5, where the mean diameter is closer to 40 nm. On the other hand, particle densities are far more varied, ranging from 30 to 440 μ m⁻².

X-ray photoelectron spectroscopy confirmed that the deposited material is gold S10, and no competing processes take place, as is expected since no other photoreactions are known to take place from chloroauric acid.

It is immediately evident that the photodeposition on sample 4 failed entirely, which makes the series unfit for the same statistical protocol that has been applied for the platinum-deposited samples. However, trends can be observed qualitatively to match the results attained by the Platinum study, supporting the evidence that the H_2 treatment and the light

intensity decrease the particle size, while precursor concentration increases the size, the precursor concentration decreases the density and the deposition time increases the density. Unlike the trend for platinum, however, the intensity of the UV light increases the particle density for gold. This is due to the fact that Au interacts with oxygen vacancies differently than Pt, and is more likely to nucleate at oxygen vacancies, resulting in larger particles (which, in turn, results in a lower particle density)^{7,8}. Otherwise, the particles seemed to respond to the changing deposition conditions in a manner similar to the Pt particles, but describing this with any sort of variance analysis will require further sample production and measurements.



Figure S7 SEM micrographs of the gold deposited samples.



Figure S8 Particle size distribution for the gold samples: histograms of the data are shown as bar graphs, while the line is the log-normal distribution fit for the data.



Figure S9 Particle nearest neighbor distribution for the gold samples: histograms of the data are shown as bar graphs, while the line is the Poisson distribution for the number of particles observed in the examined area.



Figure S10 XPS spectra from the gold-deposited samples. It is evident that in sample 4 there is no gold, as the SEM micrographs already show.



Figure S11 On the left, the average diameter and density of the gold particles for all the eight samples, and on the right the group averages highlighting the influence of all the seven process parameters.

5. Substrate treatment

One of the parameters explored in the present study is the realization of a H_2 thermal treatment on the TiO₂ layer, with the goal to increase the number of oxygen vacancies on the surface, and, as a consequence, to enhance the reduction potential of said surface. The graphs in figure show the results of X-ray photoelectron spectroscopy conducted on a non-treated sample (on the right) and on a treated sample (on the left).



(a) XPS spectrum for oxygen from a sample treated (b) XPS spectrum for oxygen from an untreated samwith H_2 ple.

Figure S12 The spectra show a peak that is coherent with the presence of an OH⁻ component, which confirms the creation of oxygen vacancies.

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