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A Simple and Ligand-Free Synthesis of Light and Durable Metal-TiO$_2$ Polymer Films with Enhanced Photocatalytic Properties

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The photocatalytic efficiency of TiO$_2$ can be increased by using co-catalysts, such as metal nanoparticles, which act as electron sinks to suppress the recombination of photogenerated electron–hole pairs. The main challenge in preparing such systems is to create intimate contact between the metal and the TiO$_2$ surface while still maintaining control over the morphology and distribution of the metal nanoparticles in the TiO$_2$ matrix. Here lightweight TiO$_2$ films are prepared by assembling a layer of TiO$_2$ nanoparticles onto a thin polymer support, followed by physical vapor deposition of metal nanoparticles onto the TiO$_2$ surface. Importantly, the fabrication does not involve any chemical modifications to the surface of NPs, which allows spontaneous formation of strong chemical bonds between deposited metal and TiO$_2$. Systematic optimization of this process gives materials 6x more catalytically active than the parent TiO$_2$ films and up to 18x more catalytically active than commercial photoactive TiO$_2$ glass. Moreover, the transparent, flexible, and robust polymer support enables the product films to be easily used for repeated photocatalytic reactions. Since the whole fabrication process is scalable and highly reproducible, this approach provides new opportunities for controlled synthesis of a new family of practical high-performance metal-semiconductor hybrid photocatalysts.

1. Introduction

Nanostructured TiO$_2$ materials are amongst the most promising and widely researched photocatalytic materials for addressing challenges associated with clean energy generation and environmental pollution.[1–5] For TiO$_2$ based catalysts, materials in the form of solid films are particularly desirable since this addresses one of the most important problems associated with traditional photocatalyst systems, which is that powder-like TiO$_2$ photocatalysts tend to agglomerate and are difficult to recover.[6] Of particular interest is solid TiO$_2$ films that are flexible, robust, and transparent since this would greatly facilitate the actual use of these photocatalysts under real-life conditions where the surface of interest is curved and/or the reaction container is irregular. In our previous research we have developed a one-pot self-assembly method that allows such films to be produced which contain only single layers of TiO$_2$ nanoparticle (NP) clusters firmly anchored on a flexible and lightweight polystyrene support.[7] Importantly, unlike traditional methods for self-assembly, which often involve the use of modifying ligands that adsorb strongly to the surface of the NP catalysts, our method allows photo-catalytically active TiO$_2$ NP powder to be assembled directly into densely packed monolayer films without introducing ligands onto the TiO$_2$ surface.[8–12] In this material, molecules have unrestricted access to the catalytic TiO$_2$ surface, which is a prerequisite for photocatalysts to exhibit high photocatalytic activity.[13] These films are therefore called “surface exposed nanoparticle sheets”, namely SENSs.

While this assembly process addresses the handling issues associated with using TiO$_2$ as a photocatalyst and creates a material that is very suitable for real world applications, the efficiency of the material is still determined by the properties of the photocatalyst itself, which in the case of TiO$_2$ is limited by the fast recombination of the electron–hole pairs created by UV excitation.[14–16] A widely adopted strategy to address this issue is to prepare hybrid metal-TiO$_2$ nanomaterials. Since metals such as Au and Pt have larger work functions than TiO$_2$, electrons flow from TiO$_2$ to metals when they are in close contact, leading to the formation of Schottky barrier which prohibits the backflowing of photogenerated electrons when TiO$_2$ is excited.[17,18] This effectively prolongs the lifetime of electron–hole pairs and...
subsequently leads to the enhancement of the photocatalytic activity of TiO2.[19–23] Apart from the formation of the Schottky barrier, loading of plasmonic metals such as Ag, Cu, and Au on the TiO2 can also enhance the photocatalytic activity of TiO2 via different mechanisms because of the localized surface plasmonic resonance effect. Depending on the exact composition of the photocatalytic system, the exact mechanism of enhancement can include hot-electron injection, near-field enhancement, resonant photon-scattering, etc., as well as a combination of several of the above.[24–26] In constructing such highly active hybrid metal NP-TiO2 nanomaterials, it is important to control the size, morphology, and distribution of the doped metal NPs and to create intimate contact between them and the TiO2 surface.[2,20,27,28] While the first requirement can be met using pre-synthesized metal NPs combined with sol–gel methods, it is difficult to achieve a homogeneous distribution of the metal NPs within the TiO2 matrix.[28–30] The even bigger challenge for sol–gel methods which use pre-synthesized metal NPs is to create intimate contact between the TiO2 and metal NPs, since the metal NPs are normally covered by organic molecules that are introduced during the synthesis and/or added to stabilize them. This significantly decreases the photocatalytic efficiency of the final catalyst since the presence of organic ligands significantly reduces electron transfer between TiO2 and metal NPs.[21,27,31–33] Currently, the most efficient way to remove such organic ligands is through high temperature calcination.[34–36] However, delicate features of metal NPs that dictate the photocatalytic properties of hybrid nanomaterials can be lost during this process.[37–39]

In this report, we present a simple approach to fabricate robust, flexible, and lightweight metal-TiO2-polymer SENSs which are convenient to use and possess superior photocatalytic efficiency and durability. The procedure is straightforward and involves interfacial self-assembly of P25 TiO2 NPs followed by physical vapor deposition (PVD) of metal NPs. We show that interfacial self-assembly allows powdered TiO2 NPs to be deposited into a densely packed layer on a support for the formation of TiO2 SENSs which maximizes the proportion of the TiO2 NPs available for catalysis. The PVD process allows the metal NPs to be deposited uniformly and with direct control over their size and loading, without the need for surface-ligands. Since the self-assembly is also achieved without the use of organic ligands this approach creates intimate contact between metal and TiO2 NPs which allows for unhindered electron-transfer between them, maximizing the performance enhancement given by the metal NPs. The product metal-TiO2 SENSs were not only dramatically lighter and more flexible that standard commercial TiO2-based photocatalytic glass but they also out-performed it by a maximum of ≈18× in standard dye degradation experiments.

2. Results and Discussion

As illustrated in Figure 1, the key step in the formation of the required TiO2 (Evonik P25) SENSs is the assembly of TiO2 NPs at a liquid–liquid (water–dichloromethane) interface. While this can be achieved through surface modification of TiO2 NPs to tune their surface charge and/or hydrophobicity, this approach is undesirable since it will compromise the activity of TiO2 NPs.[8–10] Therefore, in this work non-adsorbing “promoter” molecules were added to the mixture. These “promoter” molecules dissolved in the organic layer and screened the charge on the surface of TiO2 NPs so they could assemble at the oil–water interface.[7,38–42] In practice, this assembly process simply involved shaking an aqueous dispersion of TiO2 NPs with dichloromethane, which contained micromolar concentrations of promoters (Figure 1, step 1, see Experimental Section for details). This created particle-coated emulsion droplets which coalesced to form a two-layer liquid system with a 2D array of TiO2 NPs at the interface (Figure 1, step 2). When polystyrene was pre-dissolved in the dichloromethane, subsequent evaporation of dichloromethane could lead to deposition of a layer of polystyrene onto the assembled particles on the side of the interface which the oil resided. This yielded a flexible polymer film carrying a densely packed monolayer of TiO2 particles on one side (Figure 1, step 3). The as-prepared TiO2 SENSs were very thin (≈2.5 μm thick as shown in Figure S1, Supporting Information) but physically robust, which allowed them to be handled and deployed easily in routine use, for example in the following treatment with metal sputtering and their eventual application as convenient photocatalysts.

The optical images of an as-prepared solid TiO2 SENS and its precursor colloid are shown in Figure 2a. While the TiO2 colloid appeared to be white and opaque, the as-prepared TiO2 SENS was almost colorless and transparent, suggesting that the SENS carried only a very thin layer of TiO2 NPs. In fact, inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis showed that there was only ≈0.8 g of TiO2 NPs per square meter of TiO2 SENS. This also explains the extremely weak TiO2 signals obtained from TiO2 SENSs in the following X-ray diffraction (XRD) analysis (Figure 2b). Despite being extremely weak, the XRD patterns obtained from TiO2 SENSs were identical to those obtained from TiO2 NPs, indicating that the preparation process had an
insignificant effect on the crystalline structure of the assembled TiO₂ NPs. The nanoscale morphology of the surface TiO₂ layer in the product TiO₂ SENSs was characterized using SEM. As shown in Figure 2c, the plan view of the surface of a typical TiO₂ SENS sample confirmed a densely packed and exposed layer of P25 TiO₂ NPs. The corresponding TEM image can be found in Figure S2, Supporting Information. To study the thickness of the TiO₂ layer, a crack at the edge of the SENS was probed with SEM at a tilted angle. As shown in Figure 2d, the SEM revealed a TiO₂ layer which was tens of nanometers thick. More importantly, the image clearly demonstrated that the TiO₂ NP layer sat on top of the polymer support and was therefore exposed for further functionalization or applications. The observed morphology is also consistent with our previous work which showed that for a range of different NPs the product SENSs contained particles which were partly anchored onto the polymer support with the bulk of their surfaces exposed. This morphology constitutes a significant advantage over conventional TiO₂ film catalysts where a large proportion of TiO₂ NPs are inaccessible during catalytic reactions since they are either buried within the substrate or beneath other layers of catalyst that sit closer to the surface.

Metal NPs were deposited onto the TiO₂ SENSs using PVD treatment, as shown in Figure 3a. Au NPs were used for proof-of-principle studies since Au is one of the most widely used electron-sink material for TiO₂ photocatalysts. In practice, our method is extremely versatile since PVD can be generally applied to introduce hundreds of different nanomaterials onto the TiO₂ SENSs under mild conditions within seconds. As shown in Figure S3, Supporting Information, the XRD and UV/Vis profile for TiO₂ SENSs sputtered with Au NPs were identical to bare TiO₂ SENSs, which suggested that Au was only present in extremely small amounts. To confirm the presence of Au NPs, XPS of the sputtered and bare TiO₂ SENSs was conducted. As shown in Figure 3b, XPS characterizations of the sputtered TiO₂ SENSs showed a distinct Au (0) peak at 83.2 eV (Au 4f7/2 peak), which was slightly down-shifted compared to the 84.0 eV value of bulk Au, indicating a lower oxidation state of the sputtered Au nanoparticles compared to bulk Au. Correspondingly, XPS characterization of Ti 2p peaks showed increased binding energies of Ti after Au sputtering, indicating a higher oxidation state of Ti, and more generally, suggesting strong interactions and electron-transfer between the Au and TiO₂ NPs (Figure 3b and Figure S4, Supporting Information). To study this effect, density functional theory (DFT) calculations were performed to simulate the interaction between an Au cluster and anatase TiO₂ {1, 0, 1} slab at room temperature. As shown in Figure 3d, the calculated adsorption energies of Au on a clean TiO₂ {1, 0, 1}, and defected TiO₂ {1, 0, 1} slab with an oxygen vacancy were −0.79 and −2.11 eV, respectively, which confirms the strong interaction between the Au and TiO₂ photocatalyst suggested by the XPS results.

Another significant benefit of the PVD process is that it allows the size and loading of metal NPs to be easily and reproducibly controlled with sputtering duration. The effect of Au sputtering was characterized by TEM, as shown in Figure 3d–f and Figure S5, Supporting Information. Since the polymer layer of the polymer-supported Au-TiO₂ SENSs was sufficiently thick to interfere with direct TEM analysis, the TEM samples were fabricated by scooping the interfacial TiO₂ arrays directly from the liquid–liquid interface with TEM grids. TiO₂ layers deposited on TEM grids were similar to those obtained with the polystyrene support but had lower uniformity and particle coverage (Figure S2, Supporting Information). Nonetheless they were sufficiently uniform to represent the actual TiO₂ surface on a TiO₂ SENS and allowed the size and distribution of Au NPs created by PVD deposition to be determined. For convenience, Au-sputtered TiO₂ samples are denoted Auₙ₋ₓTiO₂, where x represents the length of Au sputtering in seconds. Based on a count of 100 individual Au NPs, the size distribution of Au NPs for each sputtering time was obtained, which is shown in insets in Figure 3e–g and Figure S5, Supporting Information. The sizes of the Au particles increased from 2.8 ± 0.7 to 3.1 ± 0.9 and 6.5 ± 1.7 nm as the sputtering time was increased from 5 to 15 and then 30 s. The mass of Au deposited was determined using ICP-OES analysis and was found to rise from 1.67 to 6.85 and finally 11.27 μg cm⁻², which translates to 0.021, 0.086, and 0.141 g/g TiO₂. It is notable that at the longest sputtering time the deposited Au NPs became slightly irregular and polydisperse due to the growth and/or merging of Au NPs. However, this was not a significant issue since this did not occur at the 15 s, which gave the optimal catalytic efficiency (see below), and the overall picture is that sputtering offers a near ideal route to depositing small (~10 nm) and uniformly distributed Au NPs on the surface of TiO₂. This contrasts drastically with colloidal systems, where the presence of organic ligands and Ostwald ripening cause issues, and with systems with in situ generated particles, such as photo-deposition of Au NPs on the surface of TiO₂, where the morphology and uniformity of the deposited particles...
are uncontrolled, as demonstrated in Figure S6, Supporting Information. As a result, the Au$_x$-TiO$_2$ SENSs outperformed Au-TiO$_2$ SENSs prepared by photo-deposition in terms of reproducibility, catalytic efficiency, and durability, as shown in Figure S7, Supporting Information.

The photocatalytic activity of the metal-TiO$_2$ SENSs was measured by monitoring the photodegradation of methyl orange (MO) through the decrease in absorbance at the $\lambda_{\text{max}}$ of MO (465 nm), as shown in Figure 4a. The fact that the produced metal-TiO$_2$ SENSs were flexible and robust means that the photocatalytic mechanism of Au$_x$-TiO$_2$ under UV light irradiation.

Figure 3. a) Schematic illustration of the metal sputtering process on a TiO$_2$ SENS. b) XPS analysis of a TiO$_2$ SENS after 30 s of Au sputtering showing the characteristic peaks of Au 4f$_{5/2}$, 4f$_{7/2}$, and Ti 2p$_{1/2}$, 2p$_{3/2}$ at 83.2, 86.5, 464.54, and 458.84 eV, respectively. c) Calculated structures of Au clusters adsorbed on the {1, 0, l} facets of clean anatase TiO$_2$ surface (left) and anatase TiO$_2$ surface with an oxygen defect (right). Yellow, red, and grey spheres represent Au, O, and Ti, respectively. d–f) TEM images (scale bars 50 nm) showing the surface of TiO$_2$ SENS (assembled without a polymer support) and sputtered for d) 5 s, e) 15 s, and f) 30 s. Insets show measured diameters of deposited Au NPs, which correspond to 2.8 ± 0.7, 3.1 ± 0.9, and 6.5 ± 1.7 nm, respectively.

Figure 4. a) The change in the UV–vis spectrum of MO during photodegradation. b) Kinetic plots showing the photodegradation of MO catalyzed by TiO$_2$ SENSs sputtered with Au for the indicated times from 0 to 30 s. Histograms showing the rate constants for photodegradation of MO by TiO$_2$ SENSs sputtered with c) Au and d) Pt for the times indicated. e) Photocatalytic mechanism of Au$_x$-TiO$_2$ under UV light irradiation.
they can be folded to fit in practically any reaction containers, which in this case was a small sample vial containing 10 mL of MO solution (Figure S8, Supporting Information). Figure 4b shows that Au sputtering for any time between 5 and 30 s increased the rate of MO decomposition compared to the control TiO2 SENS. Apart from improvement in electron–hole separation efficiency, it has been shown that the enhancement in photocatalytic activity of metal-TiO2 systems might also arise from an improvement in adsorption properties.\textsuperscript{[45,46]} To study this the adsorption of MO on TiO2 and Au(15)-TiO2 SENSs were studied using UV–vis spectroscopy. As shown in Figure S9, Supporting Information, the adsorption kinetics and capacity of the TiO2 and Au(15)-TiO2 SENSs were found to be identical, which suggests that the enhancement in photocatalytic activity of the Au(15)-TiO2 SENSs arose mainly from improved electron–hole separation efficiency due to the Au NPs acting as electron sinks.

Figure 4c summarizes the photocatalytic activity of Au(15)-TiO2 SENSs with different Au sputtering times. These results were based on tests conducted with three different batches of metal-TiO2 SENSs. In general, the photocatalytic activity of the SENS increased as the length of Au sputtering was raised from 5 to 15 s. The maximum reaction rate constant for the degradation of MO was 1.95 × 10\(^{-3}\) min\(^{-1}\) cm\(^{-2}\) at 15 s of sputtering time, which was 4\(\times\) that of the control TiO2 SENSs (0.48 × 10\(^{-3}\) min\(^{-1}\) cm\(^{-2}\)). A further increase in the duration of Au sputtering, however, led to a decrease in photocatalytic activity. This may be due to the increase in recombination centers as the loading of Au NPs increased.\textsuperscript{[47]} In addition, the increase in Au NP loading can lead to reduction in exposed TiO2 surface. Since both Au and TiO2 are needed for catalyzing the degradation of MO, this means that the optimum amount of Au would be determined by the need to balance the number of electron sinks provided by the Au NPs with the amount of exposed area of TiO2 surface.\textsuperscript{[5,27]} Apart from this, increasing the surface coverage of Au NPs will also block more of the incoming light from reaching the TiO2 catalyst surface.\textsuperscript{[5,27]} In order to confirm that the degradation of MO arises from photocatalytic effect of the SENSs rather than from its direct absorption of UV photons, photocatalytic degradation of 4-chlorophenol which has low absorbance at 365 nm was studied under the same conditions. The results, shown in Figure S10, Supporting Information, were found to be similar to those obtained for MO.

The mechanism for photocatalytic degradation of MO is illustrated in Figure 4e. Upon UV illumination of Au(15)-TiO2 SENSs, electrons are excited from the valence band of TiO2 to the conduction band while generating holes in the valence band (Equation (1)). The excited electrons are then transferred rapidly to the Au NPs attached on the surface of TiO2. Presumably the transfer of electrons from TiO2 to Au does not significantly lower the reduction potential of photogenerated electrons, the reduction potential of photogenerated electrons equals to the energy level at the bottom of conduction band of TiO2, which is \(\approx -0.5\) V.\textsuperscript{[47–49]} Therefore, photogenerated electrons are capable of reducing MO directly or alternatively reacting with electron acceptors, such as O2, which is present on the catalyst surface, thereby generating superoxide radical anions (\(E_0 (O_2/ O_2^-) = -0.28\) V, Equation (2)). The superoxide radical anion can then react with H\(^+\) to form HO2\(^-\) radicals (Equation (3)).\textsuperscript{[47–49]}

\[ \text{TiO}_2 + h\nu \rightarrow \text{TiO}_2\left(\epsilon_{cb} + h_{vb}\right) \]  

(1)

\[ \text{TiO}_2\left(\epsilon_{cb}\right) + O_2 \rightarrow \text{TiO}_2 + O_2^- \]  

(2)

\[ O_2^- + H^+ \rightarrow HO_2^- \]  

(3)

\[ \text{TiO}_2\left(h\nu B^-\right) + H_2O \rightarrow \text{TiO}_2 + H^+ + OH^- \]  

(4)

\[ \text{TiO}_2\left(h\nu B^-\right) + OH^- \rightarrow \text{TiO}_2 + OH^- \]  

(5)

Similarly, since the oxidation potential of photogenerated holes is the energy level at the top of the valence band of TiO2 (which is \(\approx 2.7\) V), these photogenerated holes can either oxidize MO directly or react with H\(_2O\) or OH\(^-\) to form OH\(^+\) radicals (Equations (4) and (5)).\textsuperscript{[47–49]}

Since it is possible that OH\(^+\) radicals and O\(_2^-\) radicals were both involved in the photocatalytic degradation of MO, corresponding radical scavengers (benzoquinone for O\(_2^-\) radicals and tert-butyl alcohol for OH\(^+\) radicals) were added to MO solution to provide further insight into the photocatalytic mechanism. It was found that the addition of both scavengers led to decrease in MO degradation efficiency. The degradation efficiency dropped by over 80\% after addition of tert-butyl alcohol, indicating that OH\(^+\) played the main role in degrading MO in the current photocatalytic system.\textsuperscript{[50,51]}

To showcase the versatility of our approach Pt(10)-TiO2 SENSs were produced via the same procedure. The size and distribution of Pt NPs were determined by analyzing the corresponding TEM images (Figure S11, Supporting Information), which followed the same pattern as for the Au NPs discussed above. As a result, the general trends for the effect of Au and Pt sputtering were also found to be quite similar, in that the photocatalytic activity of three different batches of Pt(10)-TiO2 SENSs also showed a rise and then a fall with increased Pt sputtering time (Figure 4d). The increase in photocatalytic activity with Pt was found to be even higher than that observed with Au. This is most likely due to a larger difference between the work functions of Pt and TiO2 compared to Au and TiO2, which enables electron–hole pairs to be more efficiently separated in Pt(10)-TiO2 SENSs, thereby leading to significantly more enhanced photocatalytic activity.\textsuperscript{[52,53]} The maximum reaction rate constant for MO degradation with Pt(30)-TiO2 SENSs was almost 6\(\times\) (2.89 × 10\(^{-3}\) min\(^{-1}\) cm\(^{-2}\)) than that of TiO2 SENSs. Moreover, since we have previously shown that even the pure TiO2 SENSs were already \(3\times\) more photocatalytically active than their commercial counterparts, Pilkington Activ, this means the optimal Pt(10)-TiO2 SENSs are \(18\times\) more photocatalytically active than Pilkington Activ.

Apart from being highly photocatalytically active, the metal-TiO2 SENSs were also found to be stable under the UV irradiation conditions used for photocatalysis. Although it has been reported that polystyrene can be photo-oxidized by TiO2,\textsuperscript{[54]} our previous research suggested that the polystyrene side of these
TiO₂ SENSs remained unchanged after week-long intense UV irradiation.[7] Moreover, as shown in Figure 5a, due to the strong interaction between metal and TiO₂, the Au₁₅−TiO₂ SENSs can sustain at least four complete cycles of reaction without any noticeable changes to their photocatalytic activity. This is supported by the XPS results in Figure 5b, which show that the oxidation state of the Au NPs in the Au₁₅−TiO₂ SENSs remained unchanged even after 12 h of continuous reaction. Similarly, ICP-OES analysis revealed that there was a negligible change in the amount of Au on the sputtered film, which shows the excellent durability of the product SENSs (Table S1, Supporting Information).

3. Conclusions

In summary, we have shown a simple and rapid method to prepare highly photocatalytically active, light, and durable metal-TiO₂ SENSs under mild conditions. The hybrid SENSs contained a near monolayer of TiO₂ NPs anchored onto the surface of a thin, flexible polystyrene film support, with small (<10 nm) Au or Pt NPs distributed evenly on the TiO₂ surface. Importantly, our approach is completely ligand-free, which allows intimate contact between the metal NP electron-sinks and TiO₂ catalyst to be achieved without the need for any further processing steps. These properties combine to make the production of functional materials for direct applications.

4. Experimental Section

Chemicals: P25 TiO₂ colloids (40 wt%) were supplied by Evonik Industries AG. Chloroaic acid (HAuCl₄·3H₂O), polystyrene (M.W. ≈192,000), tetrabutylammonium nitrate (TBA⁺NO₃⁻), 4-chlorophenol, MO, and dichloromethane were purchased from Sigma Aldrich and used without further treatment. All solutions were prepared from distilled, deionized water (resistivity = 18.2 MΩ). 

Preparation of TiO₂ SENSs: Polymer-supported TiO₂ SENSs were prepared using the self-assembly method previously reported by our group with slight modifications.[7] Typically, 5 mL of TiO₂ colloids which were diluted by a factor of 2000 were mixed with 0.14 mL of 1 mmol of TBA⁺NO₃⁻ and 3 mL of polystyrene/dichloromethane (0.06 g mL⁻¹) solution. The mixture was vigorously shaken for ~1 min to facilitate the migration of TiO₂ NPs to the surface of emulsion droplets. After shaking, the emulsion droplets covered with TiO₂ NPs were poured immediately into a petri dish covered with a lid to prevent solvent evaporation. After all the emulsion droplets had coalesced to form an interfacial 2D array of TiO₂ NP-clusters, the cover of the petri dish was removed to allow evaporation of dichloromethane at room temperature, which led to the deposition of a thin polystyrene film on the TiO₂ array at the interface. After complete evaporation of the dichloromethane phase, solid TiO₂ SENSs were mounted onto Sellotape for further characterizations and applications.

Preparation of Au/Pt Sputtered TiO₂ SENSs: Au NPs were sputtered onto TiO₂ SENSs using a plasma-assisted reactive direct current sputtering deposition (PAR-DC-MS) system. The sputtering process was carried out at room temperature and in argon environment with a constant pressure of 7 × 10⁻² kPa and a constant current at 30 mA. 

Preparation of Au/Pt TiO₂ SENSs via Photo-Deposition: Au NPs were synthesized by illuminating the surface of a 5 cm² TiO₂ SENS immersed in 2 mL of 10⁻³ M HAuCl₄·3H₂O aqueous solution using a UV lamp with a peak wavelength at 365 nm and an overall output of 1.05 W. The distance from the lamp to the surface of the TiO₂ SENS was kept constant at 5 cm. 

Degradation of MO/4-chlorophenol under UV Light: In a typical experiment, an Au/Pt deposited TiO₂ SENS was mounted on Sellotape and immersed in 10 mL of 1 × 10⁻³ M MO (or 1 × 10⁻⁴ M 4-chlorophenol) solution in the dark for 1 h to reach adsorption equilibrium. The sample solution containing the catalytic SENS was then irradiated continuously using a UV-LED (forward voltage of 3.5 V DC; forward current of 0.3 A; overall power of 1.05 W) under constant stirring. The wavelength of the LED was centered at 365 nm. 2.5 mL of solution sample was taken every 15 (60) min to be analyzed using a Perkin Elmer Lambda 800 UV–vis spectrometer to monitor the degradation of MO (4-Chlorophenol).
were carried out in the canonical (NVT) ensemble employing Nose-
Henderson thermostat. After equilibration, MD trajectories were saved every 10 ps for the next 20 ps of production run, to generate a total of 200 frames per molecule. The simulations were then analyzed using the Gromacs utilities. The diffusion coefficient was calculated using Einstein's relation, which is defined as the ratio of the mean square displacement (MSD) of the center of mass of the molecule to the time, assuming a random walk of a point mass, as follows:

\[ D = \frac{\langle r^2(t) \rangle}{6t} \]

where \( D \) is the diffusion coefficient, \( \langle r^2(t) \rangle \) is the mean square displacement of the center of mass, and \( t \) is the time interval. The MSD was calculated as the average of the squares of the displacements of the center of mass of the molecule at different time intervals.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

X.L. and Y.X. contributed equally to this work. All authors have given approval to the final version of the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

2D nanoparticle arrays, photocatalysis, self-assembly, sputtering, TiO₂.

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