Effect of Au Antidot Array Pore Size on Photocatalytic Performance of Au/TiO2 Composite Thin Films Postprint

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Abstract

Through inverse replication of colloidal crystal templates, Au/TiO composite thin films with varying antidot array apertures were prepared. The structure and photocatalytic properties of the composite thin films were characterized by means of SEM, AFM, XRD, UV-Vis spectroscopy, and four-point probe measurements. By calculating geometric models of the colloidal crystal template and antidot array, the relationship between the coverage area of Au antidot arrays on the TiO thin film surface and the microsphere diameter in the template was discussed. The results demonstrate that the antidot array aperture exerts a significant influence on the photocatalytic performance of the composite thin films. An increase in aperture enhances the electrical conductivity of the antidot array and improves charge carrier transport efficiency, thereby promoting photocatalytic performance; concurrently, however, the larger aperture also increases the recombination probability of photogenerated electrons during their migration toward the antidot array, which conversely diminishes photocatalytic performance. The interplay of these two effects leads to a variation pattern wherein the photocatalytic performance of the Au/TiO composite thin films initially increases and subsequently decreases with increasing aperture of the Au antidot array, reaching its optimum at an aperture of 3.3 m.

Full Text

Preamble

Effect of Pore Sizes of Au Antidot Arrays on Photocatalytic Performance of Au/TiO Composite Films

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Abstract

Au/TiO composite films with varying pore sizes of antidot arrays were fabricated through inverse replication of colloidal crystal templates. The microstructure and photocatalytic performance of the composite films were characterized using SEM, AFM, XRD, UV-Vis spectroscopy, and four-point probe measurements. By calculating geometric models of the colloidal crystal templates and antidot arrays, the relationship between the coverage area of Au antidot arrays on the TiO film surface and the diameter of template microspheres was discussed. The results demonstrate that the pore size of Au antidot arrays significantly influences the photocatalytic performance of the composite films. As pore size increases, the conductivity of the antidot arrays improves and charge carrier transport efficiency enhances, which promotes photocatalytic performance. However, simultaneously, the increased pore size raises the recombination probability of photogenerated electrons during their migration toward the antidot arrays, thereby reducing photocatalytic performance. The combined effect of these two competing mechanisms leads to a non-monotonic variation in photocatalytic performance with pore size, which first increases and then decreases, reaching its maximum at a pore size of 3.3 m.

Keywords: Au antidot arrays, TiO , pore size, photocatalytic performance

TiO photocatalytic materials can degrade and mineralize pollutants in water and air using low-density solar energy and can also convert low-density solar energy into high-density hydrogen energy, showing tremendous potential for addressing energy and environmental challenges. In recent years, TiO has demonstrated broad application prospects in pollutant degradation, air purification, anti-fogging, self-cleaning, and solar photoelectric conversion. The TiO photocatalytic process derives its energy entirely from sunlight, making it a truly energy-saving and green technology. As calls for developing a "low-carbon economy" and "circular economy" grow louder, the use of photocatalytic materials for environmental purification and new energy development has become a major focus of competition in high-tech sectors worldwide. However, TiO suffers from a high recombination probability of photogenerated electron-hole pairs, resulting in low quantum efficiency and slow overall reaction rates, which significantly limits its practical applications.

Noble metal modification is an effective approach to enhance TiO photocatalytic efficiency, with Au, Ag, Pd, and Pt being the most commonly used metals. The difference in work functions between TiO and noble metals creates a Fermi level mismatch that drives electron migration from the semiconductor to the metal, promoting carrier redistribution at the catalyst surface and achieving photogenerated carrier separation. Conventional modification methods include sol doping, metal ion implantation, and co-sputtering surface modification, all of which involve embedding noble metal clusters either within the material bulk or onto the TiO surface. However, several problems exist with these approaches. First, metal clusters embedded in the bulk cannot contact external reactants and thus cannot release separated electrons; instead, the charged metal clusters become recombination centers for holes, reducing quantum efficiency. Second, randomly distributed noble metal particles on the TiO surface are disconnected from each other, leading to severe redox reaction imbalance during photocatalysis—holes are consumed extensively on the TiO surface while electrons accumulate on the noble metal surface, creating recombination centers that fail to significantly improve quantum efficiency. Additionally, the disordered and random distribution of noble metal particles reduces controllability and reproducibility in research, making underlying patterns difficult to discern. Therefore, precise controlled design and synthesis of noble metal structures for photocatalyst surface modification to efficiently suppress electron accumulation warrant in-depth investigation.

Based on these considerations, this work employs colloidal crystal template technology to design and controllably modify TiO film surfaces with Au antidot arrays, aiming to enhance carrier mobility and mutual utilization among TiO particles. By varying the microsphere diameter in the templates, Au/TiO composite films with antidot pore sizes ranging from 1.3 to 5.6 m were synthesized. Through geometric model calculations of the colloidal crystal templates, the relationship between antidot array coverage area and pore size was discussed. Combined with surface morphology analysis and photocatalytic performance testing, the influence of pore size variation on photocatalytic performance was investigated.

Experimental Methods

TiO films were prepared via a sol-gel method. Ten milliliters of tetrabutyl titanate (C H O Ti) were added to 60 mL of anhydrous ethanol (C H O). After uniform dispersion, appropriate amounts of concentrated hydrochloric acid (HCl), acetylacetone (C H O), and distilled water were sequentially added to obtain a TiO sol with suitable viscosity. Films were deposited on quartz substrates using dip-coating at a withdrawal speed of 0.5 mm/s, with a coating temperature of 25 °C and humidity of 30%. After several cycles of drying-dipping-withdrawal, TiO films were obtained and annealed at 450 °C for 2 h.

Monodisperse polystyrene (PS) microspheres with diameters of 1.6, 2.9, 4.1, 5.2, and 7.0 m were used, prepared according to reference [20]. In a 250 mL crystallizing dish, 200 mL of deionized water was injected, and a stable vortex was formed under magnetic stirring. PS microsphere emulsion was slowly dropped onto the vortex until the water surface was fully covered. Stirring was then stopped, allowing the liquid surface to return to a planar state, whereupon the microspheres self-assembled into a dense, ordered monolayer under contraction forces. The TiO film was then vertically immersed into the liquid surface, withdrawn at a constant speed after 1 min, and dried at 80 °C for 10 min to obtain an ordered monolayer colloidal crystal template on the TiO film surface. Au was sputtered onto the template surface using an FJL560 ultra-high vacuum sputtering system. After evacuating to a base pressure of 1×10 Pa, pure Ar gas was introduced at a flow rate of 20 mL/min for 5 min of sputtering. The antidot array morphology was modulated by varying the PS microsphere diameter. The sample was ultrasonicated in tetrahydrofuran solution for 10 min to remove the template, followed by ultrasonic rinsing in acetone and deionized water, yielding a series of Au/TiO composite films with different pore sizes. A schematic diagram of the structure is shown in [Figure 1: see original paper].

The microstructure of the composite films was observed using an FEI-SIRION scanning electron microscope (SEM), with composition of the Au antidot arrays analyzed by energy-dispersive spectroscopy (EDS). The height of Au antidot arrays on the TiO film surface was measured using a CSPM4000 atomic force microscope (AFM). Crystal structure was examined using an X Pert Pro automated X-ray diffractometer (XRD) with Cu K radiation at a scanning step of 0.02°/s. Sheet resistance was measured using a D41-3 four-point probe system. Photocatalytic performance was evaluated using a U-3010 UV-Vis spectrophotometer: samples were placed in 3 mL of methylene blue (MB) solution (5 mg/L) and irradiated for 1 h using a 20 W UV-254 lamp positioned 30 cm above the solution surface, with the sample 0.5 cm below the liquid surface. The degradation rate was calculated from the absorbance of the remaining solution.

Results and Discussion

2.1 Structure and Microstructure

The TiO film preparation involved multiple cycles of dipping-withdrawal-drying followed by annealing, resulting in a morphology consisting of discrete nanoparticles with uniform grain sizes of 30–40 nm, as shown in [Figure 2a: see original paper]. The self-assembled monolayer colloidal crystal on the film surface, shown in [Figure 2b: see original paper], exhibited no defects such as vacancies, dislocations, or particle stacking, demonstrating a highly ordered hexagonal close-packed arrangement over large areas.

The XRD pattern of the TiO film is presented in [Figure 3: see original paper]. The main diffraction peaks at 25.35°, 37.78°, 48.07°, 53.92°, and 55.11° correspond to the (101), (004), (200), (105), and (211) crystal planes of anatase TiO , respectively, with the (101) peak being the strongest. This indicates that the prepared TiO film is anatase phase. The grain size was calculated using the Scherrer formula:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where D is the average grain size, k is the Scherrer constant, λ is the incident X-ray wavelength, β is the full width at half maximum of the diffraction peak, and θ is the Bragg angle. The calculated grain size is approximately 34 nm, consistent with the SEM results.

SEM images of Au antidot arrays on TiO film surfaces are shown in [Figure 4: see original paper], with pore sizes of 1.3, 2.3, 3.3, 4.2, and 5.6 m. The microstructure exhibits high long-range order, with each pore surrounded by six neighboring pores in a regular hexagonal arrangement. The pores are circular, and the inter-pore regions consist of fine metal particles identified as Au by EDS analysis. SEM measurements reveal that both pore size and spacing are directly proportional to the PS microsphere diameter, with pore spacing equal to approximately one-fifth of the corresponding microsphere diameter.

2.2 Photocatalytic Performance

MB solution exhibits a distinct absorption peak at 664 nm in the visible light region, which decreases during photocatalytic reaction. Therefore, photocatalytic performance can be evaluated by measuring the absorbance of MB solution before and after degradation. [Figure 5a: see original paper] shows the absorption spectrum of the original MB solution, with an absorbance of 1.44 at 664 nm before reaction. After 1 h of degradation by the composite photocatalysts, the absorbance at 664 nm decreased to below 0.3 for all samples, significantly lower than that obtained with TiO film alone, as shown in [Figure 5b: see original paper]. These results demonstrate that Au antidot arrays substantially enhance the photocatalytic performance of TiO films.

In the low concentration range, the absorbance of MB solution is proportional to its mass concentration, following the Lambert-Beer law:

$$A = Kcb$$

where A is absorbance, K is the concentration proportionality coefficient, c is the mass concentration, and b is the solution thickness. The degradation rate can be calculated using:

$$\eta = \frac{c_0 - c_1}{c_0} \times 100\% = \frac{A_0 - A_1}{A_0} \times 100\%$$

where η is the degradation rate, c_0 and c_1 are the initial and final mass concentrations, and A_0 and A_1 are the initial and final absorbance values.

The relationship between antidot array pore size and degradation rate is shown in [Figure 6: see original paper]. The degradation rate increases rapidly with pore size, reaching a maximum of 88.7% at a pore size of 3.3 m. Further increasing the pore size leads to a noticeable decrease in degradation rate. These results indicate that antidot array pore size significantly affects the photocatalytic performance of the composite films. Additionally, the degradation rate of bare TiO film is only 58.1%, while all composite photocatalysts achieve rates above 80%, demonstrating superior performance.

3.1 Theoretical Calculation

The geometric model of a two-dimensional colloidal crystal template is illustrated in [Figure 7a: see original paper]. The prepared colloidal crystals exhibit highly ordered hexagonal close-packing over large areas, as shown in [Figure 2b: see original paper]. This close-packed structure can be modeled as an ordered array of equilateral triangles, where the side length equals the PS microsphere diameter. When metal is deposited in the interstices of the microsphere template and the template is subsequently removed, assuming Au deposits only in the gaps between close-packed microspheres, the minimal coverage of antidot arrays on the TiO surface can be determined by calculating the ratio of the microsphere gap area (shaded region in [Figure 7a: see original paper]) to the equilateral triangle area. The minimal coverage Ψ_1 can be expressed as:

$$\Psi_1 = \frac{S_\Delta - S_1}{S_\Delta} = \frac{S_\Delta - 3S_2}{S_\Delta} = 1 - \frac{\pi}{2\sqrt{3}} \approx 0.0931$$

where S_Δ is the area of the equilateral triangle, S_1 is the area occupied by Au antidot arrays within the triangular region, S_2 is the area of the sector region, and d_1 is the PS microsphere diameter.

Equation (4) shows that under conditions where antidot arrays are disconnected, the minimal coverage Ψ_1 is a constant independent of microsphere diameter. However, under magnetron sputtering conditions, high-voltage-accelerated Ar bombardment of the target produces Au atoms with high momentum that can diffract through the template gaps during deposition, resulting in Au deposition beneath the microspheres and forming interconnected antidot array structures, as shown by the shaded region in [Figure 7b: see original paper]. With constant sputtering parameters, the antidot array spacing (r) is directly proportional to the PS microsphere diameter (d_1) with a constant ratio: $r = d_1/n$ (where n is a non-zero constant). Since the antidot array diameter $d_2 = d_1 - r$, the actual coverage Ψ_2 can be expressed as:

$$\Psi_2 = \frac{\pi(d_1 - r)^2}{2\sqrt{3}d_1^2} = \frac{\pi(1 - 1/n)^2}{2\sqrt{3}}$$

Thus, the actual coverage Ψ_2 is also independent of PS microsphere diameter. Therefore, with constant magnetron sputtering parameters, the coverage area of Au antidot arrays on the TiO surface remains constant regardless of microsphere diameter.

3.2 Sheet Resistance of Antidot Arrays

Pore size significantly affects the sheet resistance of the composite photocatalysts. As pore size increases from 1.3 m to 5.6 m, the sheet resistance decreases from 107 Ω/ to 9.4 Ω/ , as shown in [Figure 8: see original paper]. These results indicate that the conductivity of Au antidot arrays gradually improves with increasing PS microsphere diameter, with the improvement trend slowing after the pore size reaches 3.3 m.

3.3 Height of Antidot Arrays

AFM was used to investigate the height of Au antidot arrays. [Figure 9: see original paper] shows the AFM analysis results for a composite film with a pore size of 2.3 m. Line scanning across the film surface, as indicated in [Figure 9a: see original paper], reveals the height variation of antidot arrays on the TiO surface, shown in [Figure 9b: see original paper]. The lowest and highest points correspond to the centers of pores and pore skeletons, respectively. For the 2.3 m pore size, the antidot array height on the TiO film surface is 49.2 nm.

Similar analysis was performed for other pore sizes, with the relationship between array height and PS microsphere diameter shown in [Figure 10: see original paper]. The height increases gradually with microsphere diameter, following the linear equation:

$$H = 0.017d_1 + 0.002$$

where H is the array height, with an adjusted R-squared value of 0.99629. The array height exhibits an excellent linear relationship with microsphere diameter, approximately equal to 1/59 of the microsphere diameter. Since the microstructure of Au antidot arrays is an inverse replica of the colloidal crystal template, larger microspheres create larger interstitial voids, providing greater space for Au atom diffraction during deposition and enabling higher and wider Au deposition on the TiO film surface. This linear increase in both height and width is the fundamental reason for the variation in sheet resistance with pore size.

3.4 Mechanism of Pore Size Effects

The combination of Au antidot arrays with TiO films creates a dense, ordered conductive network on the film surface. Photogenerated carriers on TiO particle surfaces can be rapidly separated and transported, preventing electron accumulation on the semiconductor surface and enhancing carrier mobility and photon utilization efficiency. Consequently, Au antidot arrays significantly improve the photocatalytic performance of TiO .

[Figure 11: see original paper] illustrates charge carrier migration within antidot array pores. Since pore sizes are on the micrometer scale while TiO particles are only tens of nanometers, each pore contains dozens or even hundreds of

TiO particles. For simplicity, the carrier migration behavior at TiO particles A, B, C, and D is considered. Upon UV excitation, electron-hole pairs are generated in the TiO particles within the pores. Photogenerated electrons must transfer through adjacent particles to reach the antidot arrays. During this migration, electrons generated at particle B can easily recombine with holes at particle A, and electrons at particle C can recombine with holes at particle D, dissipating light energy as heat or other forms and causing energy loss. Only electrons at particles A and D can reach the antidot arrays through adjacent particles. Since pore size increases on the micrometer scale, the number of TiO particles within each pore increases by 20–30 with increasing pore size. Therefore, photogenerated electrons have a higher probability of recombining with holes in adjacent particles during migration toward the antidot arrays. Overall, this increases the carrier recombination probability in the TiO film, leading to greater energy loss and reduced degradation efficiency and photocatalytic performance. On the other hand, increasing pore size rapidly enhances the conductivity of antidot arrays, facilitating electron transport and improving carrier transport efficiency, which increases degradation efficiency and photocatalytic performance. The combined effect of these two competing mechanisms results in the observed non-monotonic variation in photocatalytic performance with pore size, reaching a maximum at 3.3 m.

Conclusions

1. Au antidot arrays on TiO film surfaces exhibit a highly ordered hexagonal close-packed structure. Both the height and width of antidot arrays increase linearly with PS microsphere diameter. The coverage area of Au antidot arrays on TiO film surfaces remains constant and does not vary with microsphere diameter.
2. The degradation rate of MB solution by composite films shows a non-monotonic trend with increasing Au antidot array pore size, reaching a maximum at a pore size of 3.3 m. All composite photocatalysts achieve degradation rates above 80%, significantly outperforming bare TiO film (58%).
3. Sheet resistance decreases with increasing Au antidot array pore size, indicating rapidly improved conductivity. This enhances carrier transport efficiency in the antidot arrays, thereby improving degradation efficiency and photocatalytic performance.
4. Increasing Au antidot array pore size raises the recombination probability of photogenerated electrons during migration toward the antod arrays, reducing the photocatalytic performance of composite films.
5. The combined effects of conductivity variation in Au antod arrays and changes in the number of TiO particles within array pores lead to the observed non-monotonic variation in photocatalytic performance with pore size.

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Note: Figure translations are in progress. See original paper for figures.