Research Article

Anodic Titanium Oxide Layers Modified with Gold, Silver, and Copper Nanoparticles

Karolina Syrek, Joanna Grudzień, Aneta Sennik-Kubiec, Anna Brudzisz, and Grzegorz D. Sulka

Department of Physical Chemistry and Electrochemistry, Faculty of Chemistry, Jagiellonian University in Krakow, Gronostajowa 2, 30-387 Krakow, Poland

Correspondence should be addressed to Grzegorz D. Sulka; sulka@chemia.uj.edu.pl

Received 26 July 2018; Revised 15 October 2018; Accepted 22 October 2018; Published 7 February 2019

Titanium(IV) oxide is commonly used in photocatalysis. However, it has some drawbacks, e.g., a high rate of electron-hole recombination and a wide bandgap. In here, the surface of anodic titanium(IV) oxide (ATO) was modified with metal nanoparticles (gold, silver, and copper) in order to enhance its photoelectrochemical (PEC) and photocatalytic (PC) properties. SEM analysis revealed that Au, Ag, and Cu nanoparticles obtained on an ATO surface by chemical methods had an average diameter of 50 ± 10 nm, 30 ± 6 nm, and 25 ± 3 nm, respectively. Enhancement of photoelectrochemical water-splitting current efficiency in the wavelength range of 300–400 nm was observed due to the occurrence of the Schottky barriers. However, the nanoparticles had no effect on the current efficiency in the range of 400–600 nm which meant that the surface plasmon resonance (SPR) effect was not observed. A rate of methyl red photodecomposition was improved after the modification of the ATO surface. The best results were obtained for ATO decorated with gold nanoparticles.

1. Introduction

Titanium(IV) oxide is an n-type semiconductor that is known from its good stability, high resistance to corrosion, nontoxicity, biocompatibility, and low cost of production. Due to these properties, TiO₂ is widely used in medicine, industry, and the military. Recently, titanium(IV) oxide nanostructures, like nanoparticles [1], nanowires [2], nanorods [3], nanotubes [4], or nanopores [5] are being intensively studied because of their unique properties. They can be obtained by methods such as the sol-gel process [6], solvothermal synthesis [7], electrodeposition [8], and anodization [4, 5, 9]. Among those techniques, anodic oxidation of titanium substrate is favorable due to the possibility of obtaining highly ordered nanostructures in a simple, non-time-consuming, and low-cost production way. What is more, dimensions (tube length and diameter) of those structures can be easily controlled by several parameters, like external voltage, time, temperature, and type and composition of the electrolyte [10–13].

As is well known, TiO₂ is commonly used in photocatalysis due to its ability to absorb the UV irradiation. It is possible because of the value of its bandgap, which is 3.2 eV and 3.0 eV for anatase and rutile, respectively [14, 15]. When a semiconductor absorbs UV light, an electron from the valence band is excited to the conduction band. Simultaneously, an electron hole is created in the valence band. Then, electron-hole pairs can recombine, but this process is undesirable. What is beneficial from the point of view of photocatalysis is that electrons and holes, responsible respectively for reduction and oxidation reactions, can migrate to the surface of a material and react with adsorbed compounds, e.g., water molecules [16]. What is worth mentioning is the fact that the band edge positions of conduction and valence bands of the efficient photocatalyst have to be close to the redox potential of the adsorbed species. For titanium(IV) oxide, those band edges
are located near the redox potential of water molecules [15]. As a result of the reaction occurring at the surface of the catalyst, highly reactive oxygen species, e.g., radicals are produced which can react in the next step with other compounds from the electrolyte.

Despite the advantages mentioned above, TiO$_2$ has some crucial drawbacks that limit its utilization in photocatalytic processes. Titanium(IV) oxide has a wide bandgap which allows absorbing light only from the UV range. On the other hand, the solar spectrum consists of approximately 5% of UV and 40% of visible light. That is why TiO$_2$ cannot be used as a photocatalyst under sunlight irradiation which would have been preferable in terms of lowering processing costs. Additionally, the rate of electron-hole recombination is high and significantly decreases photocatalytic efficiency. In order to extend potential applications of TiO$_2$, numerous modifications have been performed that expand the spectrum of the light absorption and enhance the efficiency of photocatalysis and photoelectrolysis [17]. Strategies are based on, e.g., nonmetal [18, 19] and metal [20, 21] doping, coupling with other semiconductors [22, 23], and surface decoration with nanoparticles [24, 25].

The decoration of the TiO$_2$ surface with metal nanoparticles can be made by using photo- or electrodeposition, precipitation, and ion-exchange techniques. The most commonly used metals are noble metals (Au, Ag, and Pt [24–26]) and some transition metals (Ni, Fe, and Cu [27–29]). It is well known that coupling some metals with the semiconductor results in Schottky junctions at their interface [30]. This phenomenon is described as a flow of electrons from the semiconductor to the metal, that leads to bending of the energy bands of the semiconductor. The presence of the Schottky barrier prevents a return of electrons to the semiconductor. In other words, electrons can be trapped into the metal, and thus the rate of recombination of the electron-hole pair is reduced. That is why this type of junction can enhance photocatalytic and photoelectrochemical efficiencies. Paramasivam et al. [24] compared the photocatalytic efficiency of the degradation of acid orange 7 on an unmodified flat TiO$_2$ film and nanotubular anodic TiO$_2$ with anodic TiO$_2$ nanotubes decorated with gold and silver nanoparticles. It was found, that in the presence of the catalyst loaded with noble metal nanoparticles the rate of dye degradation significantly increased.

On the other hand, the second phenomenon that can occur at the metal-semiconductor interface is the surface plasmon resonance (SPR). Surface plasmons are defined as the collective oscillation of conduction electrons (surface plasmons) at the interface between a metal and other materials. Under light irradiation, charge-density oscillations might occur and the formation of the electric field can be observed [31]. Metals such as gold [32], silver [33], and copper [34] are known for their ability to undergo the SPR effect. According to the literature, there are three possible mechanisms of the SPR that may have an influence on photocatalytic reactions, namely scattering of resonant photons by metal, plasmon resonance energy transfer, and hot electron transfer [31, 35–37].

Silver, gold, and copper nanoparticles, which are characterized by the presence of absorption bands at 400 nm, 520 nm, and 580 nm, respectively, are of particular interest [38]. Zhao et al. [39] studied the effect of size, distribution, and morphology of gold-covered TiO$_2$ nanotubes on their photoelectrochemical properties. The theoretical calculations and experimental results confirmed that the SPR effect led to a significant increase in the magnitude of generated photocurrents. Other examples of the effect of nanoparticle deposition on photoelectrochemical and/or photocatalytic properties are presented in Table 1.

In this work, we present the photoelectrochemical and photocatalytic properties of anodic titanium(IV) oxide decorated with chemically deposited metal nanoparticles. The anodic materials were compared in terms of the morphology, amount of nanoparticles on the oxide surface, generated photocurrent at different wavelengths and applied potentials, and rate of methyl red decolorization. Additionally, we showed whether the SPR effect or Schottky barrier occurs during surface modification of anodic TiO$_2$ under the proposed experimental conditions.

### 2. Materials and Methods

#### 2.1. Synthesis of Anodic Titanium Oxide (ATO)

Titanium foil (99.5% purity, 0.25 mm thick) was polished electrochemically,
and then chemically [46]. The anodization process was carried out in a two-electrode cell, where the polished Ti sample was used as an anode, and a titanium plate was used as a cathode. Electrodes were kept at the constant distance of 2 cm. nanoporous anodic titanium oxide layers were synthesized in an ethylene glycol-based solution containing NH₄F (0.38 wt.%) and H₂O (1.79 wt.%). A three-step anodization was carried out at the constant voltage of 40 V at 20°C. The first and second anodizing steps lasted 3 h, and after each step, an adhesive tape was used to remove the resulting oxide layer. The third anodizing step was carried out for 10 min in a freshly prepared electrolyte. Each anodizing step was performed at the constant stirring rate of 200 rpm [47]. Afterwards, TiO₂ samples were annealed in air at 500°C for 2 h with a heating rate of 2°C min⁻¹ using a muffle furnace (FCF 5SHM Z, Czylok) [48].

The morphology of ATO layers was characterized using a field emission scanning electron microscope (SEM, Hitachi S-4700).

2.2. Deposition of Nanoparticles. Copper nanoparticles (CuNPs) were deposited using a SILAR method [41]. In the first step, anodic TiO₂ was immersed in a 0.01 M copper (II) acetate solution for 10 min. Then, the sample was rinsed with distilled water and placed in a 0.01 M NaBH₄ solution for 10 min. This cycle was performed five times. Silver nanoparticles (AgNPs) were synthesized using the citrate method [41]. The same volume (5 mL) of 1 mM silver nitrate solution and 1 mM sodium citrate were mixed together in a beaker and placed in an ultrasonic bath. Anodic TiO₂ was immersed in the solution and 2.5 mL of a 0.01 M sodium borohydride solution was added dropwise. Finally, ATO was rinsed with water and dried in air. Gold nanoparticles (AuNPs) were obtained in a mixture of 1 mM sodium citrate and 1 mM chloroauric acid(III) (3:1 in vol.) heated to 60°C. Anodic TiO₂ was immersed in the mixture, and 1 mL of 0.01 M sodium borohydride was added. The samples were rinsed with water and dried in air.

In order to confirm the presence of gold and silver nanoparticles, the postreaction solutions were analyzed by using a UV-Vis spectrophotometer (Evolution 220, Thermo Fisher Scientific). UV-Vis spectra of Au and Ag nanoparticles were recorded against distilled water in the range of 200–780 nm.

2.3. Photoelectrochemical Measurements. Photoelectrochemical measurements were performed using a three-electrode cell with a quartz window, where the nanostructured ATO layer was used as a working electrode (WE), a platinum foil was used as a counter electrode (CE), and a Luggin capillary with a saturated calomel electrode (SCE) was used as a reference electrode. The generated photocurrents were measured using a photodlectric spectrometer (Instytut Fotonowy, Poland) equipped with the 150 W xenon arc lamp and combined with a potentiotstat [47, 48]. The photoelectrochemical characterization was carried out in 0.1 M KNO₃ at the potential range of 0–1 V vs. SCE and wavelengths ranging from 200 to 800 nm. Incident photon to charge carrier efficiency (IPCE) was calculated from the following equation [49]:

\[ IPCE = \frac{I_p(\lambda)}{P(\lambda) A} \cdot 1240, \]

where \( I_p(\lambda) \) and \( P(\lambda) \) are the photocurrent density (A m⁻²) and incident power density of light (W m⁻²), respectively, at wavelength \( \lambda \) (nm). The constant of 1240 has the unit W nm A⁻¹.

2.4. Photocatalytic Tests. Photodegradation of methyl red, MR (pure p. a., POCH S.A.), was carried in a UV reactor (Instytut Fotonowy, Poland) consisting of 20 UV-A lamps (160 W). All experiments were performed using a 5 mg L⁻¹ dye solution in 0.01 M HCl. For the photodegradation tests, 10 mL of the MR solution was used. During experiments, at given reaction intervals, the concentration of dye was determined spectrophotometrically (Evolution 220 UV-Vis Spectrophotometer, Thermo Scientific) in the range of 200–600 nm. The percentage of dye loss (DEG%) was determined using the following equation:

\[ \text{DEG} = \left( \frac{C_0 - C_i}{C_0} \right) \cdot 100\%, \]

where \( C_0 \) is the initial MR concentration and \( C_i \) is the MR concentration after illumination.

3. Results and Discussion

Typical morphology of anodic TiO₂ layers obtained by three-step anodization at the potential of 40 V is shown in Figure 1(a). Such nanostructures are characterized by a top porous layer and nanotube structure in cross-sectional view (Figure 1(a) insert). A thickness of the oxide layers was 2.2 ± 0.2 μm. The surface of anodic TiO₂ layers with deposited copper, gold, and silver nanoparticles is presented in Figures 1(b)–1(d), respectively. Prior to the deposition of noble metal nanoparticles, titanium oxide layers were heat treated at 500°C in order to transform amorphous oxide into the anatase phase [48].

As shown in Figure 1, nonaggregated nanoparticles are randomly distributed over the ATO surface regardless of the type of deposited metal. The presence and distribution of nanoparticles on the surface of ATO layers was confirmed by EDS analyses (Figures 2 and 3), and the content of metals was different depending on the applied method of synthesis. The size of metal nanoparticles was estimated on the basis of SEM micrographs. In the case of copper nanoparticles obtained by the SILAR method, the average diameter equal to 50 ± 10 nm, and the copper content in the ATO layer was found to be 0.4 at.%. The deposited gold nanoparticles have the average diameter of 30 ± 6 nm, and the Au total content of 2.2 at.% was estimated in the sample. The average size of silver nanoparticles was 25 ± 3 nm, and the Ag content determined by EDS was about 0.1 at.%. According to XPS studies performed for similar anodic materials [42, 50, 51], there are no chemical bonds between a noble metal and Ti. After deposition of Au and Ag nanoparticles on the surface of ATO layers, the solutions with metal nanoparticles were subjected to
spectrophotometric analyses (Figure 3). The obtained spectrum characterized by maximum absorbance at approx. 520 nm (Figure 3(a)) confirms the presence of gold nanoparticles. A similar analysis performed for a solution containing silver nanoparticles revealed that AgNPs absorb at approx. 400 nm, which is in good agreement with the literature reports [52]. For both nanoparticle solutions, the observed wide band in the UV-Vis spectrum (instead of a narrow well-defined peak) can be attributed to an agglomeration of nanoparticles, which can occur in aqueous solutions.

Figure 1: Top view of nanostructured ATO layers ((a), insert – a cross-sectional view) with deposited copper (b), gold (c), and silver (d) nanoparticles.

Figure 2: EDS spectra of ATO layers modified with metal nanoparticles (a). UV-Vis spectra of chemically synthesized gold and silver nanoparticle solutions (b).
(AuNPs ~ 520 nm, AgNPs ~ 400 nm, and CuNPs ~ 570 nm) might be observed as a result of a modification of the anodic TiO$_2$ surface with gold, silver, and copper nanoparticles. However, for all tested anodic materials, there was no significant increase observed in the generated photocurrent in the wavelength range of 400–600 nm. In the case of a photoanode modified with copper nanoparticles, the metal surface could have oxidized and, therefore, the SPR effect was not observed [53]. In other cases, it is possible that the amount of metal nanoparticles on the ATO surface was too small to observe the SPR effect or/and the size of particles was too big to observe quantum effects. On the other hand, an improvement in photoelectrochemical properties was seen in the wavelength range of 300–400 nm (Figure 4). These results suggest that for the studied photoanodes the Schottky barrier is present. The radiation is absorbed by the semiconductor, and the photogenerated electrons are trapped in metal nanoparticles, which promotes the charge separation and contributes to the efficiency of the process.

The complex photoelectrochemical behavior of the tested photoanodes was studied at the potential range of 0–1 V vs. SCE and wavelengths ranging from 300 to 400 nm. The photocurrent densities as a function of incident light wavelength and applied potential were recorded for anodic TiO$_2$ samples annealed at 500°C and decorated with CuNPs, AuNPs, and AgNPs (Figure 5). For the nonmodified anodic TiO$_2$ layer, the maximum photocurrent density of about 70 μA cm$^{-2}$ is observed at 350 nm (Figure 5(a)). In general, the deposition of nanoparticles results in an improvement of the photoelectrochemical response of nanostructured anodic TiO$_2$ films, which is in good agreement with the literature (see Table 1). For instance, the maximum photocurrent densities of about 90 μA cm$^{-2}$ and 80 μA cm$^{-2}$ were recorded at 350 nm and 1 V vs. SCE for samples modified with copper (Figure 5(b)) and silver (Figure 5(d)) nanoparticles, respectively. For the ATO sample decorated with AuNPs, much higher photocurrents (about 100 μA cm$^{-2}$) at 350 nm were observed. However, it should be mentioned that the estimated atomic content of deposited noble metals was
different for each electrode. What is more, IPCE values obtained for the samples modified with metal nanoparticles are mostly higher than those observed for bare anodic titania (Figure 5(e)). For the ATO surface decorated with Au nanoparticles, the higher conversion efficiencies close to 45% are visible at the higher applied potentials.

Figure 5: Photocurrent density as a function of incident light wavelength and applied potential recorded in 0.1 M KNO₃ for the ATO layers annealed at 500°C (a) and decorated with copper (b), gold (c), and silver (d) nanoparticles. IPCE values obtained at 0, 0.5, and 1 V vs. SCE for bare ATO and ATOs decorated with noble metals (e).
In order to verify the photocatalytic effectiveness of ATO layers decorated with metal nanoparticles in decomposition of MR, photodegradation tests were performed. Prior to photocatalytic tests, a series of standard solutions to generate a calibration curve was prepared at the MR concentration range of 0–5 mg L\(^{-1}\). The typical UV-Vis spectra obtained in 0.01 M hydrochloric acid are presented in Figure 6(a). During the photocatalytic tests, the dye solution was irradiated with 350 nm UV light in the presence of ATO samples decorated with different nanoparticles. MR concentration (c) and ln(C) (d) vs. irradiation time curves.

Figure 6: UV-Vis spectra of methyl red solutions (0–5 mg L\(^{-1}\)) prepared in 0.01 M HCl (a). Calibration curve used for MR determination (b). Photocatalytic degradation of 5 mg L\(^{-1}\) MR under 350 nm UV irradiation in the presence of ATO samples decorated with different nanoparticles. MR concentration (c) and ln(C) (d) vs. irradiation time curves.

| Sample      | DEG (%) | k (h\(^{-1}\)) |
|-------------|---------|---------------|
| ATO         | 75 ± 2  | 0.24 ± 0.01   |
| ATO CuNPs   | 76 ± 2  | 0.22 ± 0.02   |
| ATO AuNPs   | 84 ± 2  | 0.30 ± 0.01   |
| ATO AgNPs   | 79 ± 1  | 0.25 ± 0.01   |
| MR solution | 12 ± 2  | 0.02 ± 0.01   |

Table 2: Percentage of dye loss (DEG%), and decomposition rate of MR in the presence of ATO-based photocatalysts.

In order to verify the photocatalytic effectiveness of ATO layers decorated with metal nanoparticles in decomposition of MR, photodegradation tests were performed. Prior to
similar regardless of the type of photocatalyst used. A simple photolysis of the MR solution without any photocatalyst during irradiation tests was also investigated (see MR solution in Figure 6(c)). In order to determine the kinetic rate constant, the ln(C) values were plotted with respect to time for all studied ATO samples (Figure 6(d)). The plotted data were best fitted by straight lines of different slopes which indicate that the reaction follows pseudo-first order kinetics. From the slopes of those plots, the reaction rate constants were determined. The best photocatalytic properties, indicated by the highest rate constant of 0.30 h$^{-1}$ when compared with nonmodified ATO ($k = 0.24$ h$^{-1}$), were observed for the ATO layer decorated with AuNPs. A slight improvement in photocatalytic properties was found also for the ATO layer modified with silver nanoparticles ($k = 0.25$ h$^{-1}$). For ATO decorated with CuNPs, no enhancement in the photodegradation rate was observed. It can be attributed to a partial oxidation of copper nanoparticles during the photocatalytic process. What is more, the percentages of dye loss (DEG%) obtained after 6 hours of irradiation was calculated and gathered in Table 2. As it can be seen, the most effective photocatalytic behavior was observed for ATO decorated with gold nanoparticles (about 84% of MR decomposition), and the second promising modification of the ATO surface was deposition of silver nanoparticles (DEG% = 79%).

The synthesized Au-ATO photocatalysts have been used multiple times in order to determine the stability of such materials. As can be seen in Figure 7(a), the decolorization rate of methyl red is similar when using the same sample four times. The average MR degradation percent was determined to be $84 \pm 2\%$ as shown in Figure 7(b). Both gold and silver nanoparticles are known for their antibacterial properties [54]. Covering TiO$_2$ nanotubes with noble metal particles can be a great advantage in the context of the use of such materials for water purification. The presence of Au and Ag may prevent the growth of microorganisms near the photocatalyst, thus allowing its permanent exposure to solar radiation.

4. Conclusions

In this study, the effect of the ATO surface decorated with Cu, Au, and Ag nanoparticles on photoelectrochemical and photocatalytic properties were investigated. Nanoparticles were synthesized by a chemical method, and the presence of metals on TiO$_2$ was confirmed by EDS analysis. All obtained materials were used as photoanodes in photoelectrochemical water splitting and as photocatalysts in a methyl red decomposition process. It was found that in studied conditions the Schottky barrier is formed between the metal/ATO interface, which leads to enhancing photocurrent generation in the range of 300–400 nm. However, in the visible light spectrum (400–600 nm) no additional effect from SPR was observed. Nevertheless, deposition of noble metal nanoparticles on the ATO surface resulted in improved efficiencies in both studied processes. It was shown that deposition of gold nanoparticles resulted in high photocurrent densities (100 $\mu$A cm$^{-2}$ for 350 nm and 1 V) with a high IPCE value of $\sim$45%. The best photocatalytic properties was observed for ATO samples with AuNPs (DEG% = 84%, $k = 0.30$ h$^{-1}$) and AgNPs (DEG% = 79%, $k = 0.25$ h$^{-1}$).

Data Availability

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

Additional Points

Highlights. (i) Nanostructured TiO$_2$ (ATO) layers were obtained by electrochemical oxidation. (ii) Copper, gold, and silver nanoparticles were deposited on ATO surface. (iii) The effect of ATO surface modification was studied. (iv) Photoelectrochemical performance of obtained materials was investigated. (v) Photodegradation of methyl red in the presence of modified ATO was performed.
Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

The authors gratefully acknowledge financial support from the Jagiellonian University. The SEM imaging was performed in the Laboratory of Field Emission Scanning Electron Microscopy and Microanalysis at the Institute of Geological Sciences, Jagiellonian University, Poland.

References

[1] R. K. Keswani, H. Ghodke, D. Sarkar, K. C. Khilar, and R. S. Srinivas, “Room temperature synthesis of titanium dioxide nanoparticles of different phases in water in oil microemulsion,” *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, vol. 369, no. 1-3, pp. 75–81, 2010.

[2] B. Liu, J. E. Boercker, and E. S. Aydil, “Oriented single crystalline titanium dioxide nanowires,” *Nanotechnology*, vol. 19, no. 50, pp. 505604–505611, 2008.

[3] Z. Zander, R. Yagloski, J. DeCoste, D. Zhang, and B. G. DeLacy, “One-pot synthesis of high aspect ratio titanium dioxide nanorods using oxalic acid as a complexing agent,” *Materials Letters*, vol. 163, pp. 39–42, 2016.

[4] J. M. Macak, H. Hildebrand, U. Marten-Jahns, and P. Schmuki, “Mechanistic aspects and growth of large diameter self-organized TiO₂ nanotubes,” *Journal of Electroanalytical Chemistry*, vol. 621, no. 2, pp. 254–266, 2008.

[5] G. D. Sulka, J. Kapusta-Kołodziej, A. Brzózka, and M. Jaskula, “Fabrication of nanoporous TiO₂ by electrochemical anodization,” *Electrochimica Acta*, vol. 55, no. 14, pp. 4359–4367, 2010.

[6] J. H. Jung, H. Kobayashi, K. J. C. van Bommel, S. Shinkai, and T. Shimizu, “Creation of novel helical ribbon and double-layered nanotube TiO₂ structures using an organogel template,” *Chemistry of Materials*, vol. 14, no. 4, pp. 1445–1447, 2002.

[7] X. Sun and Y. Li, “Synthesis and characterization of iron-exchangeable titinate nanotubes,” *Chemistry - A European Journal*, vol. 9, no. 10, pp. 2229–2238, 2003.

[8] P. Hoyer, “Formation of a titanium dioxide nanotube array,” *Langmuir*, vol. 12, no. 6, pp. 1411–1413, 1996.

[9] H. Omidvar, S. Goodarzi, A. Seif, and A. R. Azadmehr, “Influence of anodization parameters on the morphology of TiO₂ nanotube arrays,” *Superlattices and Microstructures*, vol. 50, no. 1, pp. 26–39, 2011.

[10] J. M. Macak, H. Tsuchiya, A. Ghicov et al., “TiO₂ nanotubes: self-organized electrochemical formation, properties and applications,” *Current Opinion in Solid State and Materials Science*, vol. 11, no. 1-2, pp. 3–18, 2007.

[11] G. D. Sulka, J. Kapusta-Kołodziej, A. Brzózka, and M. Jaskula, “Anodic growth of TiO₂ nanopore arrays at various temperatures,” *Electrochimica Acta*, vol. 104, pp. 526–535, 2013.

[12] J. M. Macak and P. Schmuki, “Anodic growth of self-organized anodic TiO₂ nanotubes in viscous electrolytes,” *Electrochimica Acta*, vol. 52, no. 3, pp. 1258–1264, 2006.

[13] S. Bauer, S. Kleber, and P. Schmuki, “TiO₂ nanotubes: tailoring the geometry in H₃PO₄/HF electrolytes,” *Electrochemistry Communications*, vol. 8, no. 8, pp. 1321–1325, 2006.

[14] S.-D. Mo and W. Y. Ching, “Electronic and optical properties of three phases of titanium dioxide: rutile, anatase, and brookite,” *Physical Review B*, vol. 51, no. 19, pp. 13023–13032, 1995.

[15] I. Paramasivam, H. Jha, N. Liu, and P. Schmuki, “A review of photocatalysis using self-organized TiO₂ nanotubes and other ordered oxide nanostructures,” *Small*, vol. 8, no. 20, pp. 3073–3103, 2012.

[16] Y. Smith, R. Ray, K. Carlson, B.arma, and M. Misra, “Self-ordered titanium dioxide nanotube arrays: anodic synthesis and their photo/electro-catalytic applications,” *Materials*, vol. 6, no. 7, pp. 2892–2957, 2013.

[17] X. Chen and S. S. Mao, “Titanium dioxide nanomaterials: synthesis, properties, modifications, and applications,” *Chemical Reviews*, vol. 107, no. 7, pp. 2891–2959, 2007.

[18] J. Xu, Y. Ao, M. Chen, and D. Fu, “Photoelectrochemical property and photocatalytic activity of N-doped TiO₂ nanotube arrays,” *Applied Surface Science*, vol. 256, no. 13, pp. 4397–4401, 2010.

[19] J. H. Park, S. Kim, and A. J. Bard, “Novel carbon-doped TiO₂ nanotube arrays with high aspect ratios for efficient solar water splitting,” *Nano Letters*, vol. 6, no. 1, pp. 24–28, 2006.

[20] L. Sun, J. Li, C. L. Wang, S. F. Li, H. B. Chen, and C. J. Lin, “An electrochemical strategy of doping Fe³⁺ into TiO₂ nanotube array films for enhancement in photocatalytic activity,” *Solar Energy Materials and Solar Cells*, vol. 93, no. 10, pp. 1875–1880, 2009.

[21] J. Gong, W. Pu, C. Yang, and J. Zhang, “A simple electrochemical oxidation method to prepare highly ordered Cr-doped titania nanotube arrays with promoted photoelectrochemical property,” *Electrochimica Acta*, vol. 68, pp. 178–183, 2012.

[22] Y. Liu, H. Zhou, B. Zhou et al., “Highly stable CdS-modified short TiO₂ nanotube array electrode for efficient visible-light hydrogen generation,” *International Journal of Hydrogen Energy*, vol. 36, no. 1, pp. 167–174, 2011.

[23] Q. Shen, T. Sato, M. Hashimoto, C. Chen, and T. Toyoda, “Photoacoustic and photoelectrochemical characterization of CdSe-sensitized TiO₂ electrodes composed of nanotubes and nanowires,” *Thin Solid Films*, vol. 495, no. 1-2, pp. 299–305, 2006.

[24] I. Paramasivam, J. M. Macak, and P. Schmuki, “Photocatalytic activity of TiO₂ nanotube layers loaded with Ag and Au nanoparticles,” *Electrochemistry Communications*, vol. 10, no. 1, pp. 71–75, 2008.

[25] S. Zhang, F. Peng, H. Wang et al., “Electrodeposition preparation of Ag loaded N-doped TiO₂ nanotube arrays with enhanced visible light photocatalytic performance,” *Catalysis Communications*, vol. 12, no. 8, pp. 689–693, 2011.

[26] A. Pearson, H. Zheng, K. Kalantar-zadeh, S. K. Bhargava, and V. Bansal, “Decoration of TiO₂ nanotubes with metal nanoparticles using polyoxometalate as a UV-switchable reducing agent for enhanced visible and solar light photocatalysis,” *Langmuir*, vol. 28, no. 40, pp. 14470–14475, 2012.

[27] H. He, P. Xiao, M. Zhou, Y. Zhang, Q. Lou, and X. Dong, “Boosting catalytic activity with a p–n junction: Ni/TiO₂ nanotube arrays composite catalyst for methanol oxidation,” *International Journal of Hydrogen Energy*, vol. 37, no. 6, pp. 4967–4973, 2012.

[28] D.-M. Yun, H.-H. Cho, J.-W. Jang, and J.-W. Park, “Nano zero-valent iron impregnated on titanium dioxide nanotube array film for both oxidation and reduction of methyl orange,” *Water Research*, vol. 47, no. 5, pp. 1858–1866, 2013.
Z. Liu, W. Hou, P. Pavaskar, M. Aykol, and S. B. Cronin, “Enhancing photocatalytic activities of titanium dioxide via well-dispersed copper nanoparticles,” *Chemosphere*, vol. 204, pp. 193–201, 2018.

R. T. Tung, “The physics and chemistry of the Schottky barrier height,” *Applied Physics Reviews*, vol. 1, no. 1, article 011304, 2014.

D. B. Ingram, P. Christopher, J. L. Bauer, and S. Linic, “Predictive model for the design of plasmonic metal/semiconductor composite photocatalysts,” *ACS Catalysis*, vol. 1, no. 10, pp. 1441–1447, 2011.

Z. Liu, W. Hou, P. Pavaskar, M. Aykol, and S. B. Cronin, “Plasmon resonant enhancement of photocatalytic water splitting under visible illumination,” *Nano Letters*, vol. 11, no. 3, pp. 1111–1116, 2011.

Z. Jiang, Q. Ouyang, B. Peng, Y. Zhang, and L. Zan, “Ag size-dependent visible-light-responsive photocatalytic activity of Ag–TiO2 nanostructure based on surface plasmon resonance,” *Journal of Materials Chemistry A*, vol. 2, no. 46, pp. 19861–19866, 2014.

S. Zhang, B. Peng, S. Yang et al., “Non-noble metal copper nanoparticles-decorated TiO2 nanotube arrays with plasmon-enhanced photocatalytic hydrogen evolution under visible light,” *International Journal of Hydrogen Energy*, vol. 40, no. 1, pp. 303–310, 2015.

P. Christopher, D. B. Ingram, and S. Linic, “Enhancing photocatalytic activity of semiconductor nanoparticles with optically active Ag nanostructures: photochemistry mediated by Ag surface plasmons,” *The Journal of Physical Chemistry C*, vol. 114, no. 19, pp. 9173–9177, 2010.

Y. H. Tseng, I. G. Chang, Y. Tai, and K. W. Wu, “Effect of surface plasmon resonance on the photocatalytic activity of Au/TiO2 under UV/visible illumination,” *Journal of Nanoscience and Nanotechnology*, vol. 12, no. 1, pp. 416–422, 2012.

Y. Tian and T. Tatsuma, “Plasmon-induced photoelectrochemistry at metal nanoparticles supported on nanoporous TiO2,” *Chemical Communications*, vol. 10, no. 16, pp. 1810-1811, 2004.

A. Zuber, M. Purdey, E. Schartner et al., “Detection of gold nanoparticles with different sizes using absorption and fluorescence based method,” *Sensors and Actuators B: Chemical*, vol. 227, pp. 117–127, 2016.

Y. Zhao, N. Hoivik, and K. Wang, “Microstructure and photocurrent response of gold nanocrystalline on TiO2 nanotube arrays,” *The Journal of Physical Chemistry C*, vol. 122, no. 14, pp. 7877–7884, 2018.

K. A. Soliman, A. F. Zedan, A. Khalifa et al., “Silver nanoparticles–decorated titanium oxynitride nanotube arrays for enhanced solar fuel generation,” *Scientific Reports*, vol. 7, no. 1, p. 1913, 2017.

Q. Wang, J. Qiao, X. Xu, and S. Gao, “Controlled synthesis of Cu nanoparticles on TiO2 nanotube array photoelectrodes and their photoelectrochemical properties,” *Materials Letters*, vol. 131, pp. 135–137, 2014.

J. Chen, M. Guo, H. Su et al., “Improving the efficiency of dye-sensitized solar cell via tuning the Au plasmons inlaid TiO2 nanotube array photoanode,” *Journal of Applied Electrochemistry*, vol. 48, no. 10, pp. 1139–1149, 2018.

N. Nyein, W. K. Tan, G. Kawamura, A. Matsuda, and Z. Lockman, “Anodic Ag/TiO2 nanotube array formation in NaOH/fluoride/ethylene glycol electrolyte as a photoanode for dye-sensitized solar cells,” *Nanotechnology*, vol. 27, no. 35, pp. 355605–355620, 2016.

M. Nischl, P. Mazierski, Z. Wei et al., “Enhanced photocatalytic, electrochemical and photoelectrochemical properties of TiO2 nanotubes arrays modified with Cu, AgCu and Bi nanoparticles obtained via radiolytic reduction,” *Applied Surface Science*, vol. 387, pp. 89–102, 2016.

K. Lee, R. Hahn, M. Altomare, E. Selli, and P. Schmuki, “Intrinsic Au decoration of growing TiO2 nanotubes and formation of a high-efficiency photocatalyst for H2 production,” *Advanced Materials*, vol. 25, no. 42, pp. 6133–6137, 2013.

M. Jarosz, J. Kapusta-Kołodziej, M. Jaskula, and G. D. Sulka, “Effect of different polishing methods on anodic titanium dioxide formation,” *Journal of Nanomaterials*, vol. 2015, Article ID 295126, 10 pages, 2015.

K. Syrek, J. Kapusta-Kołodziej, M. Jarosz, and G. D. Sulka, “Effect of electrolyte agitation on anodic titanium dioxide (ATO) growth and its photoelectrochemical properties,” *Electrochimica Acta*, vol. 180, pp. 801–810, 2015.

M. Jarosz, K. Syrek, J. Kapusta-Kołodziej et al., “Heat treatment effect on crystalline structure and photoelectrochemical properties of anodic TiO2 nanotube arrays formed in ethylene glycol and glycerol based electrolytes,” *The Journal of Physical Chemistry C*, vol. 119, no. 42, pp. 24182–24191, 2015.

A. Takai and P. V. Kamat, “Capture, store, and discharge. Shuttling photogenerated electrons across TiO2-silver interface,” *ACS Nano*, vol. 5, no. 9, pp. 7369–7376, 2011.

S. Noothongkaew, J. K. Han, Y. B. Lee, O. Thumthan, and K.-S. An, “Au NPs decorated TiO2 nanotubes array candidate for UV photodetectors,” *Progress in Natural Science: Materials International*, vol. 27, no. 6, pp. 641–646, 2017.

Y. Lai, Y. Chen, H. Zhuang, and C. Lin, “A facile method for synthesis of Ag/TiO2 nanostructures,” *Materials Letters*, vol. 62, no. 21-22, pp. 3688–3690, 2008.

S. T. Dubas and V. Pimpan, “Green synthesis of silver nanoparticles for ammonia sensing,” *Talanta*, vol. 76, no. 1, pp. 29–33, 2008.

M. R. Khan, T. W. Chuan, A. Youssuf, M. N. K. Chowdhury, and C. K. Cheng, “Schottky barrier and surface plasmonic resonance phenomena towards the photocatalytic reaction: study of their mechanisms to enhance photocatalytic activity,” *Catalysis Science & Technology*, vol. 5, no. 5, pp. 2522–2531, 2015.

C. M. Ramakritinan, E. Kaarunya, S. Shankar, and A. K. Kumaraguru, “Antibacterial effects of Ag, Au and bimetallic (Ag-Au) nanoparticles synthesized from red algae,” *Solid State Phenomena*, vol. 201, pp. 211–230, 2013.
