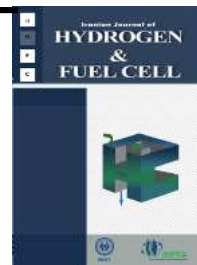


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Optimization of Ag loaded TiO₂ nanotube arrays for plasmonic photoelectrochemical water splitting

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Abstract

In this paper we report on a notable improvement of the photoelectrochemical (PEC) properties of highly ordered Ag loaded TiO₂ nanotube arrays (Ag/TNT). Electrochemical anodization and sequential chemical bath deposition with an optimum ratio of precursors were employed for the production of an Ag/TNT nanocomposite. X-ray diffraction analysis (XRD) and scanning electron microscopy SEM images indicate that the Ag nanoparticles were deposited completely on the surface of the pore wall of TiO₂ nanotube arrays. The photoelectrochemical measurements, including LSV, chronoamperometry and EIS, indicate that the Ag/TNT sample with a ratio of 1 precursors exhibited the maximum photoelectrochemical efficiency with a photocurrent density of about 300 μ A, which is at least 3 times greater than a pure TNT sample. PEC and EIS measurements show that because of the localized surface plasmon resonance (LSPR) effects of Ag nanoparticles, an effective separation of photogenerated electron-hole pairs occurs that led to a reduction of charge transfer resistance at the interface and enhanced the PEC properties of the Ag/TNT sample.

1. Introduction

Photoelectrochemical (PEC) water splitting is one of the most interesting methods of hydrogen production

for use in energy issues in the future [1]. Different semiconductor materials, such as TiO₂ [2], Fe₂O₃ [3, 4], WO₃ [5] and Cu₂O [6], have been used for PEC. Among various semiconductors, titanium dioxide

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TiO₂ is a favorable candidate as a photoelectrode for PEC applications due to better chemical stability, photocorrosion resistance, and low cost [7]. For the first time, Fujishima used TiO₂ as a favored semiconductor electrode for water photolysis [8, 9], then Gratzel used it for a dye sensitized solar cell as a low cost and high efficiently semiconductor [10]. Mainly due to large surface area and high photoactivity, TiO₂ nanotube arrays have received extensive attention [11]. However, because of TiO₂'s (3.2 eV) wide band gap, its light absorption range is limited to UV; and due to its high density of trap states, the photogenerated electron-hole pairs easily recombine [11]. These restrictions have caused lower charge separation and photoelectron transfer during the PEC process for solar water splitting. Different approaches have focused on improving the photoactivity of TiO₂ during PEC process [12]. Two significant solutions are broadening the absorption of sunlight range using plasmonic nanoparticles and reducing the recombination of photogenerated carriers [11].

In recent years, noble metal nanoparticles, such as Ag, Au and Cu, have received much consideration for applications in photoelectrochemical processes because of their localized surface plasmon resonance (LSPR). This LSPR resonance wavelength depends on the size, shape, and dielectric environment around the nanoparticles [13-21]. Recently, Ag-doped semiconductor nanoparticles have received much attention in PEC processes, to increase the photo conversion yield and to absorb visible light to wide band gap semiconductors such as TiO₂ [22-26].

There are different explanations used to verify the role of metal nanoparticles in the improvement of the PEC process. First, increasing absorption of metal nanoparticles due to surface plasmons and light trapping effects [27]; second, metal nanoparticles acting as an electron donor to prompt electron transfer from metal to semiconductor [28-31]; and finally, metal nanoparticles acting as an electron trapping media to reduce the surface charge recombination in the semiconductor [32-36].

In this paper, TiO₂ nanotube arrays, used as the

photoanode, were synthesized by electrochemical anodization by optimizing the length and the diameter of the nanotubes [37]. Ag nanoparticles were used as the plasmonic medium. There are several methods to prepare the plasmonic nanoparticles such as chemical method [38], electrodeposition [39], and UV photo reduction [40] of metal salts. Here, the Ag nanoparticles were deposited on the TiO₂ nanotubes by sequential chemical bath deposition S-CBD to obtain the Ag/TNT nanocomposite, and photoelectrochemical properties were measured under simulated sunlight. Previously, we have reported the effects of different cycles of S-CBD on photoelectrochemical properties of Ag/TNT photoanode and obtained the optimum cycle of deposition [41]. In this work, by applying that optimum condition, we have investigated the effect of different concentrations of precursors with different ratios on photoelectrochemical properties of Ag/TNT nanocomposite. The crystalline structure of the Ag/TNT nanocomposites are characterized by X-ray diffraction XRD analysis. Also, field-emission scanning electron microscope FESEM analysis was used to investigate the surface morphology of the synthesized Ag/TNT samples. Finally, photoelectrochemical properties of the Ag/TNT samples were investigated under visible irradiation. Few works have focused on the PEC water splitting of Ag-loaded TiO₂ nanotubes. Comparing the results with previous works showed a noteworthy improvement in the photocatalytic activity of the Ag/TNT samples [11, 15, 22]. The EIS analyses indicate that enhancement of the electron mobility by reducing the recombination of electron-hole pairs improved photoelectrochemical efficiency of the Ag/TNT photoelectrodes.

2. Materials and methods

2.1. Preparation of TiO₂ nanotube layers

The TiO₂ nanotube layers were prepared by the anodization method [25]. The titanium foils (99.5%, 25 mm × 15 mm × 1 mm) were mechanically polished

with sandpaper. Then the polished titanium foils were cleaned with acetone, 2-propanol, and distilled water ultrasonic baths for 10 min. Then the foils were air dried. Finally, the titanium substrates were anodized using a direct current voltage source (100V DC POWER SUPPLY) consisting of a two-electrode configuration with a piece of Cu foil with the same size of Ti foil (25 mm × 15 mm) as cathodes. The electrolytes consist of 0.3M NH₄F with 2 vol% H₂O in ethylene glycol. The anodization process was carried out under constant potential of 60 V for 3 hour at 5°C in a cold water and ice bath. After the anodization process, the anodized TiO₂ samples were rinsed with distilled water and ethanol then air dried, and then annealed at 500°C for 2h in an atmosphere to obtain the crystalline phase.

2.2. Photodeposition of Ag nanoparticles

Ag nanoparticles were loaded onto TiO₂ nanotubes by the four step photochemical reduction method S-CBD. In this method, the electrolytes consisting of 1 mM AgNO₃ and 2 mM NaBH₄ were prepared separately. First, the foils with annealed TNT were immersed in 1 mM AgNO₃ solution for 1 min then immersed in deionized water for 30 s. Subsequently, they were immersed in a prepared 2mM NaBH₄ solution for 3 min and then again in deionized water for 30 s. This four step process was carried out in an ice bath and in the dark. This process was repeated for 8 cycles then the samples were irradiated with a Xenon lamp for 20 min to reduce the Ag⁺ ions to Ag⁰ nanoparticles. To compare the different amounts of Ag nanoparticles on the TNT substrate, different concentrations of AgNO₃ and NaBH₄ precursors with different ratios of 0.5, 1, 2 and 3 were deposited on the TiO₂ nanotube arrays, respectively.

2.3. Characterization

The morphology of the fabricated photoelectrodes was examined by scanning electron microscopy (SEM). The structure of the samples was also analyzed using X-ray diffractometer (XRD, Xpert,

Philips) with CuK α radiation ($\lambda=1.54 \text{ \AA}$).

Photoelectrochemical tests of the photoelectrodes were conducted using a three-electrode PEC cell with Pt wire as the counter electrode and Ag/AgCl as the reference electrode. A potentiostat (Model Biologic SP 300) was used as the workstation. The Ag/, as the working electrode, is immersed in 0.1M Na₂SO₄ electrolyte and then illuminated by a 300 W Xenon lamp (Oriel) with an intensity of 100 mW/cm² (the intensity of AM 1.5). The linear sweep voltammetry (LSV), chronoamperometry, and electrochemical impedance spectroscopy (EIS) were carried out using the abovementioned setup. The chronoamperometry was measured under a chopped light irradiation (on/off cycles of 60 s) in 1.2 V vs RHE for all the samples. Linear sweep voltammetry with a scan rate of 50 mV/s was used for the current-voltage measurements. EIS measurements were carried out using the EIS mode of the potentiostat with an AC component amplitude of 10 mV from 100 kHz to 100 mHz.

3. Results and Discussion

In order to identify the crystal phase of the TiO₂ nanotube arrays and Ag/TNT nanocomposite, the X-ray diffraction (XRD) measurement was used and the results are shown in Fig. 1-a.

For the TiO₂ nanotube arrays TNT, all peaks miare indexed to the TiO₂ anatase phase (JCPDS file no: 01-1167) and the Ti metal phase (JCPDS file no: 01-1198). The characteristic peaks of (101), (004), (200), (105), (211), (204) and (301) at the angles 29.5°, 44.5°, 56.7°, 63.8°, 64.9°, 74.8° and 92.5° all obviously show formation of anatase TiO₂ nanotubes on the Ti substrate. Additionally, the peaks of Ti are recognized in the XRD pattern. Diffraction peaks at angles of 44.8° and 93° could be attributed to the (111) and (311) crystal planes of the cubic Ag phase (JCPDF file no: 01-1167). It should be noted that because of overlapping the other diffraction peaks ascribed to the cubic Ag phase and those of anatase TiO₂ and pure Ti metal could not be clearly

distinguished. The XRD results indicated that the Ag/TNT nanocomposite electrodes prepared by the mentioned method were composed of Ag nanocrystals and crystalline TiO₂ anatase.

The UV-Vis spectroscopy of the samples is shown in Fig. 1-c. The results indicate that loading Ag nanoparticles on TiO₂ nanotube arrays increase the light absorption of the samples, except the ratio 3 sample that shows even less light absorption than bare TiO₂.

Fig. 2-a shows the field emission scanning electron microscope (FESEM) image of the as-prepared TiO₂ nanotube array. A distinctive top layer with a periodically porous structure could be clearly observed. The average diameter of the nanotubes was 85-90 nm, and the thickness of the walls was about 20-30 nm. The height of the TiO₂ nanotube layer was about 2 μm. It should be noted that the maximum penetration depth of light in a TiO₂ nanotube is about 2.0 μm [2]. From Fig. 2-b, it can be clearly seen that silver nanoparticles were deposited on the surface of the pore wall of TiO₂ nanotube arrays with

an average size of about 15-20 nm via the proposed photochemical reduction deposition method. After deposition of Ag nanoparticles, the diameter of TiO₂ nanotubes dropped to 72-82 nm, indicating that the silver nanoparticles are located on both sides of the inner and outer surface of the nanotubes [41].

To study the photoelectrochemical properties of Ag a loaded TNTs linear sweep voltammetry (LSV) was carried out to obtain I-V figures under xenon lamp illumination. For comparison, photoelectrochemical activity of pure TiO₂ nanotube arrays was also measured. Fig. 3-a shows the photocurrent density measurements of the pure TNT samples and Ag loaded TiO₂ nanotube arrays with different ratios of precursor concentrations both in the dark and under illumination.

It is seen that the photocurrent density increases linearly in all the cases with the applied potential in the range of -0.2 to +1 V. The dark current density measured in all the samples is negligibly small, which shows that there is no significant electrochemical reaction. For light illumination the photocurrent density increases

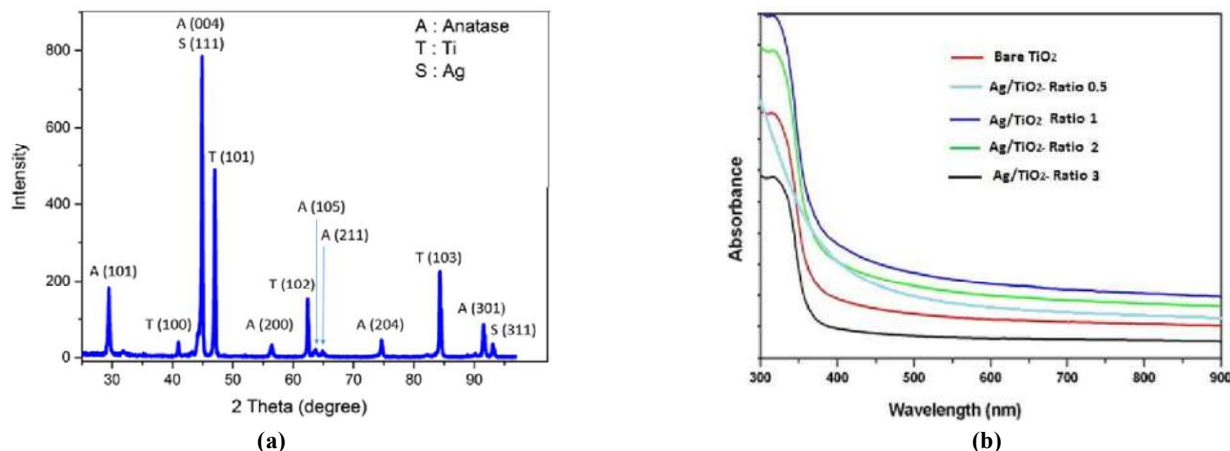


Fig. 1 a) XRD pattern of Ag/TNT nanocomposite and b) UV/Vis spectroscopy of samples.

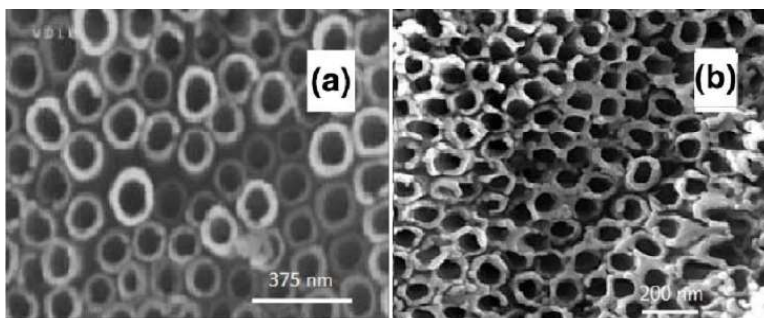


Fig. 2 FE-SEM image of TiO₂ nanotubes a) before, and b) after the Ag deposition.

linearly with the applied potential in the range of -0.2 to +0.4 V, then it reaches a saturated level in the region of +0.4 V to +1 V. Obviously, the photocurrent density of the Ag/TNT samples is greater than that of pure TNT arrays with the exception of the ratio 3 Ag/TNT sample, which increases with an increase in concentration ratio of precursor until ratio 1. However, it decreases with an increase in concentration ratio up to 2. The reason for this decrease may be due to the amount of saturation of Ag nanoparticles on the TNT which prevents the TNT from efficient absorption of light. The best photocurrent density was achieved from the Ag/TNT sample of ratio 1. In the Ag/TNT samples, the best observed photocurrent was produced by the generation and efficient separation of photogenerated electron-hole pairs at the TNT/Ag/electrolyte interface, where the holes move to the semiconductor surface and the electrons are transported to the back contact Ti substrate through the Ag/TNT.

The chronoamperometry measurements I-t of the pure TNT sample and Ag/TNT samples are shown in Fig. 3-b. The results of this figure are consistent with the I-V measurement data. The best photocurrent density was obtained from the sample ratio 1.

The interfacial properties between the photoelectrode and the electrolyte were studied by electrochemical impedances spectroscopy (EIS) measurements. A semi-circle in the Nyquist plot at high frequency represented the charge-transfer properties, and the diameter of the semicircle revealed the charge-transfer resistance (Fig. 4). It is clear that the arc for Ag/TNT

under the light illumination is much smaller than that for pure TNT, implying that decoration with Ag could meaningfully enhance the electron mobility by reducing the recombination of electron-hole pairs. Comparing the different samples, the arc value for Ag/TNT ratio 1 is the smallest and this sample showed the best performance in the photoelectrochemical water splitting process, which is in agreement with the I-V measurements. It was noted that the loaded Ag nanoparticle exhibited an important role in the solution-action process of the electron transfer.

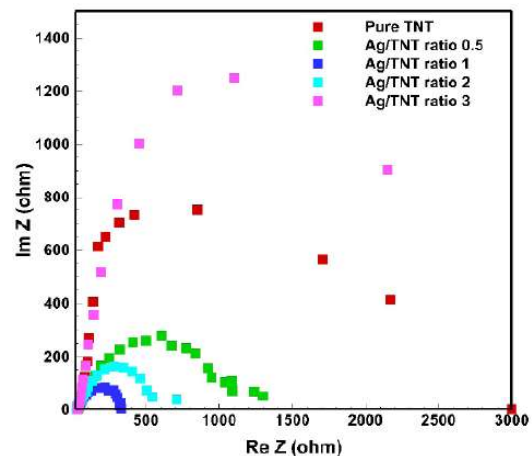
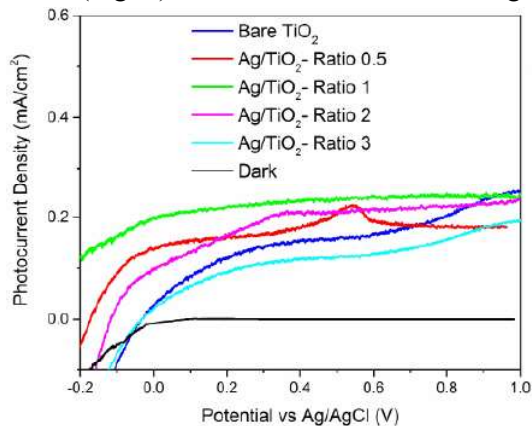


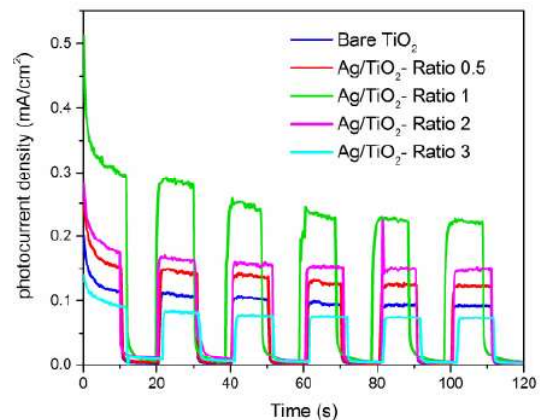
Fig. 4. Nyquist plots of pure TNT and different ratios of Ag/TNT samples under light illumination condition.

4. Conclusion

In summary, we have developed a highly ordered Ag loaded TiO_2 nanotube arrays Ag/TNT by a combination



(a)



(b)

Fig. 3 a) Linear sweep voltammetry I-V measurements of pure TNT and different concentration ratios of Ag/TNT nanolayers. b) Chronoamperometry measurements of bare TiO_2 and different amounts of Ag loaded TNT.

of anodization and sequential chemical bath deposition (S-CBD). Such a nanocomposite structure displays an effective separation of photogenerated charge carriers and significantly enhances TiO_2 photoelectrochemical performance. The increased photocurrent also resulted from the LSPR effect of silver in the Ag/TNT samples. From the observed results, the Ag/TNT ratio 1 sample achieves the maximum efficiency with photocurrent density of about $300 \mu\text{A}$, which is at least 3 times greater than pure TNT sample illumination under xenon lamp.

References

- [1] A. Fujishima, K. Honda, "Photolysis-decomposition of water at the surface of an irradiated semiconductor", *Nature*, 1972, 238: 37.
- [2] A. El Ruby Mohamed, S. Rohani, "Modified TiO_2 nanotube arrays (TNTAs): progressive strategies towards visible light responsive photoanode, a review", *Energy Environ. Sci*, 2011, 4: 1065.
- [3] A. A. Tahir, K. G. U. Wijayantha, S. Saremi-Yarahmadi, M. Mazhar, V. McKee, "Nanostructured $\alpha\text{-Fe}_2\text{O}_3$ Thin Films for Photoelectrochemical Hydrogen Generation", *Chem. Mater*, 2009, 21: 3763.
- [4] L. Fu, H. Yu, C. Zhang, Z. Shao, B. Yi, "Cobalt phosphate group modified hematite nanorod array as photoanode for efficient solar water splitting", *Electrochem Acta*, 2014, 136: 363.
- [5] M.A. Butler, "Photoelectrolysis and physical properties of the semiconducting electrode WO_2 ", *J. Appl. Phys*, 1977, 48: 1914.
- [6] Q.B. Man, J.P. Hofmann, A. Litke, E.J.M. Hensen, "Cu₂O photoelectrodes for solar water splitting: tuning photoelectrochemical performance by controlled faceting", *Sol. Energy Mater. Sol. Cells*, 2015, 14: 178.
- [7] H. Li, Y. Zeng, T. Huang, L. Piao, Z. Yan, M. Liu, "Hierarchical TiO_2 Nanospheres with Dominant {001} Facets: Facile Synthesis, Growth Mechanism, and Photocatalytic Activity" *Chem. Eur. J*, 2012, 18: 7525.
- [8] A. Fujishima, "Response to comments on efficient photochemical water splitting by a chemically modified n- TiO_2 ", *Science*, 2003, 30: 1673.
- [9] K. Maeda, K. Domen, "Isotopic and kinetic assessment of photocatalytic water splitting on Zn-added Ga_2O_3 photocatalyst loaded with $\text{Rh}_2\text{-yCrO}_3$ cocatalyst", *J. Phys. Chem. Lett*, 2010, 1: 2655.
- [10] M. G. Brian O'Regan, "A low-cost, high-efficiency solar cell based on dye-sensitized colloidal TiO_2 films", *Nature*, 1991, 353: 737.
- [11] J. Jiqing, T. Jianguo, G. Wei, K. Daibin, T. Yexiang, C. Liuping, "Plasmonic silver nanoparticles matched with vertically aligned nitrogen-doped titanium dioxide nanotube arrays for enhanced photoelectrochemical activity", *Journal of Power Sources*, 2015, 274: 464.
- [12] H. Li, W. Zhang, S. Huang, W. Pan, "Enhanced visible-light-driven photocatalysis of surface nitrided electrospun TiO_2 nanofibers", *Nanoscale*, 2012, 4: 801.
- [13] V.K. Sharma, R.A. Yngard, Y. Lin, "Silver nanoparticles: green synthesis and their antimicrobial activities", *Adv. Colloid Interface Sci*, 2009, 145: 83.
- [14] M.M. Khan, S.A. Ansari, M.O. Ansari, B.K. Min, J. Lee, M.H. Cho, "Biogenic Fabrication of Au@ CeO_2 Nanocomposite with Enhanced Visible Light Activity", *J. Phys. Chem. C*, 2014, 118: 9477.
- [15] M.M. Khan, J. Lee, M.H. Cho, "Au@ TiO_2 nanocomposites for the catalytic degradation of methyl orange and methylene blue: an electron relay effect", *J. Ind. Eng. Chem*, 2014, 20: 1584.
- [16] S. Oros-Ruiz, R. Zanella, R. Lopez, A. Hernandez-Gordillo, R. Gomez, "Photocatalytic hydrogen production by water/methanol decomposition using Au/ TiO_2 prepared

- by deposition–precipitation with urea”, *J. Hazard. Mater.*, 2013, 263: 1.
- [17] R. Saravanan, S. Karthikeyan, V.K. Gupta, G. Sekaran, V. Narayanan, A. Stephen, “Enhanced photocatalytic activity of ZnO/CuO nanocomposite for the degradation of textile dye on visible light illumination”, *Mater. Sci. Eng.*, 2013, 33: 91.
- [18] R. Saravanan, V.K. Gupta, T. Prakash, V. Narayanan, A. Stephen, “Synthesis, characterization and photocatalytic activity of novel Hg doped ZnO nanorods prepared by thermal decomposition method”, *J. Mol. Liq.*, 2013, 178: 88.
- [19] R. Saravanan, V.K. Gupta, V. Narayanan, A. Stephen, *J. Taiwan Inst.*, “Visible light degradation of textile effluent using novel catalyst ZnO/ γ -Mn₂O₃”, *Chem. Eng.*, 2014, 45: 1910.
- [20] R. Saravanan, E. Thirumal, V.K. Gupta, V. Narayanan, A. Stephen, “The photocatalytic activity of ZnO prepared by simple thermal decomposition method at various temperatures”, *J. Mol. Liq.*, 2013, 177: 394.
- [21] R. Saravanan, H. Shankar, T. Prakash, V. Narayanan, A. Stephen, “ZnO/CdO composite nanorods for photocatalytic degradation of methylene blue under visible light”, *Mater. Chem. Phys.*, 2011, 125: 277.
- [22] E. Albitar, M.A. Valenzuela, S. Alfaro, G. Valverde-Aguilar, F.M. Martinez-Pallares, “Photocatalytic deposition of Ag nanoparticles on TiO₂: Metal precursor effect on the structural and photoactivity properties”, *Journal of Saudi Chemical Society*, 2015, 19: 563.
- [23] Z. Shan, J. Wu, F. Xu, F.-Q. Huang, H. Ding, “Highly effective silver/semiconductor photocatalytic composites prepared by a silver mirror reaction”, *J. Phys. Chem. C*, 2008, 112: 15423.
- [24] S.A. Ansari, M.M. Khan, M.O. Ansari, J. Lee, M.H. Cho, “Biogenic synthesis, photocatalytic, and photoelectrochemical performance of Ag–ZnO nanocomposite”, *J. Phys. Chem. C*, 2013, 117: 27023.
- [25] M.M. Khan, S.A. Ansari, M.I. Amal, J. Lee, M.H. Cho, “Highly visible light active Ag@ TiO₂ nanocomposites synthesized using an electrochemically active biofilm: a novel biogenic approach”, *Nanoscale*, 2013, 5: 4427.
- [26] M.M. Khan, S.A. Ansari, J.-H. Lee, M.O. Ansari, J. Lee, M.H. Cho, “Electrochemically active biofilm assisted synthesis of Ag@ CeO₂ nanocomposites for antimicrobial activity, photocatalysis and photoelectrodes”, *J. Colloid Interface Sci.*, 2014, 431: 255.
- [27] H.R. Stuart, D.G. Hall, “Island size effects in nanoparticle-enhanced photodetectors”, *Appl. Phys. Lett.*, 1998, 73: 3815.
- [28] S. Mubeen, G. Hernandez-Sosa, D. Moses, J. Lee, M. Moskovits, “Plasmonic photosensitization of a wide band gap semiconductor: converting plasmons to charge carriers”, *Nano Lett.*, 2011, 11: 5548.
- [29] Y. Tian, T. Tatsuma, “Plasmon-induced photoelectrochemistry at metal nanoparticles supported on nanoporous TiO₂”, *Chem. Commun.*, 2004, 16: 1810.
- [30] Y. Tian, T. Tatsuma, “Mechanisms and Applications of Plasmon-Induced Charge Separation at TiO₂ Films Loaded with Gold Nanoparticles”, *J. Am. Chem. Soc.*, 2005, 127: 7632.
- [31] N. Chandrasekharan, P.V. Kamat, “Improving the Photoelectrochemical Performance of Nanostructured TiO₂ Films by Adsorption of Gold Nanoparticles”, *J. Phys. Chem. B*, 2000, 104: 10851.
- [32] A. Takai, P.V. Kamat, “Capture, Store, and Discharge. Shuttling Photogenerated Electrons across TiO₂–Silver Interface”, *ACS NANO*, 2011, 5: 7369.
- [33] J. Liu, F. Chen, “Plasmon enhanced photoelectrochemical activity of Ag–Cu nanoparticles on TiO₂/Ti substrates”, *Int. J. Electrochem. Sci.*, 2012, 7: 9560.
- [34] N. Sakai, Y. Fujiwara, Y. Takahashi, T. Tatsuma, “Plasmon-Resonance-Based Generation of Cathodic Pho-

to current at Electrodeposited Gold Nanoparticles Coated with TiO₂ Films”, *ChemPhysChem*, 2009, 10: 766.

[35] A. Furube, L. Du, K. Hara, R. Katoh, M. Tachiya, “Ultrafast Plasmon-Induced Electron Transfer from Gold Nanodots into TiO₂ Nanoparticles”, *J. Am. Chem. Soc.*, 2007, 129: 14852.

[36] L. Liu, G. Wang, Y. Li, Y. Li, J.Z. Zhang, “CdSe quantum dot-sensitized Au/TiO₂ hybrid mesoporous films and their enhanced photoelectrochemical performance”, *Nano Res*, 2011, 4: 249.

[37] V.V. Agrawal, P. Mahalakshmi, G.U. Kulkarni, C.N. Rao, “Nanocrystalline films of Au-Ag, Au-Cu, and Au-Ag-Cu alloys formed at the organic-aqueous interface”, *Langmuir*, 2006, 22: 1846.

[38] D.W. Gong, C.A. Grimes, O.K. Varghese, W.C. Hu, R.S. Singh, Z. Chen, E.C. Dickey, “Titanium oxide nanotube arrays prepared by anodic oxidation”, *J. Mater. Res.*, 2001, 16: 3331.

[39] B. Wickman, Y.E. Seidel, Z. Jusys, B. Kasemo, R.J. Behm, “Fabrication of Pt/Ru nanoparticle pair arrays with controlled separation and their electrocatalytic properties”, *ACS NANO*, 2011, 5: 2547.

[40] J. Herrmann, J. Disdier, P. Pichat, A. Fernandez, A. Gonzalez-Eliphe, G. Munuera, C. Leclercq, “Titania-supported bimetallic catalyst synthesis by photocatalytic co-deposition at ambient temperature: Preparation and characterization of Pt-Rh, Ag-Rh, and Pt”, *J. Catalysis*, 1991, 132: 490.

[41] K. Mohammadi, A. Moshaii, M. Azimzadeh-rini, Z. Pourbakhsh, “Photoelectrochemical activity of Ag loaded TiO₂ nanotube arrays produced by sequential chemical bath deposition for water splitting”, *Journal of Materials Science: Materials in Electronics*, 2019, 30: 1878.