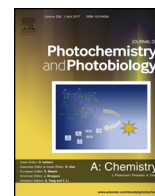




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Invited feature article

Plasmonic metal decorated titanium dioxide thin films for enhanced photodegradation of organic contaminants

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ABSTRACT

Photocatalysis using titanium dioxide as photocatalyst is an efficient way for the removal of organic contaminants in water using solar energy. In this study, thin films of copper and silver were deposited on fused silica using the thermal evaporation technique. A 100 nm film of titanium dioxide (TiO₂) was then deposited on the plasmonic metal films using a sputter coating technique. The opposite order of deposition of the film was also explored. The prepared thin films were fully characterized using high resolution scanning electron microscopy (HRSEM), X-ray diffraction (XRD), atomic force microscopy (AFM) and Rutherford backscattering spectrometry (RBS). The effect of plasmonic metal film thickness, order of deposition and the use of bimetallic layers on the photocatalytic activity of the TiO₂ photocatalyst was evaluated using methyl orange as a model pollutant. It was shown that, the increase in Ag film thickness underneath the TiO₂ film increased the photocatalytic activity of the TiO₂ photocatalyst until an optimum film thickness of 20 nm was attained. In the case of copper, the increase in film thickness above 5 nm led to reduced photocatalytic activity. Silver was found to be a better plasmonic metal than copper in enhancing the photocatalytic activity of TiO₂ under UV light illumination. Cu was found to perform better when deposited underneath the TiO₂ film whereas Ag performed better when deposited on top of the TiO₂ photocatalyst film. The use of bimetallic layers was found to enhance TiO₂ photocatalytic activity more than monometallic layers.

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1. Introduction

Access to adequate and safe drinking water is vital for human health hence it will remain a high priority. Due to an increase in population sizes and industrialization, the pressure on the available water resources for safe drinking water has increased. Many contaminants such as toxic metals, persistent organic contaminants from pharmaceutical industries, endocrine disruptors and dyes from textile industries are discharged into the environment resulting in contamination of the available water resources. Among the various methods available for water purification, some conventional methods such as flocculation and coagulation, ultrafiltration and adsorption using activated carbon have the disadvantage of creating secondary pollution which requires further treatment, disposal of the solid waste and

difficult regeneration of the adsorbent which makes these expensive options [1,2]. Besides the high operational costs, these methods could generate toxic secondary pollutants which can further pollute the environment [3].

These factors have led to the rapid development of alternative treatment methods to replace conventional methods, such as advanced oxidation processes (AOPs) which are very promising methods for treating contaminated water. Much attention has been given to photocatalysis due to its potential to degrade a wide range of recalcitrant organic contaminants into less harmful products at ambient temperature [4–6].

The TiO₂ photocatalyst only absorbs UV light which is a major drawback in its application. Several ways have been used to extend its absorption into the visible region which makes about 50% of the total solar radiation available and these include noble metal loading (plasmonic elements), ion doping, anion doping, dye sensitization and the use of composite semiconductors. The introduction of metallic nanostructures such as gold and silver into a semiconductor film to enhance photocatalytic activity by strong plasmonic effects has received attention recently [7]. The

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plasmonic elements increase the light absorption to boost the excitation of electrons in TiO₂ resulting in increased photoelectric conversion efficiency. Irradiating Au nanoparticles at their plasmon resonance frequency for instance, results in the creation of intense electric fields which increase the rate of electron-hole pair generation in semiconductors. This extends the photocatalytic activity of wide band gap semiconductors into the visible region of solar radiation. Previous studies have shown that the deposition of noble metals also reduces the recombination of the photo-generated electron-hole pairs resulting in enhanced photocatalytic activity [8–10].

Previously, TiO₂ photocatalysts were mainly used as a suspension in the form of a powder but the recovery of the photocatalyst adds unnecessary costs such as the filtration to purify the water. This prompted the coating of the photocatalyst on various surfaces which include silica, zeolite, activated carbon and quartz. Therefore in this study, the nanoparticles were deposited as thin films on fused silica which is transparent to light.

2. Experimental procedures

2.1. Materials

Hydrogen peroxide was purchased from Sigma Aldrich, sulphuric acid and bisphenol A were purchased from MET-U-ED, 3-mercaptopropyltrimethoxysilane from Alfa Aesar, hydrofluoric acid and 2-propanol were supplied by Associated Chemical Enterprises (Pty)(Ltd) and methyl orange was obtained from Merck. All reagents and solvents were used as received without further purification.

2.2. Silver and copper film deposition

Thin films of copper and silver were deposited on 3-mercaptopropyltrimethoxysilane (MPTMS) surface modified fused silica with dimensions of 2.5 cm by 3.5 cm, using the thermal evaporation technique. The method for the treatment of fused silica with MPTMS was reported in literature [11]. For the deposition of copper, the copper source material was loaded onto a tungsten sample holder and placed in the centre of the thermal evaporator's dome. A desired vacuum was created using a vacuum pump. The current was then increased slowly until the copper source material started to melt and evaporate. The evaporated material was deposited on fused silica support that was placed above the copper source. This system was fitted with an acoustic crystal monitor for controlling the amount of metal deposited. When the desired thickness was achieved, the swing arm shield was closed to prevent more material from depositing onto the fused silica supports followed by switching off the vacuum pump and allowing air into the chamber to release the vacuum. The same procedure was repeated for the deposition of silver. Table 1 shows the parameters used for the deposition of the metal thin films on the MPTMS treated fused silica.

Different thicknesses of the plasmonic elements were prepared and QPod.exe software was used for the film thickness determination. Bimetallic films were also prepared using the same procedure. The metal films were deposited one at a time, layer

Table 1
Experimental conditions used to prepare Cu and Ag thin films.

Parameter	Copper	Silver
Vacuum Pressure (Pascal)	3.0×10^{-3}	3.2×10^{-3}
Current (Amps)	95	100
Rate of deposition (nm/s)	Variable (0–1.2)	Variable (0–1.2)
Frequency (Hz)	591365.25	591365.25

by layer. The sample description and codes of the prepared samples are given in Table 2.

2.3. TiO₂ thin film preparation

TiO₂ was deposited on top or below of the noble metal films using the electron sputter coating technique. In a typical experiment, the titanium source material and fused silica support to be coated were placed in the chamber of the sputter coating instrument. A vacuum was created and oxygen gas was introduced into the chamber to react with titanium to form the desired product (TiO₂). The voltage used was between 460 and 465 V and the deposition rate of the TiO₂ film was approximately 1 nm per minute. In order to obtain a 100 nm TiO₂ film, the deposition was done for about 1 h 40 min. The parameters used for depositing the thin film of TiO₂ were: current 0.28 amps, power 129 W, voltage 460–465 V and a pressure of 60 mmHg. TiO₂ photocatalysts with metal films layered above TiO₂ were also prepared using the same procedure.

2.4. Photocatalyst characterization

The crystallographic properties of the prepared Ag/TiO₂ and Cu/TiO₂ thin films were obtained using X-ray diffraction using a Bruker D8 Advance instrument with a Cu-K α 1 (λ – 1.54060 nm) X-ray tube and a LynxEye detector. The scanning range was from 2 theta value of 25° to 90°. The structure and morphology of the nanoparticles forming the thin films were analysed by HRSEM using an Auriga Zeiss Field Emission Scanning Electron Microscope where the SmartSem 5 software supplied with the instrument was used to capture images and AZTEC 1.2 program was used to do EDS (energy dispersive spectroscopy). The samples were sputter coated with carbon prior to HRSEM analysis. Rutherford Backscattering Spectrometry (RBS) measurements were performed with 2 MeV alpha (4He⁺) particles using 6 MV Van de Graaff accelerator. The scattering angle was $\theta = 165^\circ$ and the detector resolution was 20 KeV. The beam current was approximately 50 nA. The AFM analysis was performed in Nanosurf and the data was handled by the easyScan software.

2.5. Photocatalytic activity evaluation

The photocatalytic activities of the thin films were evaluated based upon the removal of methyl orange as a model pollutant. The Ag/TiO₂ and Cu/TiO₂ thin films on fused silica were immersed in a 10 ppm (30.6 μ M) methyl orange solution. The methyl orange solution was prepared using distilled water. The solution was then irradiated with UV light of wavelength 254 nm. Aliquots were

Table 2
Sample description and codes.

Sample description	Sample Code
TiO ₂ film with no metal film	T1
TiO ₂ deposited on 5 nm Cu film	T5Cu
TiO ₂ deposited on 10 nm Cu film	T10Cu
TiO ₂ deposited on 20 nm Cu film	T20Cu
TiO ₂ deposited on 25 nm Cu film	T25Cu
TiO ₂ deposited on 5 nm Ag film	T5Ag
TiO ₂ deposited on 10 nm Ag film	T10Ag
TiO ₂ deposited on 20 nm Ag film	T20Ag
TiO ₂ deposited on 25 nm Ag film	T25Ag
TiO ₂ deposited on Ag (5 nm) and Cu (5 nm)	TAC
2 nm Ag film deposited on TiO ₂ film	2AgT
5 nm Ag film deposited on TiO ₂ film	5AgT
2 nm Cu film deposited on TiO ₂ film	2CuT
5 nm Cu film deposited on TiO ₂ film	5CuT

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