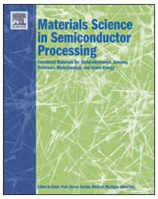
Materials Science in Semiconductor Processing 76 (2018) 25–30

Contents lists available at ScienceDirect

Materials Science in Semiconductor Processing

journal homepage: www.elsevier.com/locate/mssp



Visible active gold/carbon co-doped titanium dioxide photocatalytic nanoparticles for the removal of dyes in water

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ARTICLE INFO

Keywords:
Titanium dioxide
Doping
Photocatalysis
Nanoparticles

ABSTRACT

Gold/carbon co-doped TiO_2 photocatalysts with different contents of gold were prepared using a wet chemical technique, immobilized on fused silica and tested for their photocatalytic activity using methyl orange under visible light. Co-doping significantly red shifted the absorption edge of the photocatalysts. The synergistic effects between gold and carbon were best when the Au content was 1.0% where the lowest band gap of 2.45 eV and high photocatalytic activity towards methyl orange were achieved. Co-doping was also found to promote anatase to rutile phase transformation and the highest transformation was achieved by using 0.5% of Au. The effect of the simultaneous photodegradation of methyl orange and bisphenol A was also studied and it was observed that the photodegradation rates achieved for each contaminant was reduced in the bi-component system when compared to the mono-component system.

1. Introduction

Dyes are widely used in industries such as textile, pharmaceutical, food, cosmetic and leather industry. Among these, the textile industry is heavily polluting and consumes a lot of water during the dyeing and finishing processes. It has been reported that about 80% of the total discharge of wastewater comes from the textile industry hence; the removal of these dyes from wastewater has received worldwide concern [1]. This has resulted in over 15% of the world population lacking access to safe potable water which is a requirement to the human society [2].

The commonly used methods for the removal of dyes include adsorption, flocculation and coagulation and degradation [3]. Although the adsorption technique is simple and easy to operate, it requires proper disposal of the adsorbed organics contaminants. In recent years, researchers have been focusing mainly on advanced oxidation processes (AOP) such as photocatalysis for the removal of organics from water as it is capable of degrading and mineralizing these pollutants [4]. In photocatalysis, several semiconductor photocatalysts can be used but the most preferred and promising for environmental applications is TiO_2 because of its biocompatibility, chemical stability, cheap, high reactivity, and availability.

When TiO_2 absorbs a photon with energy equal to or greater than its band gap, an electron is excited from the valence band to the conduction band creating a positive hole in the valence band. The holes have an oxidation potential of +2.6 V and these are capable of oxidizing water or hydroxide to produce hydroxyl radicals ($OH^{\bullet}$), [5]. The $OH^{\bullet}$ radicals are very powerful oxidizing agents and indiscriminant. However, pure TiO_2 photocatalyst is only active under UV light irradiation due to its wide band gap energy of 3.2 eV [6] hence there is a need to extend its spectral response into the visible region which makes 55% of the total solar radiation.

Major efforts have been devoted in extending the use of TiO_2 efficiently under solar radiation energy [2,7]. The modification of TiO_2 through doping is one of the promising and convenient approaches to make it visible light active and enhance its photocatalytic performance. Doping has been done using metals such as Fe^{3+} [8] Cu and Zn [9], Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+} and Ba^{2+} [10], non-metals such as C [11], N [12], S [13] or both metal and non-metal for instance Ce & S co-doping [14]. Co-doping has been found by some researchers to further enhance the photocatalytic activity of TiO_2 than doping with a single element. TiO_2 co-doped with N and Fe was found to be more photocatalytically active than either N or Fe doped TiO_2 due to reduced electron-hole recombination rates [15]. In this study, in order to efficiently remove the organic dyes from water without creating secondary pollution under visible light, visible light responsive gold and carbon co-doped TiO_2 photocatalysts were developed.

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https://doi.org/10.1016/j.mssp.2017.12.008
Received 17 August 2017; Received in revised form 13 December 2017; Accepted 14 December 2017

2. Experimental

2.1. Materials

Titanium(IV) tetrachloride (99%) and potassium hydroxide were purchased from Merck (Germany), silver nitrate (99.8%) from SAARCHEM (South Africa). Methyl orange, bisphenol A and glucose were supplied by MET-U-ED (South Africa) and tetrachloro auric acid (HAuCl4) was purchased from Labstuff. All chemicals were analytical grade and were used as received without further purification.

2.2. Photocatalyst preparation

$TiCl_4$ (6.0 mL) was added drop wise to 100 mL of distilled water followed by glucose (0.01 M) solution. The role of glucose in the synthetic process was to act as a source of carbon. Six sets of the solutions were prepared and to each, suitable amounts of $HAuCl_4$ were added to get 0.2, 0.5, 0.7, and 1.0 mol percent of Au. The solution was then heated for 30 min at 95 °C and the pH was adjusted to 8.0 using potassium hydroxide and heated for another 30 min. The precipitate was separated from the solution by centrifugation followed by washing with deionised water. The resulting photocatalysts were calcined at 500 °C and then deposited on fused silica using the method from our previous work [11]. The six different photocatalysts that were prepared were given codes which are shown in Table 1.

2.3. Characterization

Fourier transform infrared (FT-IR) spectra were obtained on a Perkin-Elmer (FT-IR Spectrum 200) spectrophotometer using the KBR method. Diffuse reflectance spectroscopy (DRS) spectra of the samples were acquired from 800 nm to 200 nm at room temperature using a diffuse reflectance attachment of a Cary 500 UV–vis–NIR spectrophotometer. The crystallographic characteristics of the prepared photocatalysts were analysed by XRD technique using a Bruker D8 Advance instrument with a Cu-Kα1 (λ – 1.54060) X-ray Tube and a LynxEye detector. The Raman spectra were obtained on a Czerny-Turner micro-Raman spectrometer equipped with a cooled charged coupled device. The carbon content was determined using a Thermo Scientific CHNS-O-Analyzer; Flash 2000.

2.4. Photocatalytic activity evaluation

The photocatalytic activity of the synthesised photocatalysts was evaluated using methyl orange (MO) and bisphenol A (BPA) under visible light and also UV light irradiation using the method reported in literature [11]. In a typical experiment, the photocatalyst coated fused silica was immersed in 100 mL of 10 ppm methyl orange solution. The flask was then placed in the dark for an hour for adsorption and desorption equilibrium to take place. The system was then irradiated with visible light from an Oriel Newport solar simulator fitted with a 500 W xenon lamp. After every 30 min, aliquots of methyl orange were taken and analysed by a UV–vis spectrometer at a wavelength of 468 nm.

Table 1
Sample description and codes.

Sample description	Sample code
Undoped TiO_2	T0
Au/C co-doped TiO_2 (0.0% Au)	TAu0
Au/C co-doped TiO_2 (0.2% Au)	TAu1
Au/C co-doped TiO_2 (0.5% Au)	TAu2
Au/C co-doped TiO_2 (0.7% Au)	TAu3
Au/C co-doped TiO_2 (1.0% Au)	TAu4
Au doped TiO_2 (0.5% Au)	TAu5

3. Results and discussion

The FTIR spectrum of TAu4 showed the most pronounced peaks around 3450 cm^{-1} and 1655 cm^{-1} assigned to the hydroxyl group of adsorbed water (Fig. 1A). The intense broad band in the range 400–900 cm^{-1} common in the spectra of all samples is assigned to the stretching vibration of the Ti-O bond. The peak at 2358 cm^{-1} in the spectra of doped samples was ascribed to the presence of carbon species [16].

Well-defined Raman peaks were observed at 145 cm^{-1} (E_g), 244 cm^{-1}, 404 cm^{-1} (B_{1g}), 453 cm^{-1} (E_g), 525 cm^{-1} (B_{1g}), 617 cm^{-1} (A1g) and 641 cm^{-1}(E_g) as shown in Fig. 1B. There were no apparent Raman shifts observed with an increase in gold content. The increase in gold content from 0.2% to 0.5%, caused a major decrease in the intensity of the peak at 144 cm^{-1}, disappearance of peaks at 404 cm^{-1}, 519 cm^{-1}, and 641 cm^{-1} and an increase in intensity of peaks at 237 cm^{-1}, 451 cm^{-1} and 617 cm^{-1}. The strongest band of the anatase phase at 145 cm^{-1} in the spectra of T0 slightly shifted to 147 cm^{-1} in the spectra of doped TiO_2. The rutile phase peak at 244 cm^{-1} was observed in all doped samples except undoped TiO_2 implying that doping could have promoted anatase to rutile phase transformation. This is also supported by the reduction in intensities of anatase peaks at 404 cm^{-1} and 644 cm^{-1} and a huge increase in intensities of the rutile peaks at 453 cm^{-1} and 617 cm^{-1} in the spectra of doped TiO_2 photocatalysts.

The XRD peaks at $2\theta = 27.6°$, 36.1°, 41.1°, 43.81°, 54.6°, 68.8° were due to the rutile phase and those at $2\theta = 25.1°$, 37.6°, 47.8°, 53.9°, 56.2°, 62.5°, 68.8°, 70.4°, 74.8°, 82.4° anatase phase (Fig. 1C). The peaks at 27.6°, 36.1°, 41.1°, 43.81°, and 54.6° were only found in in the spectra of T0. New diffraction peaks were observed at 43.5° and 63.72° in the spectra of co-doped samples due to rutile and anatase respectively. The amount of rutile phase that was transformed as a mass fraction (F_R) was calculated using Eq. (1) [17].

$$F_R = \frac{1}{(1 + 0.79\frac{I_A}{I_R})} \tag{1}$$

where I_A is the integrated intensity of anatase at 25.3° and I_R is the integrated intensity of rutile at 27.45°. The percentages of anatase (A) and rutile (R) were, T0 (A: 88.13%, R: 11.88%), TAu0 (A: 2.09%, R: 97.91%), TAu1 (A: 63.32%, R: 36.68%), TAu2 (A: 23.73%, R: 76.27%), TAu3 (A: 55.96%, R: 44.04%), and TAu4 (A: 64.63%, R: 35.37%). The highest anatase to rutile phase transformation occurred when carbon was used as the only dopant (ca. 2.09% anatase and 97.91% rutile).

The BET surface areas of the prepared photocatalysts are shown in Table 2. The differences in the surface area of the same material, which otherwise may have the same physical dimensions can greatly influence its performance characteristics. The surface area of pure TiO_2 was 68.97 m^2/g and when it was doped with carbon, the surface area increased to 83.14 m^2/g but when gold was used as the only dopant the surface decreased to 50.25 m^2/g. When the TiO_2 was then co-doped, there was a further decrease in surface area of the resulting TiO_2 photocatalysts. As the gold content was increased, there was slight increase in surface area until an optimum loading of 0.7%. It is believed that a photocatalyst with high surface area is desirable since an enhanced surface area allow greater adsorption of pollutants resulting in enhancement of photocatalytic activity. The results from this analysis showed that co-doping of TiO_2 results in a decrease in the surface area of TiO_2 photocatalyst.

The percentages of carbon in the samples followed the order TAu2 (0.55%) > TAu3 (0.53%) > TAu0 (0.46%) > TAu1 (0.44%) > TAu4 (0.41%). There was no general trend observed in the amount of carbon with increase in gold content in the doped TiO_2 photocatalysts. There was also no general trend that was observed on the band gap shifts with the amount of carbon that was found in the co-doped TiO_2.

Fig. 1D shows the thermograms of the doped and undoped TiO_2