OPTOELECTRONICS AND ADVANCED MATERIALS – RAPID COMMUNICATIONS Vol. 8, No. 5-6, May - June 2014, p. 581 - 586

Photo catalytic degradation of methylene blue by Ag incorporated TiO_2 nanocrystals prepared at different pH conditions

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TiO_2 nanocrystals were synthesized under three different pH conditions by simple sol gel method. Silver is incorporated into the prepared TiO_2 nanocrystals by liquid impregnation method. The properties of the Ag incorporated TiO_2 nanocrystals were studied using XRD, SEM, EDX and UV-Visible spectroscopy. The photo catalytic activity of Ag incorporated TiO_2 nanocrystal has been investigated for methylene blue dye. The irradiation time, pH conditions of the synthesized TiO_2 nanocrystals were taken into account for the photo catalytic degradation process. The optimum irradiation time and pH condition of Ag incorporated TiO_2 nanocrystals were found to be 3 hours and pH=10.6 respectively.

(Received October 5, 2012; accepted May 15, 2014)

Keywords: Ag incorporated TiO_2, photo catalytic, Liquid impregnation

1. Introduction

Titanium dioxide is chemically stable and non toxic which makes it better photo catalyst than others do in practical application, among three phases of TiO_2 nanocrystals anatase is the most active polymorphs as photo catalyst due to its unique structure, which contains more defects; could hold more oxygen vacancies for electron trapping [1-3]. However its technological application has not yet come up to our satisfaction due to wide band gap and high recombination of electron and holes [4-6]. Ag incorporated TiO_2 nanocrystals shows enhanced photocatalytic degradation than pure anatase TiO_2 [4, 7]. Ag is one of the best noble metal due to its low cost easily incorporated with TiO_2 nano crystals and excellent photo catalytic activity. Ag inhibits the recombination of photo generated electron-hole pair due to its strong electron trap ability [4]. The band gap modification by creating oxygen vacancy was done by doping some noble metals like Ag with TiO_2 nanocrystals. The doping of Ag not only modifies the band gap of TiO_2, it significantly enhances the quick trapping of photo generated electrons by hole degradation reaction of organic species [8-10]. The discharge of several hazardous dyes from many textile industries is a main problem. When UV light falls on catalytic surface, hole-electron pairs are produced. These charge carriers involve in degradation of the organic pollution. The possible reactions between the positive holes and electrons with H_2O and O leads to peroxide super oxide radicals which considered as active species in the degradation process [11]. In the present work an attempt is made to synthesize Ag incorporated TiO_2 nanocrystals under three different pH conditions and the role of Ag on the degradation of organic compound was studied.

2. Experimental

Titanium isopropoxide (Alfa Aaser 99.9%) is used as titanium precursor. Absolute ethanol (Hayman 99.9%) is used to prepare the sol. The desired pH (pH=2.6, 7, and 10.6) of the sol was obtained by using dilute nitric acid and sodium hydroxide. Titanium isopropoxide is added drop wise to ethanol with stirring. After one hour of stirring, nitric acid/sodium hydroxide is added to achieve the desired pH of the solution. The final solution is dehydrated in air atmosphere at 70°C. Silver is incorporated with TiO_2 by adding $AgNO_3$ using liquid impregnation method. The silver incorporated TiO_2 nanocrystals thus prepared is annealed at 525°C for one hour using the programmable muffle furnace. To prepare Ag incorporated TiO_2 thin films for photo catalytic applications; the paste was prepared as follows. Briefly, paste was produced by mixing 2.0 g of Ag incorporated TiO_2 powders with a mixture consisting of 5.0 g of α-terpineol, 0.5 g of cellulose, and 20 ml of ethanol, which was sonicated for 24 h at 1,200 W cm^{-2} [12]. By using the prepared paste Ag incorporated TiO_2 thin films were prepared by coating the paste on a well cleaned glass plate using the doctor blade technique. The prepared films were annealed at 525°C for 30 min. To identify the crystal structure, X-ray diffraction studies were carried out using PANalytical X-ray diffractometer with nickel-filtered CuKa (30 kV, 30 mA). The surface morphology of the samples was studied using scanning electron microscopy

(SEM; S-4100, Hitachi). The optical properties were studied using the absorbance spectra recorded by Cary 500 spectrometer.

3. Result and discussion

The crystalline structure of TiO_2 greatly affects the photo catalytic activity. Therefore, the crystalline phase of Ag incorporated TiO_2 nanocrystals were investigated by X-ray diffraction technique. Fig. 1 shows the X-ray diffraction pattern of the Ag incorporated TiO_2 nanocrystals. This indicates that the synthesized TiO_2 nanocrystals are in anatase form, which matches well with the JCPDS data (02-0406). The other crystalline forms like rutile and brookite are not detected. The dominant peaks in the X-ray diffraction pattern for the samples synthesized using pH=2.6 & pH 10.6 are observed at 2θ about 25.5, 38.3, 48.3, 54.4, 55.3, 63.0, and 69.1 are correspond to (101), (112), (200), (106), (211), (204), and (116) planes of anatase TiO_2 respectively. The remaining peaks are corresponds to the characteristic peaks for Ag [13]. Interestingly the samples synthesized using pH=7 and 10.6 shows higher angle shift compared to sample synthesized using pH=2. The high intensity peaks such as (101), (112) and (200) displayed in Fig. 1 shows this shift clearly. The shift of peak towards lower angles corresponds to a lattice compression caused by replacement of Ti^{+} by Ag^{+} with its associated decrease in the ion radius. The replacement of Ag in the Ti site and the change in ionic radius will make the variation in 'd' induce this type of angle shift. The average grain size of Ag incorporated TiO_2 nanocrystals have been calculated using Scherer's formula, the calculated grain size and the lattice parameters 'a' and 'c' are shown in the Table 1. From the Table 1, it is clear that the particle size decreases first, then increases as pH Increases. However the values for lattice parameter 'a' are found to have more or less same value. But the value for lattice parameter 'c' is found to be greater at pH=7 than in the reaming two cases.

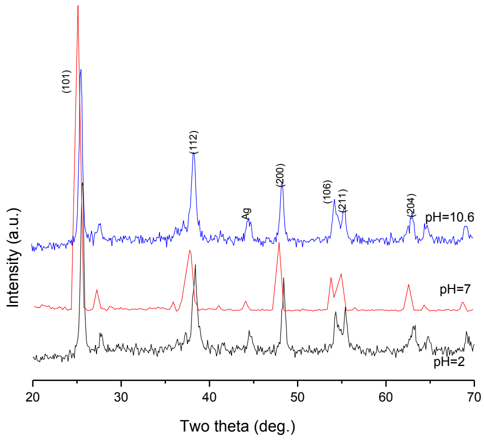

Fig. 1. X-ray diffraction patterns of Ag incorporated TiO_2 nanocrystals prepared at different pH values.

Table 1. Particle size, a, c values and band gap of the Ag incorporated TiO_2 nanocrystal synthesized using different pH conditions.

pH	Particle size (nm)	a-value (nm)	c-value (nm)	Band gap (eV)
2.6	19.76	3.75	9.18	3.74
7.0	12.62	3.79	9.87	3.80
10.6	19.92	3.76	9.18	3.67

Fig. 2 shows the optical properties of Ag incorporated TiO_2 nanocrystals synthesized at different pH values. It can be seen that the absorption of Ag incorporated TiO_2 nanocrystal synthesized using pH=10.6 shows significant red shift compared with Ag incorporated TiO_2 nanocrystals synthesized using pH=2.6 and pH=7, which is attributed to surface plasmon resonance effect of the silver [4]. The surface Plasmon resonance of Ag particle with TiO_2 enhanced the photocatalytic activity of TiO_2 in visible light; the photocatalytic activity of TiO_2 can be distinctly enhanced. Table 1 clearly shows that particle size of the nanocrystals prepared at pH =10.6 is greater than the other conditions. This greater particle size can be attributed to the narrowing band gap (reduction) of the Ag incorporated TiO_2 nanocrystals [14].

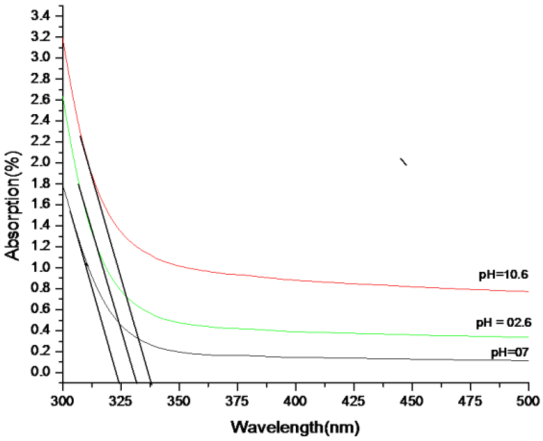

Fig. 2. UV-Vis absorption spectra of Ag incorporated TiO_2 nanocrystals prepared at different pH values.

Fig. 3 shows the SEM images of Ag incorporated TiO_2 nanocrystals prepared at different pH values. The particles are mostly in the shape of spherical [11] the aggregations of the TiO_2 particles are appeared. The sizes of the Ag particles are greater than the TiO_2 grains. The Ag particles are not uniformly dispersed in the TiO_2 matrix. During calcinations the randomly spreading Ag^{+} ions do not develop much stress on TiO_2 anatase grain. So the specific surface area of the anatase grains is not altered. During different preparation condition Ag atom will have the tendency to aggregate in to particles with various shapes. Ag-O bonding is weaker than Ti-O bonding and Ag atom processes higher surface free energy than TiO_2 [15]. It is clear from the SEM images corresponding to pH=2.6 & pH=10.6 have same particle size which are in good agreement with XRD data.

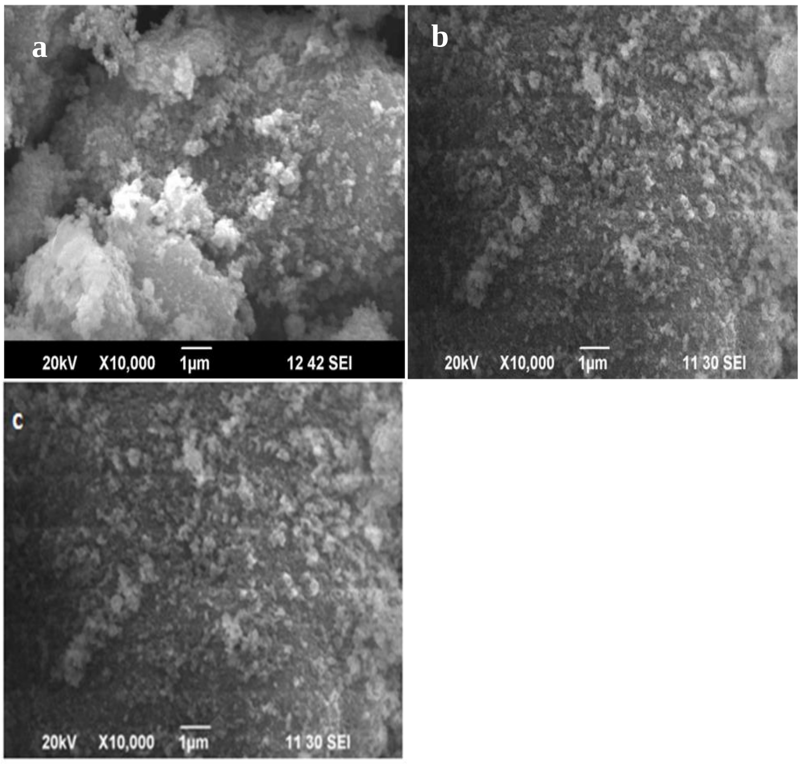

Fig. 3. SEM images of Ag incorporated TiO_2 nanocrystals prepared at pH conditions (a) 7, (b) 2.6 and (c) 10.6.

To confirm the presence of Ag on TiO_2 nanocrystal, the elemental analysis was performed on Ag incorporated TiO_2 nanocrystals prepared at pH=7 and is presented in Fig. 4. The EDXA spectrum exhibits various intense peaks which are associated with Ag, Ti and O atoms. The composition of the elements in the mixed oxide samples is in agreement with those proposed in the preparation progress.

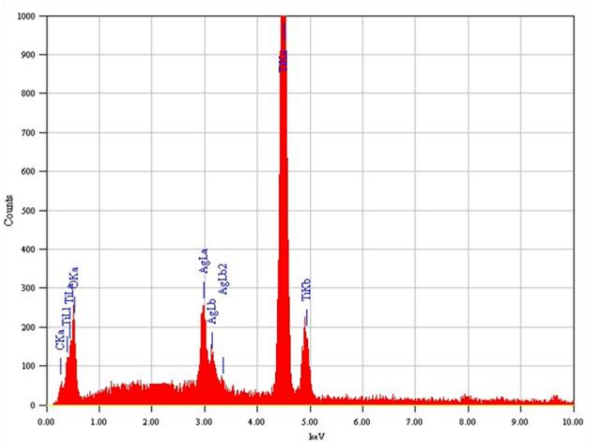

Fig. 4. EDXA of Ag incorporated TiO_2 nanocrystals prepared at pH=7.

Methylene blue is one of the hazardous organic dyes which exist in the waste water and causes serious environmental problems [11]. We use this dye as model sample to evaluate the photo catalytic activity of the Ag incorporated TiO_2 nanocrystals prepared at different pH values. The photo catalytic experiments were carried on the catalysts sample with definite dye concentration (10 ppm). The concentration of the methylene blue dye is estimated using the linear part of the absorbance spectra. Fig. 5 depicts the absorbance spectra of the typical time dependent UV–Vis spectra of methylene blue dye during photo irradiation with Ag incorporated TiO_2 nanocrystalline thin films. The rate of decolourization was recorded with respect to the change in the intensity of absorption peak in visible region. The prominent peak is observed at λ_{max} of 656.50 nm which decreased gradually with increase of irradiation time from 1 hour to 3 hour, the percentage of degradation (%D) was calculated using the following equation.

$$\text{Percentage of degradation (\%D)} = (A_0 - A_t / A_0)*100$$

Where A_0= absorbance at t = 0 minute

A_t = absorbance at t minute

For the degradation experiments, fixed amount of methylene blue dye (10ppm) was taken in a beaker and the Ag incorporated TiO_2 thin film was suspended inside the beaker. The beaker was subjected to irradiation under UV light (8WPhilips bulb TUV-08) kept at a distance of 15 cm for fixed interval of time. Fig. 6 shows the effect of irradiation time of the catalyst on the decolourization of methylene blue. It can be observed that the initial slopes of the curves representing rate of decolourization, increases greatly with increasing irradiation time. The catalyst dosage also decided by the photo catalytic destruction of other organic pollutants [16]. This can be explained on the basis of catalyst loading which is found to be dependent on initial solute concentration because with the increase in catalyst dosage, total active surface area increases. Hence availability of more active sites on catalyst surface increases [17].

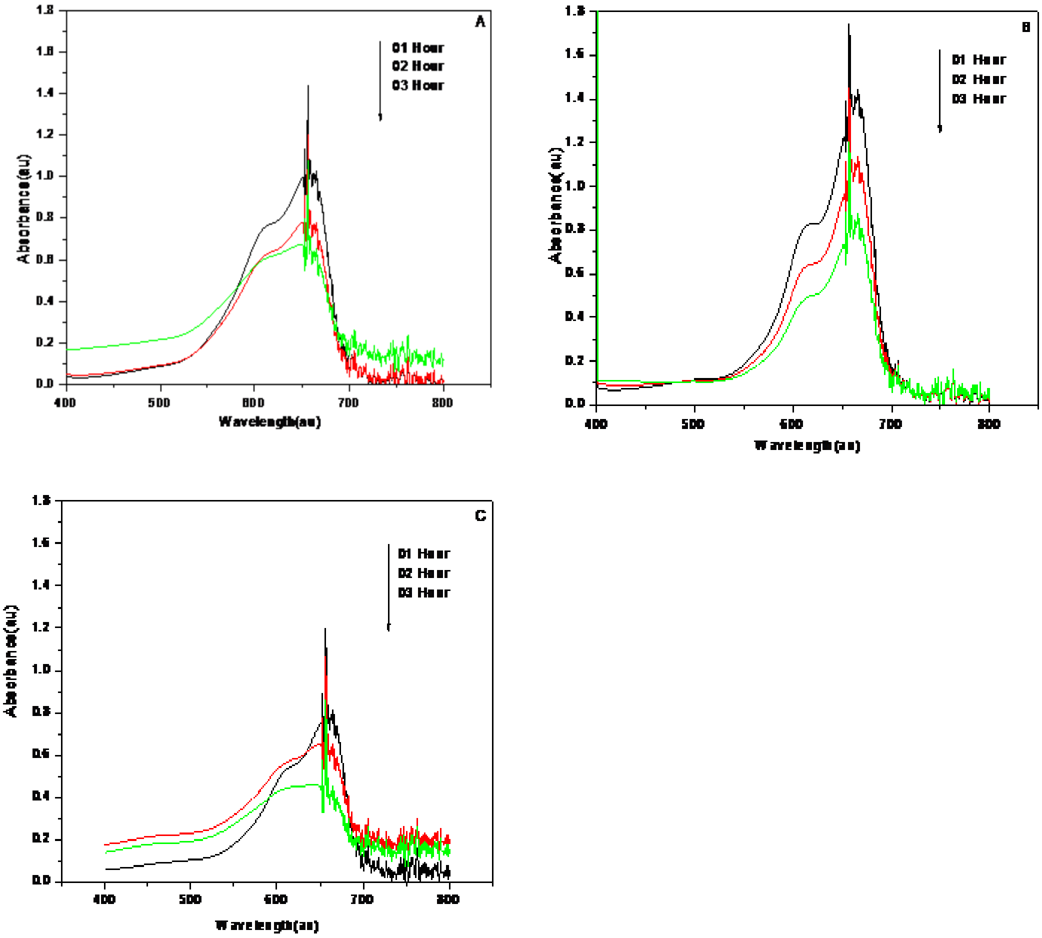

Fig. 5. The time dependent UV–Vis absorption spectra of methylene blue subjected to Ag doped TiO_2 nanocrystals prepared at pH = a) 7, b) 2.6 and c) 10.6.

The degradation of the methylene blue is studied by using UV spectrophotometer of type UV-1800 series. It is observed from the Fig. 5 that the maximum absorbance wavelength corresponds to methylene blue dye is 656.50 nm. The intensity of peaks corresponds to the maximum wavelength decreases as time increases i.e. the degradation of methylene blue is in proportion with time. The degradation of methylene blue by the Ag incorporated TiO_2 nanocrystalline thin films prepared using pH=2.6 is 45.5%. This poor degradation of methylene blue by the film is due to positive surface charge on the TiO_2 surface. The positive charge on the TiO_2 surface does not pay attention to attract the methylene blue molecule since it is a cationic dye [18]. The degradation of methylene blue by the Ag incorporated TiO_2 nanocrystalline thin films prepared using pH=10.6 is 69.4%. This may be due to the negative surface charge on the TiO_2 surface these charge readily attract the methylene blue molecule and degrade it. The degradation of methylene blue by the film prepared at pH=7 is 48.8%. It is inferior to the film prepared at pH=10.6. This result reveals that incorporating Ag with TiO_2 nanocrystals at higher pH only encourage more the decolourizations.

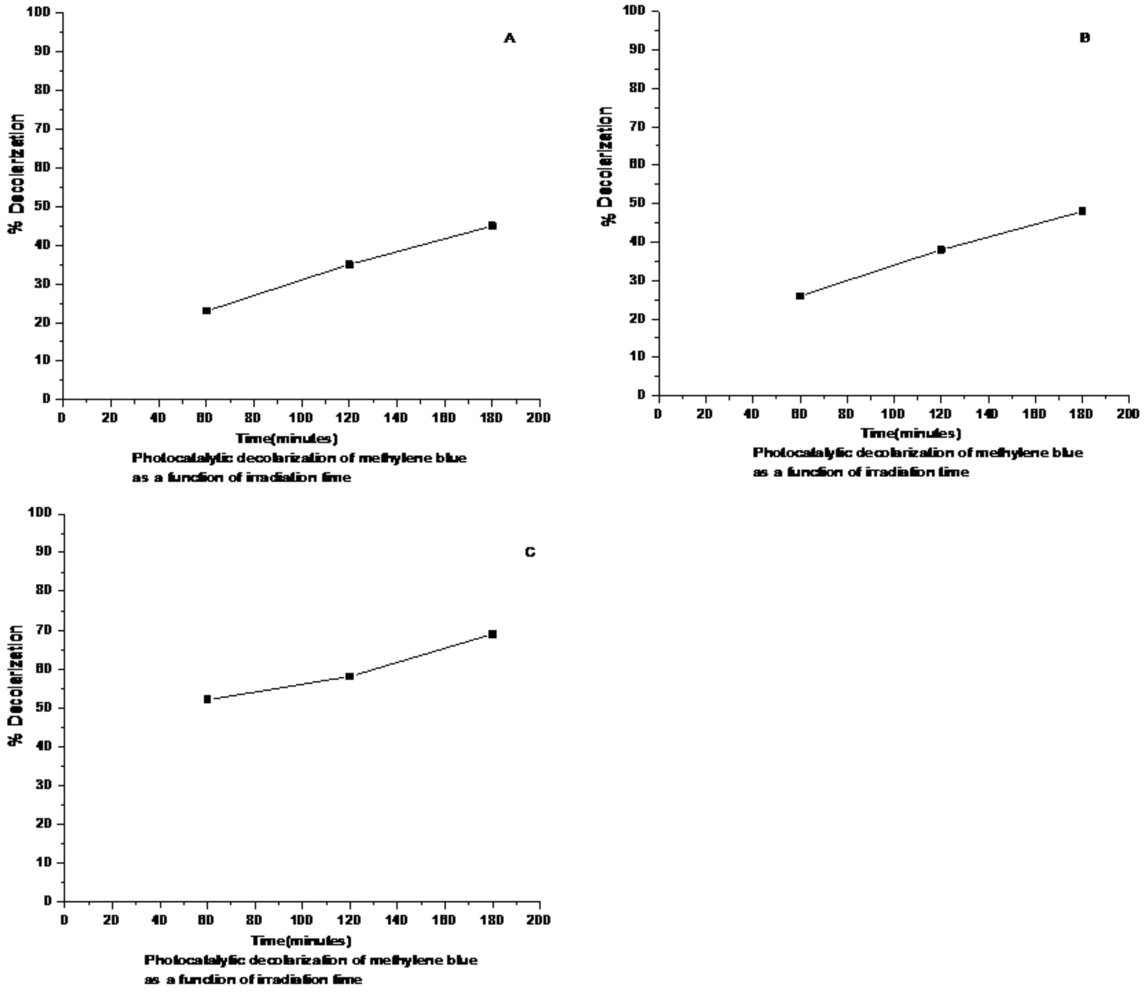

Fig. 6. photo catalytic decolorization of methylene blue as a function of irradiation time for different pH conditions A) 7 B) 2.6 and C) 10.6.

4. Conclusion

Ag incorporated TiO_2 nanocrystalline thin films have been successfully prepared at three different pH conditions. Results indicates that the light absorbance extents to the visible region for the nanocrystalline Ag incorporated TiO_2 powder synthesized using pH = 10.6. In the nanocrystalline Ag incorporated TiO_2 thin film Ag inhibits the e-h recombination and enhances the photocatalytic activity. In our paper it is found that the nanocrystalline Ag incorporated TiO_2 thin film (using the powder synthesized in higher pH condition ie pH = 10.6) has the highest photocatalytic activity.

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