

IMPACT OF SILVER DOPANT ON STRUCTURAL AND OPTICAL PROPERTIES OF TiO₂ NANOPARTICLES

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Pure and silver doped Ag_x(TiO₂)_{1-x} nanoparticles (NPs) with x= 1wt%, 3wt%, 5wt% and 7wt% were synthesized by co-precipitation method. The effect of silver concentration on structural and optical properties of Ag_x(TiO₂)_{1-x} nanoparticles was investigated using XRD, SEM, UV-Visible, FTIR and Raman spectroscopy. XRD results revealed that TiO₂ crystalline in two phases: anatase and rutile, and crystallite size varies from 31.15 nm to 7.01nm. SEM analysis indicated that shape of silver-doped NPs become regular, homogeneous with less agglomeration. UV-Visible analysis indicated that as the silver content increases, cut off wavelength (absorption) increases while band gap decreases from 3.78~ 2.89 eV. This shift from ultraviolet to visible region, which may enhance its photocatalytic activity. FTIR peaks verified that IR spectra of pure and Ag-doped TiO₂ nanoparticles remained unaltered. Raman spectroscopy illustrated that there was blue shift in peaks for Ag-doped TiO₂ nanoparticles. From all these results, it was determined that Ag-doped TiO₂ nanoparticles showed better structural and optical properties as compared to pure TiO₂ which is much suitable for photocatalytic activity.

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1. Introduction

Titanium dioxide (TiO₂) due to its unique properties has become one of the most important and innovative nanostructure. Structural and optical properties of TiO₂ are very important because of their usage in solar cells, pigments, papers and photocatalytic activities. Titanium dioxide is a potential candidate for photocatalytic process due to its suitable optical and electronic properties, corrosion resistance, chemical stability and non-toxic nature [1].

Titanium dioxide is widely used as a catalyst under ultra-violet irradiation and is pondered the best metal oxide due to its low band-gap 3.2 eV for anatase phase and 3.0 eV for rutile phase. Some visible light is absorbed by rutile phase while anatase phase shows absorbance only in ultra-violet spectrum. The best and optimal photocatalytic efficiency is achieved by mixing of anatase phase with a small content of rutile phase. At temperature 300-600°C mostly anatase phase is appeared which is much more suitable to enhance the photocatalytic performance [2].

The drawback of titanium dioxide is that it does not absorb visible light which is due to the wide band gap of titanium dioxide and it limits the application of TiO₂ under the light of sun. In order to resolve this problem, there are several approaches that are employed. These techniques are doping, sensitization, coupling and capping of titanium dioxide. Among all of these, doping by using noble metals such as platinum (Pt), gold (Au), palladium (Pd), nickel (Ni), copper (Cu), silver (Ag), strontium (Sn) are the most suitable choices[3]. Silver (Ag) is selected for doping in TiO₂ due to its high stability, electrical and thermal conductivities which strongly improves its structural and optical properties. The incorporation of silver dopants in titanium dioxide alters the band gap towards longer wavelength, which enhanced photocatalytic activity. In order to increase the absorption of light in TiO₂, larger surface area is required, and the surface area is proportional

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to particle size. The doping of silver in titanium dioxide also reduces the particle size which enhanced the absorption of light [4].

Silver doped TiO₂ NPs can be synthesized by several methods such as electrochemical method [5], mechanical ball milling method [6], chemical synthesis (co-precipitation) and hydrothermal method [7]. Among all these methods, co-precipitation is a simple, economical and relatively appropriate to synthesize NPs in laboratory without a lot of struggle and expensive instrumentation. The goal of this research work was to study the impact of silver dopants on structural and optical properties of TiO₂ NPs using XRD, SEM, UV-Vis, FTIR and Raman spectroscopy techniques.

2. Experimental procedure

To synthesize pure and silver doped titanium dioxide, the titanium tetra iso-propoxide (Ti{OCH(CH₃)₂}₄) was dissolved along with silver nitrate (AgNO₃) in solution of methanol (CH₃OH) and then kept on magnetic stirrer for continuous stirring for two hours at room temperature. During stirring the aqueous solution of sodium hydroxide (NaOH) was added drop wise. The addition of NaOH aqueous solution continues till the 10 pH of solution was obtained. After two hours stirring of solution, the precipitates were obtained at the bottom of beaker. Then this solution was filtered and washed 4 to 5 times with methanol in order to remove the impurities from the solution. After filtration and washing, gel was obtained and dried at room temperature for 24 hours. The dried gel was kept in oven for 8 hours at 80°C. After this procedure of drying, the dried precipitates were grinded in an agate mortar. Finally, the collected powder was calcined at 600 °C for four hours.

3. Results and discussion

3.1. XRD analysis

Fig.1 shows the XRD spectra of pure and Ag-doped TiO₂ NPs. The pure TiO₂ spectrum shows two phases (anatase and rutile) of tetragonal TiO₂. These two peaks appeared at (110) and (101) of rutile phase at 2θ values of 28.25° and 32.31° respectively, while (101) and (004) planes of anatase phase of TiO₂ NPs appeared at 2θ values of 30° and 37.82° [5] respectively. After the addition of Ag, there was two planes (111) and (200) appeared at 2θ values of 38° and 44° respectively. It can also be seen that most of the 2θ peak positions of major diffraction pattern in all Ag-doped TiO₂ samples showed no planes shifting except the intensities of these peaks. There was no change in phases of TiO₂ NPs due to Ag doping. It showed that Ag doped TiO₂ NPs are in good homogeneity and also there is no significant change in TiO₂ crystallinity, because Ag⁺ ion radii (126Å) was too large to replace Ti⁴⁺ (68Å) ions in the TiO₂ matrix. So, addition of Ag didn't change the phase structure of the TiO₂, which indicated that Ag was formed on the crystal grain boundary and on the surface of TiO₂.

Fig. 2 expressed that as the silver content was increased, the size of TiO₂ crystallite was decreased. The reduction in particle size by doping of Ag in TiO₂ is due to the grain-boundary pinning which is due to dopant ions, it confines the growth of grain by the symmetry-breaking effects of ions at the boundary of grain, that's why smaller size particles are formed. Hence, the particle size can be further decreased as Ag contents increases in TiO₂.

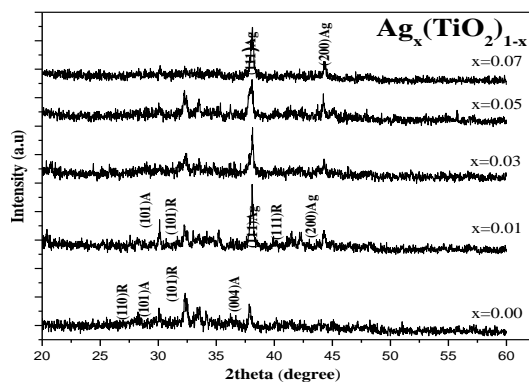


Fig.1. XRD spectra of pure and Ag-doped TiO_2 NPs.

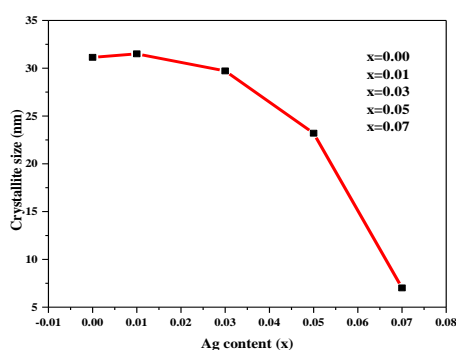


Fig.2. Crystallite size versus Ag content in TiO_2 NPs.

3.2. Scanning electron microscopy (SEM)

Fig. 3(a, b, c, d) shows the surface morphology of $\text{Ag}_x(\text{TiO}_2)_{1-x}$ nanoparticles with $x=0.00$, 0.01, 0.05 and 0.07. SEM analysis indicated that the particles of pure TiO_2 were irregular in shape and non-uniform in size. While, as the silver content was increased the particles were obtained with regular shape and uniform size. The concentration of silver also reduced the agglomeration of particles.

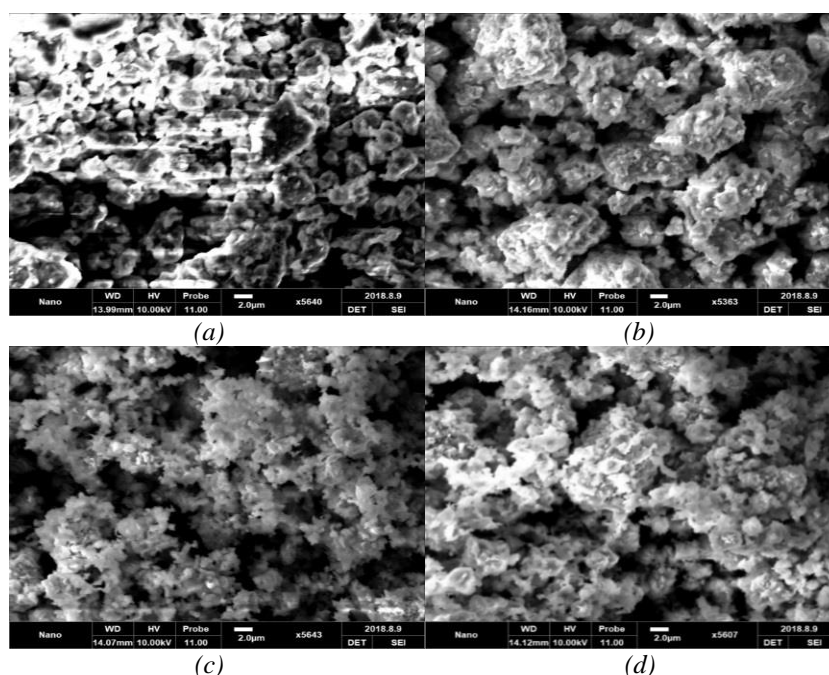


Fig. 3. SEM images of pure and Ag-doped TiO_2 NPs.

3.3. UV-visible spectroscopy

Fig.4 illustrated that pure TiO_2 has the smallest peaks, as the Ag content is increased the peak is getting sharpness which indicates the enhancement in absorbance. The cutoff wavelength (the width of peak) also increases as the silver dopant is increased which is in agreement with the results reported so far [4]. There is a red shift in the wavelength from 329 nm (ultraviolet region) to 429 nm (visible region) for the most silver doped titanium dioxide. Fig.5 shows the band gap energy of Ag-doped $\text{Ag}_x(\text{TiO}_2)_{1-x}$ NPs with $x=0.00, 0.01, 0.03, 0.05$ and 0.07 . It was found that as the silver content increases in the TiO_2 the band gap value decreases from 3.78 eV to 2.89 eV. So, there is a shift in band gap of TiO_2 from ultraviolet region (6.54 eV-3.27 eV) to visible region (3.27 eV-1.59 eV). Hence, this decline in band gap of TiO_2 nanoparticles may enhance its photocatalytic activity.

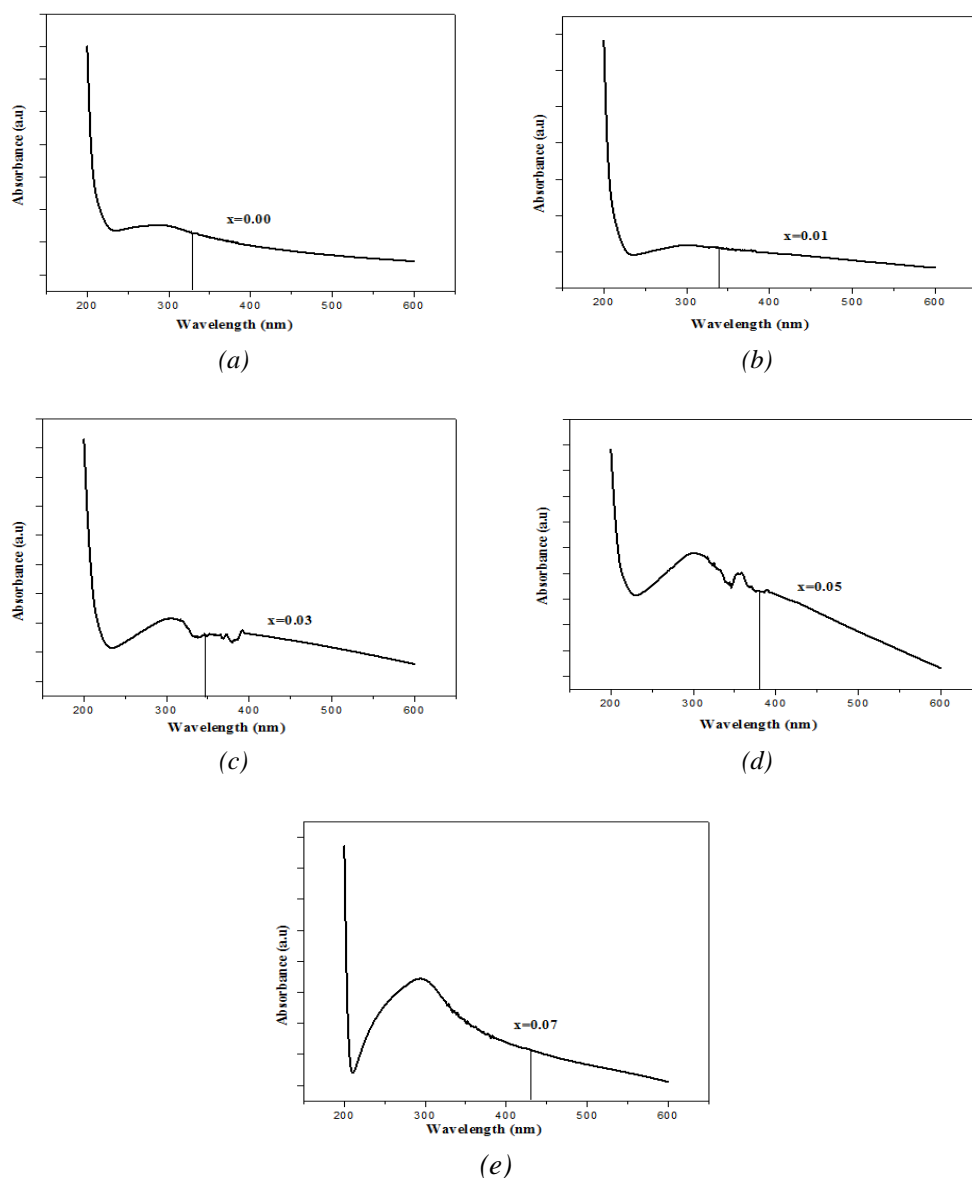


Fig.4. UV-Visible absorption spectra of pure and Ag doped TiO_2 NPs.

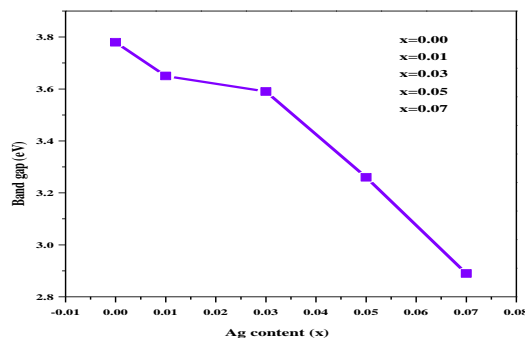


Fig. 5. Band gap versus Ag content in TiO₂ NPs.

3.4. Fourier transform infrared spectroscopy (FTIR) analysis

Fig.6 illustrated the FTIR spectra of pure and Ag-doped Ag_x(TiO₂)_{1-x} nanoparticles with x=0.00, 0.01, 0.03, 0.05 and 0.07. The peaks observed in the range 3400-3500 cm⁻¹ are ascribed to O-H stretching vibrations [8]. The peak at 1630 cm⁻¹ is observed for all the samples and this peak is attributed to the bending vibration of OH [9]. The peaks in the range 1000-1600 cm⁻¹ are associated with stretching vibrations of O-H bond [10]. The bands in the range from 400 cm⁻¹ to 900 cm⁻¹ are due to the stretching vibrations of Ti-O bond [11]. It is clear that there is no difference of spectra of peaks for pure and Ag-doped TiO₂. So, Ag dopant does not affect FTIR spectra of TiO₂ nanoparticles.

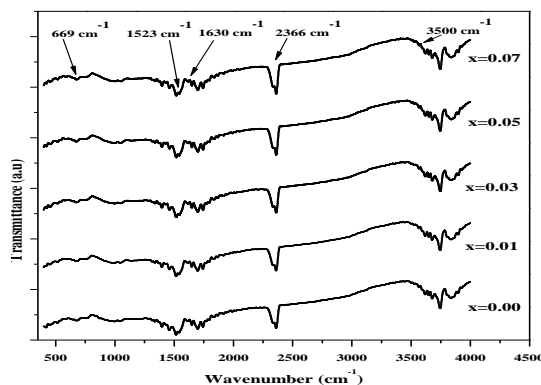


Fig.6. FTIR spectra of pure and Ag-doped TiO₂ NPs.

3.5. Raman spectroscopy analysis

Fig.7 showed the results of Raman spectroscopy of pure and Ag-doped TiO₂. It is evident that there is blue shift in peak at 297 cm⁻¹ and 637 cm⁻¹ of pure TiO₂ to 307 cm⁻¹ and 705 cm⁻¹ of Ag-doped TiO₂ respectively. It is due to the broadening of peaks and decreasing of crystallite size. As the crystallite size decreases, it affects the force constants and vibrational amplitudes of neighbouring bonds due to which blue shift and broadening of peaks occurred [12]. It is clear that there is one mode of E_g that is centered at 637 cm⁻¹. There are two modes of B_{1g} that have peaks at 380 cm⁻¹ and at 516 cm⁻¹ and they are represented by B_{1g} and B_{1g(2d)}. These peaks are in good agreement with results reported so far [8].

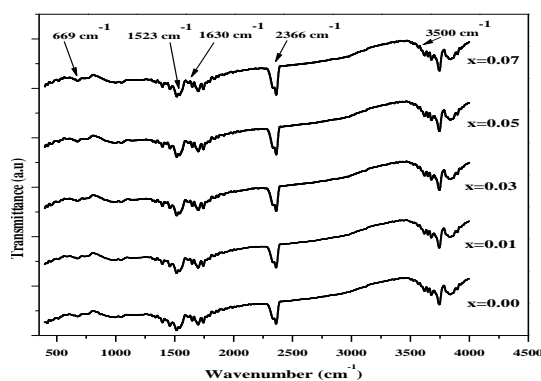


Fig.7. Raman spectra of pure and Ag doped TiO_2 NPs.

4. Conclusions

Pure and Ag-doped TiO_2 NPs were synthesized using co-precipitation method. XRD analysis confirmed two crystalline phases anatase and rutile which indicated that Ag didn't change the phase structure of the TiO_2 and Ag was formed on the crystal grain boundary and on the surface of TiO_2 . As the Ag content increases in TiO_2 the crystallite size decreases (31.14~7.01nm). SEM analysis revealed that the Ag-doped TiO_2 NPs were obtained with the most uniform shape and improved regular size. UV-Visible analysis indicated that as the silver content increases the cut off wavelength increases while band gap decreases from 3.78 to 2.89 eV (shifted from ultraviolet towards visible region). FTIR verified that silver doping did not affect the IR spectra of TiO_2 NPs. Raman spectroscopy illustrated that there was blue shift in peaks for Ag-doped TiO_2 nanoparticles due to decrease in crystallite size. These results exhibited that silver doped TiO_2 NPs do not change the phase, decrease crystallite size and band gap as compared to pure, which may enhance the photocatalytic activity.

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