Hydrothermal Synthesis of Surface Functionalized Semiconducting Nano crystals and Study of their Photo induced Interaction With Natural Dye

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Abstract - *A direct and environmental friendly synthesis method was developed to produce acetylacetone functionalized TiO2 semiconducting nanoparticle by hydrothermal synthesis. Photoinduced interaction between surface functionalized TiO2 semiconducting nanoparticles and Ceanothus thyrsiflorus dyes have been investigated. Ceanothus thyrsiflorus dye was observed as good sensitizers for TiO2 nanoparticles. The charge transfer interaction between dye and semiconducting nanoparticles was studied by UVVIS and FTIR spectroscopy, XRD, SEM and Fluorescence spectroscopic measurements. The adsorption of dye on TiO2 surface leads to increase in optical density as well as quenching of the emission intensity of the dye molecules. Spectroscopic data was used to calculate apparent association constant (Kapp) between dye and nanoparticles. The electron transfer from excited state dye to the conduction band of nano TiO2 is attributable towards quenching of dye.*

1. INTRODUCTION

Developing new nano-materials and interaction studies with organic dye molecules are raising interest in the current scenario for photovoltaic applications. The interaction between semiconductors such as TiO2 with organic dyes is an interesting and useful phenomenon that has undergone a vigorous expansion worldwide in the last few years [1, 2]. This interaction between nanoparticles with dyes is an interesting and useful phenomenon that was used to extend their absorptive range [4–5]. While colloidal crystallites of greater than 10 nm diameter behave as a bulk semiconductor, crystallite less than 10 nm has only incomplete band structure and excited electronic states [1–3]. This excited state "exciton" can luminesce, undergo non-radiative recombination through surface states or undergo redox reactions with surface adsorbed molecules having energies inside the crystallite's gap. A significant shortcoming of metal oxide semiconductors is that their photo activity is limited to the UV region. Therefore the photosensitization of stable, large-band gap semiconductors by visible light using dyes is a long term objective [6, 7]. The photosensitization can be accomplished by the adsorption of the dye molecules on the semiconductor surfaces via electrostatic, hydrophobic, or chemical interactions. From this view point, the interactions of the dye molecules with the semiconductor surfaces can be readily probed by spectroscopic techniques like absorption and fluorescence spectroscopies [8].

A dye adsorbs directly on the surface of semiconductor particle acting as an electron donor and can transfer an electron from its excited state into the conduction band of the semiconductor [9, 10]. Sensitization is achieved by adsorption of dye molecules at the passivated semiconducting surface which upon excitation inject an electron into its conduction band. The first successful experiment of this type was described by Putzeiko and Terenin [11, 12]. In literature various reports are available for the electron injection process from excited state dyes to the conduction band of semiconductors [13-15]. The present study explores the interaction between *Ceanothus thyrsiflorus* dye with passivated TiOdye and is anticipated that this study might lead to intimations on how to use TiO2 for widespread applications towards various fields of biochemical and photo-chemical research.

Experimental Materials Experimental details

All chemical solvents and reagents were of analytical grade from the sigma aldrich and were used without further purification.

Synthesis of Acetyl Acetone Functionalized TiO2Nanoparticles

In a typical synthesis process, acetyl acetone was added to alcoholic solution of Titanium isopropoxide [Ti (OC2H7)4] followed by hydrolysis with water. Resulting yellow solution was filtered and dispersed in dilute nitric acid maintaining H+/Ti ratio of 1.75 followed by continuous stirring at room temperature for 2 hrs. Peptized sol was filtered and hydrothermally treated for 4 hours at 100°C and 1200 psi. One part of obtained transparent yellowish solution was collected for UV-VIS study. Another part was dried in an air oven at 60°C and collected for FTIR, XRD and SEM charaterizations. Characterization Techniques Absorption spectra were recorded using UV-1800 Shimadzu, Japan UV-VIS spectrophotometer. The size and phase of synthesized TiO2 nanoparticles were determined using X-ray powder diffraction (XRD, PAN Analytical) with Cu Kα radiation (λ = 1.5418 Å) in the 2θ range of 10-60°. FT-IR spectra were recorded by using Perkin Elmer PE-1600 model spectrometer using KBr pellet with the resolution of 4 cm-1. The surface microstructure of the samples were observed by Scanning Electron Microscope (CARL-ZEISS-SMT-LTD, Germany, Model: SUPRA 40). The fluorescence quenching measurements were carried out with JASCO FP-6500

spectrofluorometer. The excitation and emission slit width (each 5 nm) and scan rate (500 nm/ min) were kept constant for all the experiments.

Fourier-transform infrared spectroscopy

The functional groups and chelating ligand behavior of acetyl acetone with titanium isopropoxide precursor were analyzed by a Fourier Transform Infrared Spectrometer (FTIR) in the range of 400 to 4000 cm-1 region. The FTIR spectrum of modified titanium alkoxide has been recorded at different stages as shown in Fig. 1. Figure reveals that the characteristics absorption peaks for free acetyl acetone at around 1,707 and 1726 cm-1 corresponding to the νC-C and νC-O vibrations disappearance and simultaneous two absorption peaks appearance at around 1530 and 1580 cm-1 assigned to νC-C and νC-O vibrations respectively. This observation clearly confirms the titanium-acetylacetone complex formation by the reaction of acetylacetone with titanium isopropoxide. Absorbance in the 1002–1040 cm-1 frequency range and 660 cm-1 corresponds to the OR groups attached to titanium. The broad band at around 3400 cm-1 was contributed to the stretching vibrations of Ti–OH group. Characteristic peak around 2873–2960 cm-1 corresponds to the stretching vibrations of the aliphatic -CH2 and -CH3 groups. Other broad bands below 900 cm-l are characteristic of a Ti–O–Ti network. The entire FTIR spectra hint at possible scheme of bonding between acetyl acetone and TiO2.
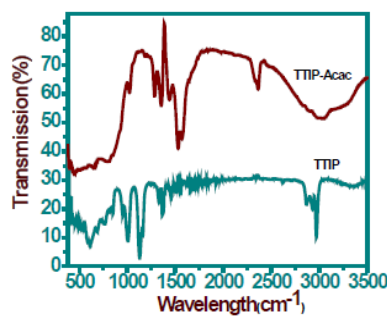

Fig 1: FTIR spectra of TTIP and acetyl acetone modified TTIP

X-ray diffraction pattern

Figure 2 shows the diffraction pattern of acetyl acetone modified TiO2; it was identified comparing with the published data (JCPDS 10-454). The crystallinity and crystal phase was evaluated by a powder X-ray diffractometer and was analyzed for phase contents and crystallite size. The nanoparticles obtained after modification with Acac is crystalline at room temperature. The diffraction angle 2θ was varied in an appropriate range and the diffracted intensity was recorded as a function of 2θ. The polycrystalline anatase phase was confirmed by (101), (004), (200), (211), and (204) diffraction peaks at 2θ values of 25.3, 38.1, 48.2, 54.0 64.2 respectively. The average crystallite size of the particles was calculated from XRD (101) peaks of anatase TiO2 by applying Scherrer's formula $D = 0.9\lambda/\beta\cos\theta$

where D is the average crystallite size, is the X-ray wavelength, β is the broadening of the diffraction line measured as the full width at half maximum intensity (FWHM), and θ is the corresponding diffraction angle. The

crystallite size of anatase TiO2 is found to be 12 nm for Acac modified TiO2.
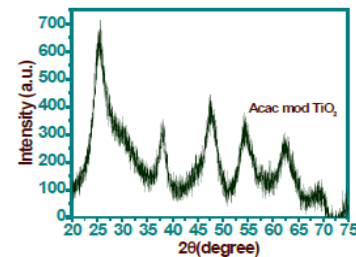

Fig 2: X-Ray Diffraction pattern of acetyl acetone modified TTIP

SEM characterization

SEM images (Figure 3) shows the surface morphology of TiO2 synthesized by using acetylacetone as surface functionalized agent. The average size of acetyl acetone modified TiO2 nanoparticles was found to be 2-5 nm. TiO2 nanoparticle of average size was found more when synthesized without capping. Particle morphology was observed using SEM. The particles present good dispersion (the loose agglomeration showed on the images could be due to the preparation technique and their average sizes are under ~ 2-5 nm, which is consistent with XRD and optical results.
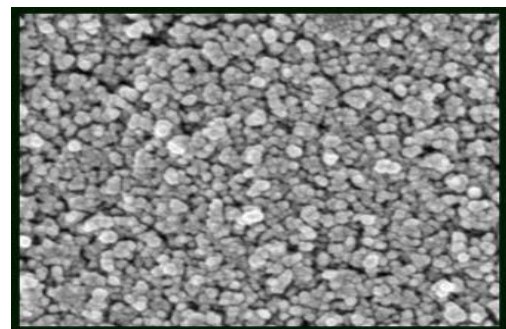

Fig 3: SEM image spectra of hydrothermally synthesized acetyl acetone modified TTIP

Further characterization of acetyl acetone modified nanoparticle was confirmed by studying the optical properties. The absorption spectra were used to monitor the reaction for the formation of TiO2 nanoparticle and their relative colloidal stability in the medium. Moreover, based on the "absorbance onset" of the curve it was possible to calculate the average nanoparticles sizes and their optical properties. It is broadly known that semiconductor nanoparticles exhibit a very pronounced change in their optical absorption properties when their sizes were reduced below a certain diameter. Optical excitation of electrons from the valence band to the conduction band produces an abrupt increase in the absorbance at the wavelength associated with the band gap energy. Due to their extreme small size, semiconductor nanoparticles with the dimensions below the so-called "Bohr-radius" will present a quantum-confinement effect, related to the strong interaction between the pair "hole-electron" generated by exciting photon. Hence in this study TiO2 colloids were extensively characterized based on the UV-visible spectroscopy results. In Figure 4, it is shown, there are significant changes in the absorption spectra

between the wavelength 200-500 nm for modified and unmodified solution. This confirms a blue shift from the bulk TiO2 which has absorption maxima at higher wavelength. That aspect can be attributed to the formation of TiO2 nanoparticles shifting the relative position of the absorption onset. The appearance of nice intense peak has proven that the acetylacetone modified TiO2 nanoparticles were successfully synthesized under these conditions.
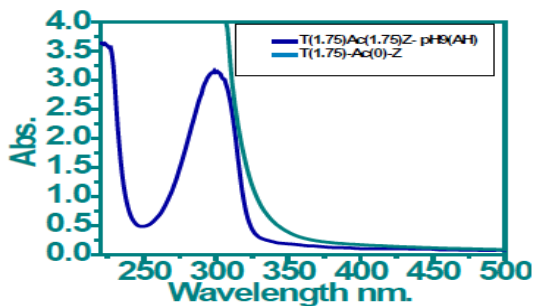

Fig 4: UV-VIS spectra of hydrothermally synthesized TiO₂ after modification with acetylacetone

The average particle size (R) of TiO2 nanoparticles were estimated using Bruss Equation as follows:

$$Eg = E + h2/8R2 [1/(me*)+1/mh*] - 1.8e2/\varepsilon R$$

Where, Eg = band gap of synthesized TiO2 nanoparticles, E = bulk band gap of TiO2 nanoparticles (2.4 eV), R = radius of particle, me = effective mass of electron mh = effective mass of hole ε = dielectric constant of material, h is Planck's constant. Band gap was calculated using the formula Eg =1240/λ Where, Eg= band gap of synthesized TiO2 nanoparticles and λ is the wavelength of absorption maxima for TiO2 nanoparticles. Energy band gap (Eg) and average particle size values are presented in Table 1.

Tabale I:

Sample Name	PH	Wavelength (λ) nm	Bandgap (E_g)eV	Size (R) nm
TiO2 nanoparticles	9	370	3.4	1.6

The UV-VIS spectra of TiO2 nanoparticles developed at different PH are shown in Figure 5. The spectra show decrease in absorption intensity with increase in PH. This observation is well attributed towards the increase in particle size of capped TiO2 nanoparticles as increase in PH.
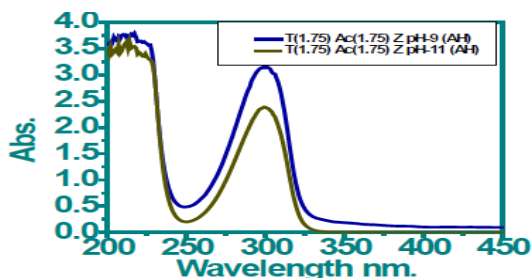

Fig 5: UV-VIS spectra of hydrothermally synthesized TiO₂ after modification with acetylacetone at different pH

Absorbance of dye- TiO2 nanoparticles solution before and after interaction was measured at different time interval using UV-VIS spectrophotometer in the photon energy range of wavelength of 200–550 nm. The charge transfer study was observed from decrease in absorption maxima of Ceanothus thyrsiflorus dye with UV-VIS spectroscopic study as shown in Figure 5. The absorption spectra reveal that while interaction of TiO2 nanoparticles with Ceanothus thyrsiflorus dye, the optical density of the dye drastically changes and both the UV-absorbance peaks disappear. It is due to the partial adsorption of Ceanothus thyrsiflorus dye on the surface of colloidal TiO2 to form a surface complex. Similar type of adsorption behavior of charged molecules on the surface of colloidal TiO2 was reported by Hilgendorff et al [17]. The equilibrium for the formation of complex between TiO2 nanoparticles with Ceanothus thyrsiflorus dye is defined by the apparent association constant Kapp calculated from the equation below [14]: [1/Aabs -1/ARdye] = [1/Ac -1/ ARdye] + 1/Kapp(Ac – Adye) [TiO2] Where, Aabs is the observed absorbance of the solution containing colloidal TiO2 at λmax. Adye and Ac are the absorbances of Ceanothus thyrsiflorus dye and the TiO2-Dye complex respectively at λmax. Kapp is the apparent association constant [TiO2] is the concentration of TiO2 It is expected a linear relationship between 1/(Aobs−Adye) and the reciprocal concentration of colloidal TiO2 with a slope equal to 1/Kapp(Ac−Adye) and an intercept equal to 1/(Ac−Adye). There is a good linear dependence of 1/(Aobs−Adye) on the reciprocal concentration of colloidal TiO2. The calculated apparent association constant (Kapp) value obtained is 6.5. The possible way of quenching is through electron transfer from excited state dye molecules to the conduction band of colloidal TiO2. Similar type of electron transfer between dyes and semiconductors has been previously reported [16–18]. Dye + CdS → [Dye….. TiO2] [Dye…..CdS]→ [Dye*….. TiO2] [Dye*…..CdS]→ [Dye•+ + CdS•-]
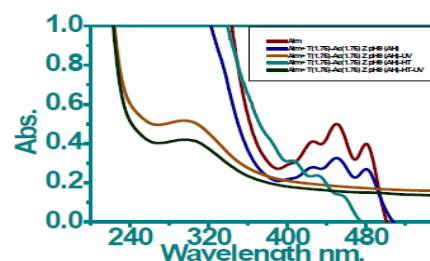

Fig 5: UV-VIS spectra for photo induced interaction between hydrothermally synthesized TiO₂ After modification with acetylacetone and *Ceanothus thyrsiflorus*

The calculated Kapp show high values due to the presence of more electronegative acetyl groups on their periphery, so they have higher electrostatic interaction with colloidal TiO2 surface. Very high Kapp value signifies the absence of any charged anchoring group in its structure, hence anchoring groups has significant effect on the adsorption process.

Photoluminescence (PL) study

The photoluminescence (PL) spectra of TiO2 are presented in Figure 6. The TiO2 nanoparticles display photoluminescence after illumination with UV light. It's important to understand the chemical nature of these traps so that they could be manipulated for a particular application. As an indirect band

gap semiconductor, TiO2 shows no band gap photoluminescence, but illumination with ultraviolet light results in broad visible photoluminescence (PL) arising from recombination of oppositely charged trapped and free carriers. The fluorescence property of the hydrothermally synthesized TiO2 colloidal nanoparticles studied by the emission spectrum confirms the presence of defect levels caused by the oxygen vacancies.

We have observed new emission bands at 360 nm and 460 nm wavelengths, second one (460 nm) being emission due to annihilation of excitons while remaining first one could be arising from surface states. The emission spectrum of annealed nanocrystallites is also having these type of band emissions. Surface functionalization has a great influence on both photoluminescence and stability of nanoparticles.
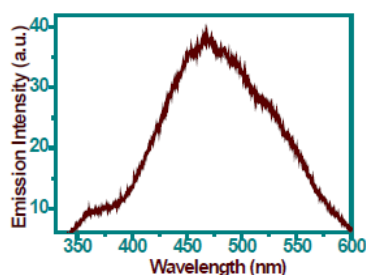

Fig 6: Photoluminescence spectra of hydrothermally synthesized acetyl acetone modified TTIP

Quenching of dyes by colloidal CdS

Interaction between dyes and colloidal TiO2 nanoparticles has also been studied by absorbance quenching measurements. Figure 5 shows the effect of colloidal TiO2 nanoparticles on the absorbance spectra of Ceanothus thyrsiflorus. The absorption spectra show that significant change in absorption spectra of Ceanothus thyrsiflorus dye after interaction with TiO2 before and after UV irradiation. We can express the equilibrium between the adsorbed and unadsorbed dye molecules by using Kapp. High apparent association constant value is due to the presence of more electronegative acyl group in its structure, increasing the interaction of this dye with colloidal TiO2. The feasibility of electron transfer from excited state of dyes to TiO2 can be explained on the basis of energy level diagram based on the excited state oxidation potential of dye.

Importance of molecular structure in energy conversion implications

In recent years, many researchers have tried to design and develop suitable low cost organic dyes, which can be used in solar cells with higher efficiency. Molecular structure of the organic dyes is an important factor to get higher efficiency. It has been observed that even a small structural change can increase the electron injection efficiency of dyes to semiconductor nanoparticles. In the present investigation we observed that Ceanothus thyrsiflorus dye shows more efficiency than the others due to TiO2 structure containing acyl group as substituents for interaction with the dye.

CONCLUSIONS

TiO2 colloidal nanoparticles and nanocrystals are prepared by hydrolysis of titanium isopropoxide employing an acetyl acetone modified synthetic hydrothermal method. The analysis of synthesized samples confirms complex formation as well as formation of small size colloidal TiO2 nanocrystals of size around 4 nm. The fluorescence property of the TiO2 colloidal nanoparticles studied by the emission spectrum confirms the presence of defect levels caused by the oxygen vacancies. The interaction of TiO2 nanoparticles with colloidal TiO2 nanoparticles has been studied by using spectroscopic technique. The apparent association constant (Kapp) has been calculated from absorption changes. In this very preliminary work, we have successfully investigated Ceanothus thyrsiflorus dye as a photosensitizer for TiO2.

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