Modification of Energy Band Gap in Natural Dye-Sensitized ZnO Nano Particles

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Abstract - Nanocrystalline particles of ZnO have been prepared by sol gel method. Prepared nano particles were used to prepare mesoporous electrodes for dye-sensitized solar cells. The anatase phase of ZnO has been confirmed using XRD. Transmission Electron Microscopy (TEM) has been used to confirm the particle size of the ZnO nano particles. The coating of natural dyes extracted from spinach and marry gold has been done on ZnO nano particles. The Scanning Electron Microscope and EDX study reveals the morphology and elemental composition of the pure and natural dye coated ZnO nano particles. Tauc's plot confirmed decrease in band gap of ZnO nanoparticles with natural dye coating. Raman scattering spectra reveal active phonon modes for all of the synthesized samples. The natural dye coated nano particles are found to be better candidates for DSSCs.

I. INTRODUCTION

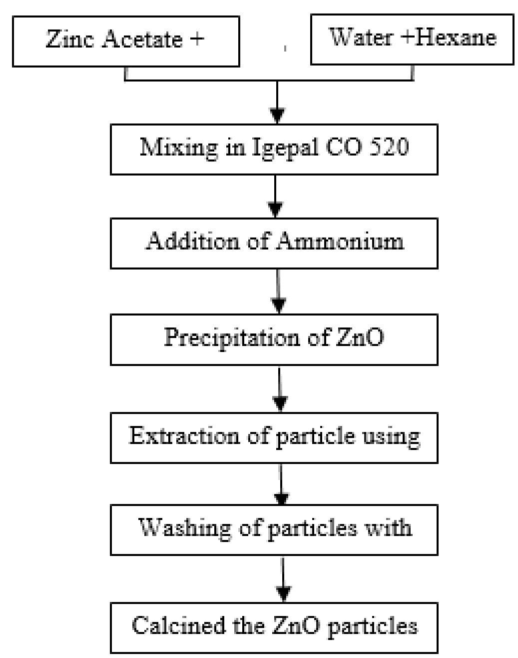
Solar cell is a device which convert solar energy to electrical energy directly. Solar cells based on dye-sensitized nanostructured metal oxides have attracted much attention as an inexpensive alternative to conventional silicon- based photovoltaic devices [1]. The dye-sensitized solar cells (DSSCs) based on nano crystalline TiO_2 have exhibited high power conversion efficiency of about 11% and remain to be one of the most commonly substitutes for low cost solar-energy-conversion devices at high temperature [2-3]. ZnO is another promising metal-oxide semiconductor that can be replace TiO_2 because of its higher electronic mobility as compare to TiO_2 and its energy level of conduction band is similar as in TiO_2 [4]. ZnO is a well-known as n-type extrinsic semiconductor having wide band gap 3.37 e V and high exciton binding energy of 60 meV. With its band gap corresponding to UV light of 365 nm, ZnO is transparent throughout the visible spectrum [5]. In recent days, nanosized ZnO has attracted much attention because of its wide applications as a base material for dye-sensitized solar cells, photocatalyst and sensors. Nano rod, Nano fiber and nanowire structure of ZnO were mostly often utilized as photoanodes in DSSCs development [6-9].

In DSSCs, dye play a role of an electron donor to metal-oxide semiconductor layer excited when the dye molecules exposed by sunlight. So for, to enhance the chemical and physical properties of ZnO, some modifiers are applied as coatings on the pure nanosized ZnO. Recently, synthetic and natural dyes have been used as a photosensitizer in DSSCs. The synthetic dyes are quite expensive as compare to natural dyes. Natural dye extracted from parts of plants such as leaves, flowers or fruit can be used as photosensitizer in DSSCs as it very inexpensive as compare to synthetic dye [10-12].

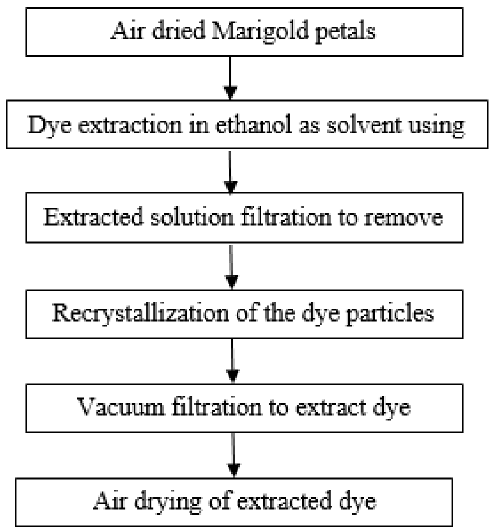
The nanosized ZnO particles have been prepared by different techniques. Sol-gel process is the most commonly used technique to synthesize nano particles of ZnO. This is very simple means of synthesize the nano particles at room temperature [13-14]. In the present study, ZnO nano particles will be synthesized by using green synthesis (sol-gel) and the dyes extracted from the natural plants sources like spinach and marry gold will be coated on these nano particles. The natural dye coated ZnO nano particles will be studies for structural, microstructural, compositional and optical properties.

II. EXPERIMENTAL PROCEDURE

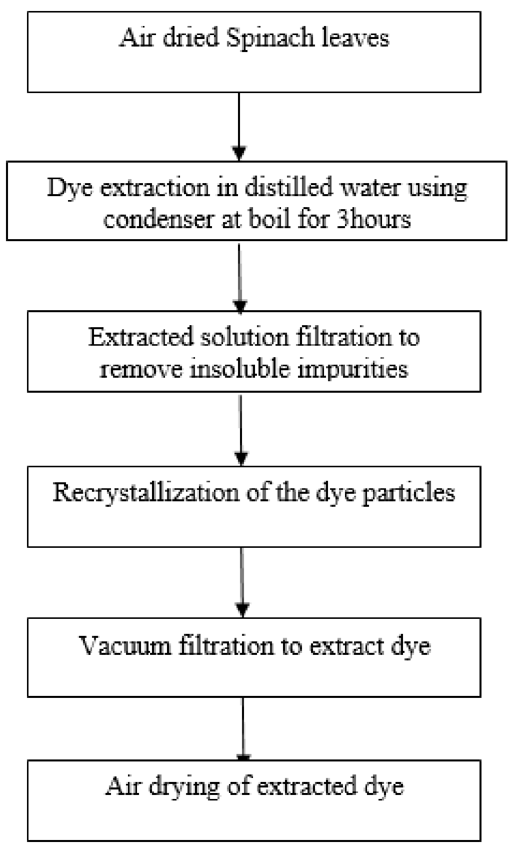
The ZnO nano particle has been prepared using sol gel method. The flow chart of the synthesis is as follows.



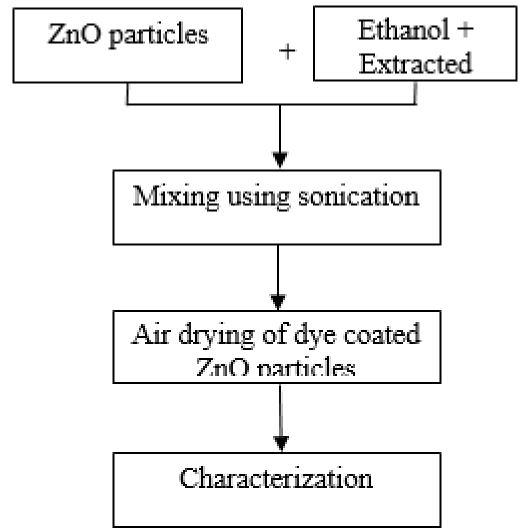
Then the extraction of the natural dyes has been done as follows.



Extraction of Marigold Dye



Extraction of Spinach Dye



Coating of the dyes on the ZnO nano particles

III. RESULTS AND DISCUSSIONS

Crystal structure of ZnO was studied by X-ray diffraction (XRD) analysis. Diffraction pattern of ZnO is shown in fig 1.1. The XRD pattern clearly reveals the crystalline nature of the sample. All the peaks in ZnO nanoparticles are indexed according to the Anatase phase of ZnO.

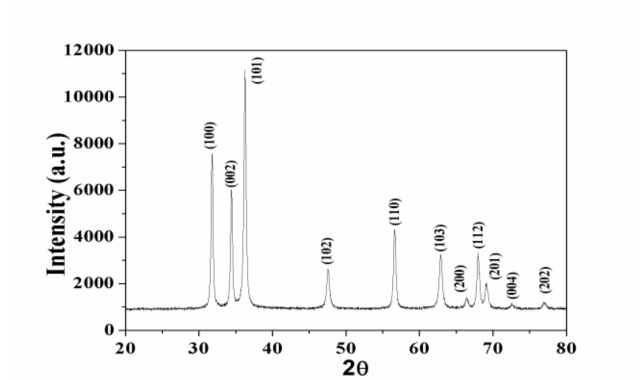


Fig.1. X-Ray diffraction patterns for the pure ZnO nano particles, using Cu Kα radiations.

No secondary phase has been detected in the XRD pattern. All peaks show that this result is appropriate with the hexagonal wurzite ZnO crystal structure. This diffraction pattern has shown the compatibility with JCPDS data no. 36-1451 as reported by Shah et al. [15]. Lattice parameters a and c were found 3.224 A° and 5.112 A° respectively.

The crystallite size of the ZnO powder has been calculated using Scherer equation.

$$\tau = K\lambda / \beta \cos\theta$$

Where τ is the mean size of the ordered (crystalline) domains, which may be smaller or equal to the grain size. K is a dimensionless shape factor, with a value close to unity. The shape factor has a typical value of about 0.9, but varies with the actual shape of the crystallite. λ is the X-ray wavelength. β is the line broadening at half the maximum intensity (FWHM), after subtracting the instrumental line broadening, in radians. θ is the Bragg angle. The typical value of the crystallite size was calculated for the ZnO powder from XRD pattern is ~23.729 nm.

The transmission electron micrograph (TEM) of the ZnO particles has been observed (Fig 2 (a)). HRTEM images shown that the uniform particle has been formed by this synthesis method. The average particle size is found to be~20 nm. HRTEM image of particle at very high magnification ~ 500000 X has also been taken. The Fringes are also clearly seen.

The morphology of the ZnO nanoparticles was studied using Scanning electron Microscope (Carl Zeiss, Germany). The micrographs were taken by spreading the powder particles of ZnO on the carbon tape. The SEM micrographs were taken at various magnifications and at different locations of sample to analyze the same extensively.

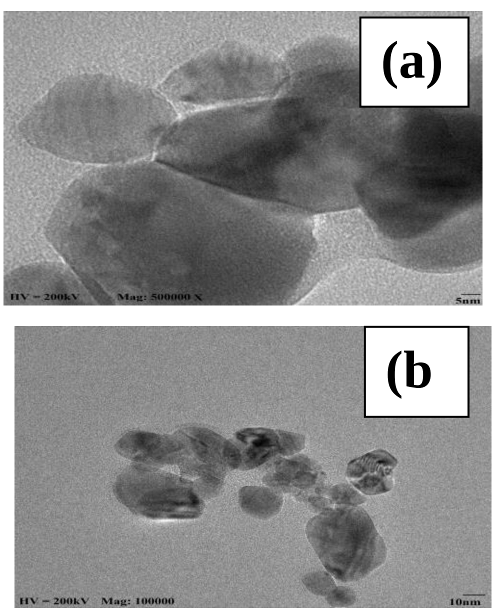


Fig.2: (a) TEM image of the ZnO nano particles. The average size of the particle is found to be ~20 nm (b) HRTEM image of ZnO nanoparticles clearly evident the crystal planes.

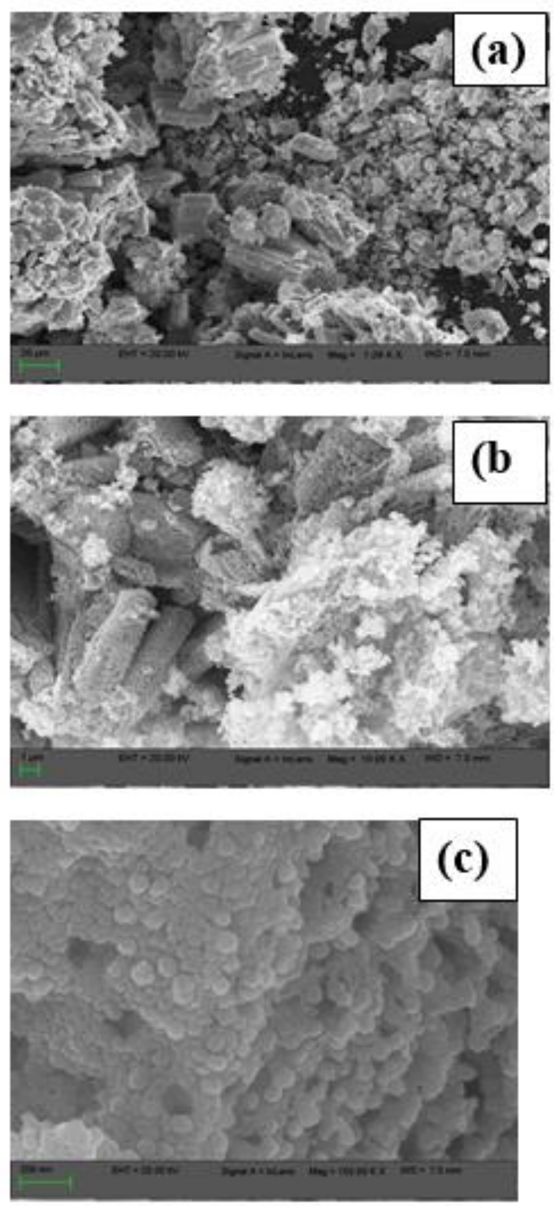


Fig.3: The SEM micrographs for the pure ZnO powder at various magnifications.

Figure 3.1 shows various SEM micrographs. Figure 3.1 (a) shows the morphology of the samples at low magnification ~1000 X. It is clearly evidence from the image that the morphology is same and uniform. As the magnification was increased two different kinds of morphologies are observed. The figures 3.1 (b) and (c) show both type of morphologies.

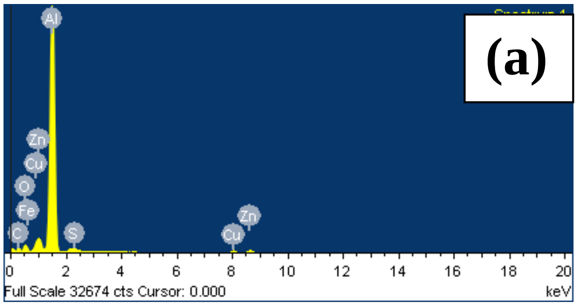


Fig.4 (a): Energy dispersive X-ray analysis of pure ZnO nano particles.

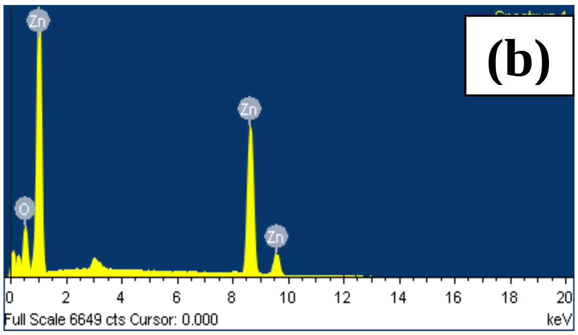


Fig.4(b): Energy dispersive X-ray analysis of spinach dye coated ZnO nano particles.

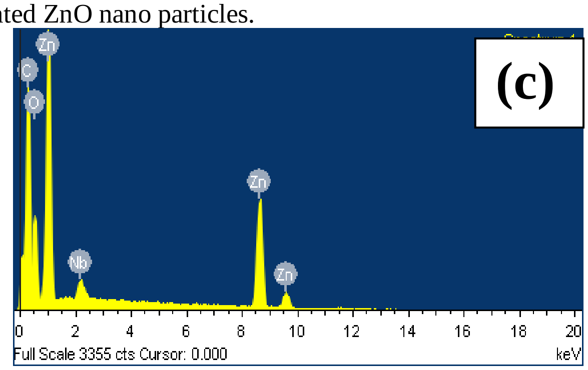


Fig.4(c): energy dispersive X-ray analysis of marry gold flower dye coated ZnO nano particles.

The energy dispersive X-ray analysis of the pure ZnO nano particles, spinach dye coated nano particles and marry gold flower ZnO nano particles have been shown in fig. 4(a), 4(b) and 4(c) respectively. It is clearly evident that the pure ZnO nano particles does not has any other element except Zn and O, whereas the presence of Cu and Nb has been found in spinach dye coated and marry gold dye coated ZnO.

Element	Weight %
Zn	86.09
O	13.91

Element	Weight %
Zn	26.27
C	51.17
O	21.47
Nb	1.10

Element	Weight %
C	20.03
O	11.00
Al	58.73
S	0.26
Fe	0.35
Cu	3.91
Zn	5.72

The UV Visible spectrum has been observed for the pure ZnO nano particles, spinach dye coated nano particles and marry gold flower ZnO nano particles with UV Visible spectrometer in the wavelength range 200nm -900nm. The Tauc's plots ($(\alpha h\omega)^{1/2}$ vs. energy) are derived from the absorption vs. wavelength graphs. The pure ZnO nano particles clearly shows that a sharp absorption edge at ~ 400 nm and the band gap calculated from the Tauc's plots is ~3.1 e V. The Tauc's plots of spinach dye coated nano particles and pure ZnO shows almost similar behavior. The Tauc's plots of marry gold dye and marry gold dye coated ZnO nano particles has been shown in the fig.6. For the comparison the Tauc's plot for pure ZnO nano particles has also been given in the figure. The marry gold dye coated nano particles show a decreased band gap ~1.41 e V. This decreased band gap may be due to the presence of Cu in marry gold dye coated ZnO nano particles. So it is also evident that these dye coated nano particles are good materials for the application of solar cell.

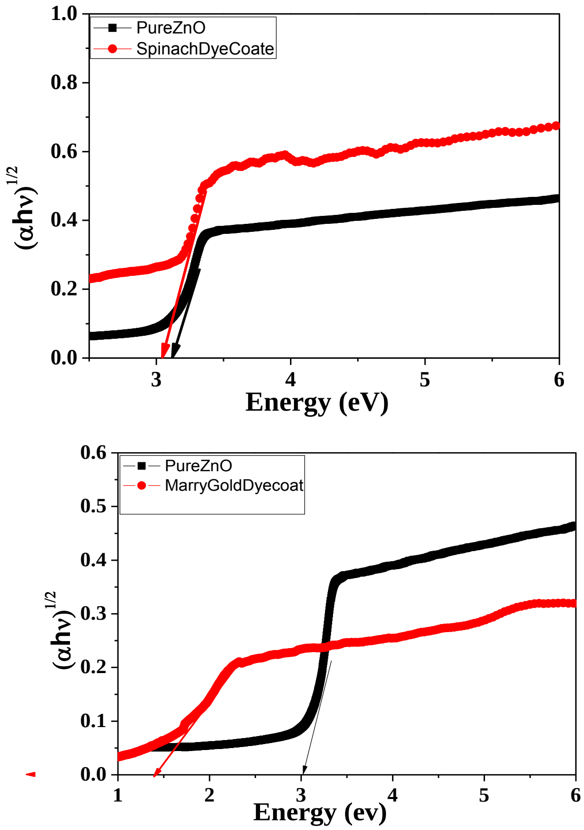


Fig.5: The Tauc's plot for the pure ZnO nano particles, spinach dye coated nano particles and pure extracted spinach dye (a) Spinach dye coated ZnO nanoparticles (b) Marry Gold dye coated ZnO nanoparticles.

IV. CONCLUSION

The pure ZnO nanoparticles are synthesized using Sol Gel method (Green synthesis). The XRD confirms the pure phase formation. The particle size of nanoparticles is found to be ~ 20nm. The optical properties of ZnO nanoparticles has been observed and found that the band gap of ZnO nanoparticle is ~3.1 eV. The dye extracted from spinach and marry gold has been coated on nanoparticles of ZnO. It has been found that with spinach dye coating, the band gap is almost same as that of pure ZnO whereas marry gold dye coating decreases the band gap from 3.1eV to ~1.41eV. The decreased band gap makes the ZnO nanoparticles suitable candidates for solar cells.

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