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Structural, morphological and optical properties of silver doped polyvinylpyrrolidone composites

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Polyvinylpyrrolidone (PVP) doped with different silver concentration (Ag: PVP) composites were prepared by simple solution casting technique using PVP and silver nitrate. The structural, morphological and optical properties of these as grown composites were characterized by powdered X-ray diffraction, SEM, FTIR and UV-VIS techniques. XRD patterns confirm the incorporation of Ag particles in PVP matrix and indicate the improvement in polycrystalline behaviour by the appearance of more diffraction peaks with increased intensity on increasing $AgNO_3$ concentration in the composites. SEM images reveal the uniform dispersion and increased densification of Ag particles in PVP matrix. Infrared transmission spectra recorded in 4000-400 cm^{-1} region show the characteristic peaks of PVP bonding groups with the minor shift in their position due to Ag doping. UV-VIS spectroscopy results reflected that absorption increases in asymmetric manner and the absorption peak showed red shift with increasing dopant concentration. These results showed that the simple synthesis process can be used for the preparation of such composites suitable for various practical applications.

Keywords: Optical properties, Structural properties, X-ray diffraction, Spectroscopy

1 Introduction

The rapid development of polymer-based composites in recent years, has gained considerable interest of the researchers due to their wide range of applications in the field of catalysis, magnetic recording and microelectronics[1-7] etc. The doping of the polymers with metal particles helps in improving the kinetics of the ionic species through the compound by inducing greater proximity of the required ions within the polymer/metal composites. The composites of polymer/metal have a magnificent phenomenon which has special potential applications in the field of displays in modern electronics. Conventionally, the polymerization of monomers and formation of metal particles are performed separately, and then the polymer and metal particles are mechanically mixed to form composites. However, it is difficult to disperse the metal particles homogeneously into the polymer matrix due to the easy agglomeration of the metal particles and the high viscosity of the polymer. PVP polymer is found to be one of the most suitable polymer matrix in terms of good environmental stability, reducing/capping agent, tendency for complex formation, charge storage capacity, transparency and optimization of dopant-dependent electrical and optical properties. The different physical and chemical methods have been applied for the preparation of metal polymer composites[8-15]. PVP controls the reduction rate of the silver ions and the formation of silver atoms. In order to prevent agglomeration and stabilization of silver particles, PVP also act as capping agent in these composites.

In the present work, Ag: PVP composites have been prepared by varying 20-80 wt% $AgNO_3$ concentration. The structural, morphological and optical properties of these composites have been studied by using XRD, SEM, FTIR and UV-VIS spectroscopy technique. XRD technique was used for studying the structural information of the composites and crystallite size of particles in pure and doped analogues. SEM micrographs help in understanding the surface morphology of the composites and role of Ag particles content on the structural morphology.

Infrared (IR) transmission spectra are used to investigate the various bonding groups present in these composites and influence of silver particles on IR peaks. UV-VIS spectroscopy has been used in the evaluation band gap energy and their variation with increase in silver particles concentration. These studies will help in optimizing the synthesis parameters for the formation silver dispersed composites for microelectronics application.

2 Experimental Details

1g PVP (AR grade) was dissolved into 50 ml of double distilled water. 20 wt%, 40 wt%, 60 wt% and

80 wt% AgNO3 (AR grade) solutions were prepared in 20 ml of doubled distilled water. Then, $AgNO_3$ solutions of different wt% were added into 50 ml each PVP solutions drop by drop at a rate of one drop per second with constant stirring. These resulted solutions were allowed to swell for half an hour at room temperature. Further, these solutions were magnetically stirred for 5 h with last 30 min of heating at 60°C, so that the colour of these solutions changes to yellow. Then these viscose solutions were poured on quartz slides to form transparent films of Ag: PVP composites. The films were dried for 36 h in air at 40°C.

The as grown composite films were characterized by using XRD, SEM, FTIR and UV-vis techniques. XRD patterns were recorded on Philips make PW-1830 powder X-ray diffractometer by using Cu Kα radiation. SEM images of these composite samples were studied on LEO 440 SEM instrument. IR transmission spectra were recorded in the range 4000-400 cm^{-1} at ambient temperature by using Perkin Elmer, 1720 FTIR spectrophotometer.

Powder XRD measurements were made on PW-1830 machine using monochromatic CuK_α (8.04 keV and $\lambda = 0.154$ nm). The scanning range was set from (5° to 90°), the step size was 0.04 with a scanning rate of 1 step/s. The operating conditions were 30 kV and 25 mA employing a 0.15-mm slit in front of the detector. Chemical study was carried out by using Perkin Elmer, Fourier transform infrared (FTIR) spectrophotometer, Model 1720 at 0.5 cm^{-1} resolution in the range 4300-500 cm^{-1}. UV-VIS measurements were carried out in 190-1100 nm region on M550 Camspec UV-VIS spectrometer.

3 Results and Discussion

Ag: PVP composites can be prepared by two ways and represented by the following chemical equations as Scheme 1 and Scheme 2:

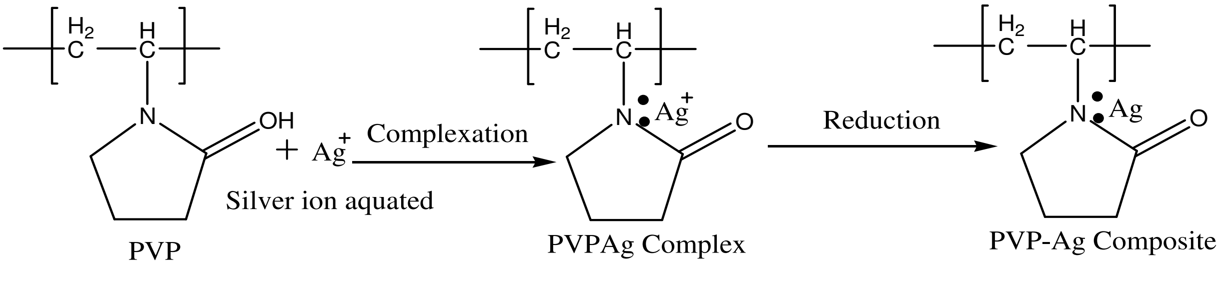
In the present paper, Scheme 1 is adopted for the synthesis of Ag: PVP composite films. The rate for the growth of Ag particles was found to be dependent on the ratio of PVP-$AgNO_3$. PVP used for the preparation of the silver based composites which play dual role of capping as well as reducing agent due to sodium hydroxide and glucose are not used as reported in earlier investigations[16]. PVP reduces silver nitrate to silver and provides the matrix for homogeneous distribution and immobilization of the silver particles. These composite films with different silver concentration were characterized by the following techniques.

Figure 1 shows the X-ray diffraction patterns of pure PVP and Ag: PVP composites. The XRD of pure

$$AgNO_3 \xrightarrow[\text{Solvation}]{H_2O} Ag^+ (aq.) + NO_3^- (aq.)$$

$$\begin{tikzcd} PVP + Ag^+ (aq.) \arrow[r, "\text{Complexation}"] & {[Ag(PVP)]^+} \arrow[d, "\text{Reduction}"] \\ & {[Ag(PVP)]} \end{tikzcd}$$

Scheme 1



Scheme 2

PVP exhibited the amorphous[17-19] nature of the prepared polymer film due to appearance of broad diffraction peaks located at 2θ value 11° and 21°. The noticeable changes in terms of the appearance of new peaks and improvement in intensity of some peaks were observed Ag related peaks in doped composites as shown in Fig. 1(c, d, e). In Fig. 1(c), a sharp peak of [311] plane at 33.05° of face centered cubic (*fcc*) structure as per JCPDS card no. 011164[20] indicates the crystalline nature of the composites due to doping of Ag in PVA polymeric network. The increase in the intensity of some peaks and appearance of new peaks on increasing $AgNO_3$ concentration in composites from 20 wt% to 80 wt% is observed and attributed to the increase in degree of crystallinity[21] by the incorporation of Ag in composites. In Fig. 5(d, e) the other peaks of *fcc* Ag at 2θ value 38.14º, 44.34º and 64.44º of [111], [200] and [211] planes, respectively are obtained and found to be in good agreement with the literature values of silver nanoparticles. Hence, these studies confirmed the incorporation of Ag in PVA polymeric network.

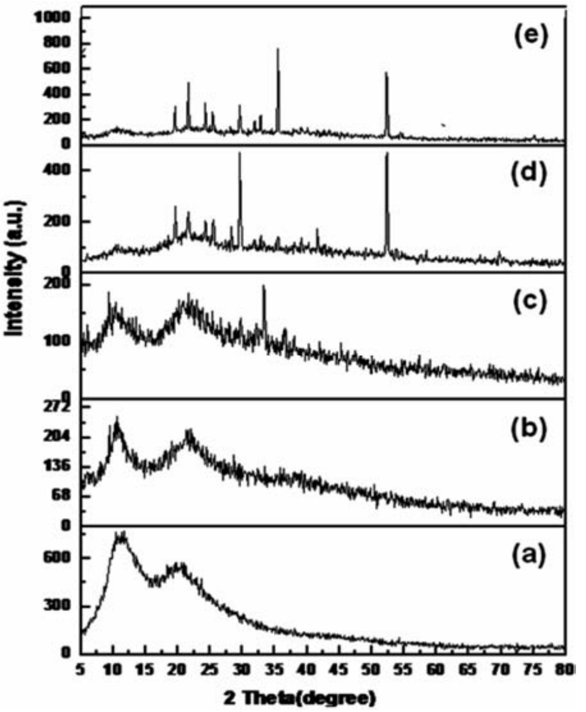


Fig. 1 — XRD pattern of (a) PVP, (b) 20% Ag: PVP, (c) 40% Ag: PVP, (d) 60% Ag: PVP and (e) 80% Ag: PVP composites

SEM images of the pure, 20 wt%, 40 wt%, 60% and 80% of AgNO3-doped PVP are shown in Fig. 2. As shown in Fig. 2(a), a texture containing spheres of average diameter 2 µm are noticed for the micrograph of pure PVP. This confirms the amorphous nature of pure PVP. In the 20 wt% $AgNO_3$-doped PVP film, Fig. 2(b) shows the formation of Ag particles. While 40 wt% $AgNO_3$-doped PVP films, Fig. 2(c) shows some region of increasing crystallinity. However, growth of the Ag particles in 60 wt% $AgNO_3$-doped PVP film Fig. 2(d) has been found to be reduced. From Fig. 2(e), it is observed that the morphology of Ag particles is spherical and the average size is about

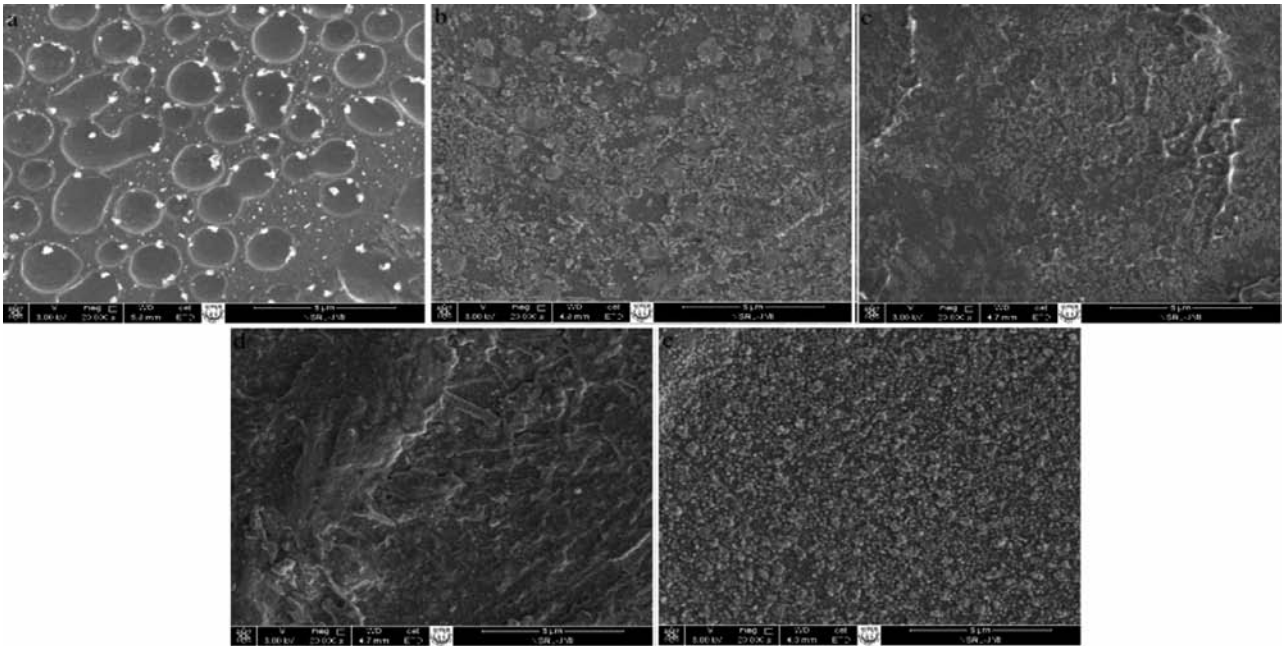


Fig. 2 — SEM micrographs of (a) pure PVP, (b) 20% $AgNO_3$: PVP, (c) 40% $AgNO_3$: PVP, (d) 60% $AgNO_3$: PVP and (e) 80% $AgNO_3$: PVP

0.01 µm. These micrographs imply that there is a drastic influence of $AgNO_3$ content on the structural morphology of PVP films. In the 80 wt% $AgNO_3$-doped PVP film, the continuous Ag particles are formed and then stuck to grow the dendritic structures by diffusion.

IR transmittance spectra of pure and $AgNO_3$: PVP composites were recorded in 4000-400 cm^{-1} region at ambient temperature and shown in Fig. 3. The FTIR spectrum of pure PVP film clearly indicated that the observed absorption peaks[22] were corresponding to the characteristic chemical bonds present in PVP. The peak at 1334 cm^{-1} represents the functional unit C-N present in PVP and disappeared after adding $AgNO_3$, confirming the completion of polymerization. However, another characteristic peak at 1658 cm^{-1} in pure PVP due to C=O stretching of the pyrrolidone ring was also found. In the literature, the researchers have projected that a blue shift of the C=O group in PVP is attributed to the change of $\pi \rightarrow \pi$ conjugation associated with the amide group of PVP arising from the dissociation of PVP chains due to the incorporation of silver.

It is possible that the interaction between the complexes and PVP leads to the dissociation of aggregated PVP chains, resulting in the blue shift of the C=O vibration band. The bands at 795, 900 and 1210 cm^{-1} are attributed to C-C stretching, C-N stretching and C-H bending vibrations of the PVP, respectively[23]. The C-H asymmetric stretching of CH_2 absorption band located at 2950 cm^{-1} became narrow and was located at 2970 cm^{-1}, 2980 cm^{-1}, 2985 cm^{-1} and 2990 cm^{-1} as the concentration of the dopant increased (Fig. 3). The hydrogen bonded O-H stretching mode of pure PVP appeared in 3500-3200 cm^{-1} region. It is also observed that by the incorporation of Ag that these bands shifted to lower wave number with the increase in wt 80% of $AgNO_3$, respectively. The obtained results from this study are found to be in good agreement with the earlier reports in literature[24]. The appearance of new peaks along with changes in position and intensity of some existing peaks in IR transmittance spectra shows the formation of complex ion between PVP and Ag^+ ions[25].

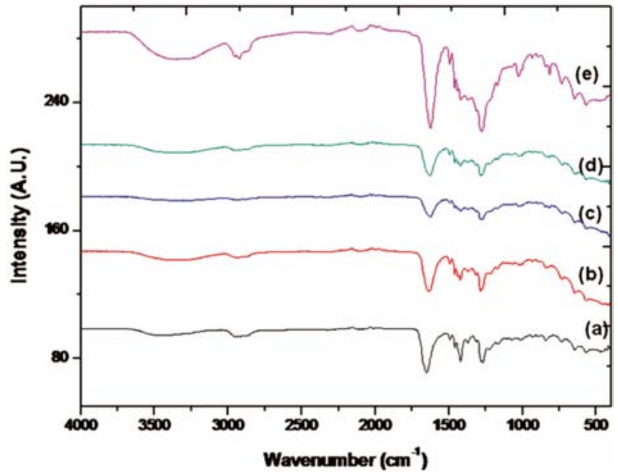


Fig. 3 — IR transmittance spectra of (a) pure PVP, (b) 20% $AgNO_3$: PVP, (c) 40% $AgNO_3$: PVP, (d) 60% $AgNO_3$: PVP and (e) 80% $AgNO_3$: PVP in 4000 – 400 cm^{-1} region

The optical absorption spectra of pure PVP and PVP-$AgNO_3$ composites are shown in Fig. 4(a-e) in the wavelength range 190-1100 nm. The absorption is increasing from 325 nm which is associated with $\pi \rightarrow \pi^*$ transition of conjugated ring system[15]. The spectra of pure PVP indicated that the maximum absorption occurred at 419 nm as shown in Fig. 1(a) as reported in literature[26].

The absorption varies asymmetrically with increasing wavelength. The maximum absorption peak shifted towards the longer wavelength and the peak broadening with increasing $AgNO_3$ concentration was also observed. The shifting of absorption peak may be correlated with the formation of conjugated bonds and the possibility of formation of carbon clusters[27]. This is in agreement with the creation of new electronic level in the forbidden gap. The optically induced transitions provide information about the bond structure and energy gap in crystalline and non-crystalline materials.

The observed shift in the fundamental absorption edge of UV-VIS spectra can be correlated with optical band gap E_g by Mott and Davies[19].

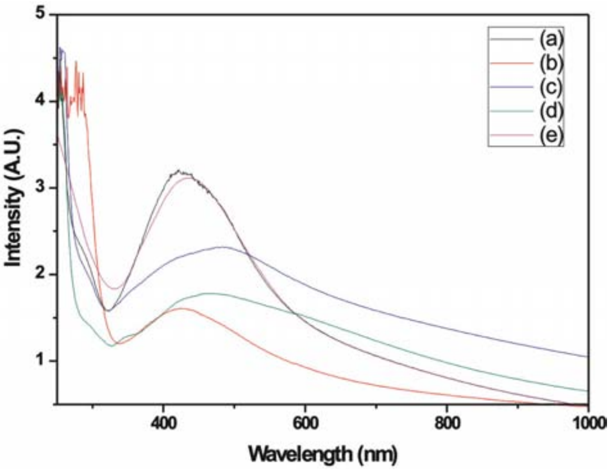


Fig. 4 — UV-VIS spectra of (a) pure PVP, (b) 20% $AgNO_3$: PVP, (c) 40% $AgNO_3$: PVP, (d) 60% $AgNO_3$: PVP and (e) 80% $AgNO_3$:PVP in 190-1100 cm^{-1} region

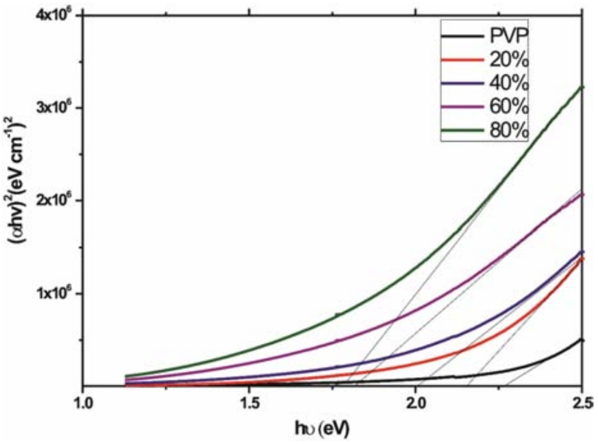


Fig. 5 — $h\nu$ (eV) versus $(\alpha h\nu)^2$ (eV.cm)^2

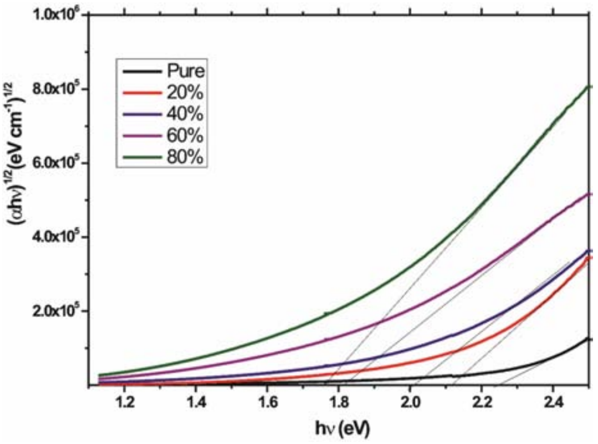


Fig. 6 — $h\nu$(eV) versus $(\alpha h\nu)^{1/2}$ (eV.cm)$^{1/2}$

$$\alpha(\nu) = \frac{B(h\nu - E_g)^n}{h\nu} \qquad \ldots(1)$$

Table 1 — Direct and indirect energy band gaps for pure and $AgNO_3$ doped PVP

% of dopant	Direct energy band gap (eV)	Indirect energy band gap (eV)
Pure	2.30±0.002	2.25±0.002
20	2.15±0.002	2.13±0.002
40	2.01±0.002	2.02±0.002
60	1.85±0.002	1.83±0.002
80	1.80±0.002	1.78±0.002

where factor B depends on the transition probability and may be assumed to be constant within the optical frequency range, $\alpha(\nu)$ is the absorption coefficient at frequency ν, E_g is the value of the optical energy band gap between the valence band and conduction band, n is index which characterizes the electronic transition.

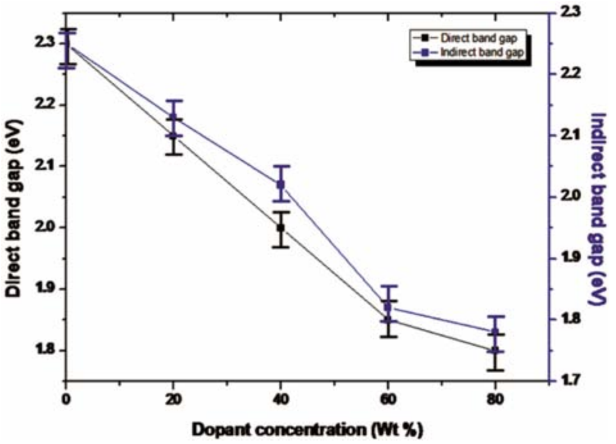


Fig. 7 — Direct band gap energy, indirect band gap energy versus dopant concentration

For the determination of direct and indirect energy band gap, $(\alpha h\nu)^2$ and $(\alpha h\nu)^{1/2}$ were plotted separately as a function of photon energy ($h\nu$) taking into account the linear portion of the fundamental absorption edge of the UV–visible spectra (curves ‘a’–‘e’ in Fig. 4). Such plots are shown in Figs 5 and 6, respectively.

From the intercept of the best-fit lines on the x-axis, direct and indirect energy band gaps have been calculated for pure and $AgNO_3$ doped PVP and the results are presented in Table 1.

It has been observed that the value of direct energy band gap decreases from (2.30 ± 0.002) eV to (1.80 ± 0.002) eV with increasing dopant concentration of $AgNO_3$ from 20 to 80 wt %. Similarly, the value of indirect energy band gap was also found to be decreased from (2.25 ± 0.002) eV to (1.78 ± 0.01) eV with increasing dopant concentration. Such a decrease in the value of E_g is attributed to the formation of coordinate bonds between silver and PVP polymer molecules, which form the trap levels between the HOMO and LOMO energy state, making the lower energy transitions feasible and resulted in the reduction of optical band gap (Fig. 7).

The error bars are marked by taking the standard deviation of the five repeated measurements under similar instrumental and environmental conditions. The decrease in the energy band gap endorse that the ionic conductivity of the material increases with increase of $AgNO_3$ dopant concentration i.e. Ag particles in PVP polymer.

4 Conclusions

Ag:PVP composites were prepared by solution casting method with different concentrations of silver particles. The comparative study suggested that the properties of the material were found to be changed due to the varying dopant concentrations. XRD patterns showed that the crystallinity of the composites increases with increasing dopant concentration. The SEM images showed a drastic influence of $AgNO_3$ content on the structural morphology of PVP films. IR transmittance spectral analysis confirmed the formation of conjugated structure between the functional groups of PVP and embedded silver particles. Both direct and indirect energy band gaps are found to be decreased with increase in the dopant concentration due to increase in ionic conductivity.

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References

1 Kojarnovitch V (Ed.), *New & Advanced Materials, Emerging Technologies Series*, United Nations Industrial Development Organization, Vienna, (1997).

2 *PVP-Polyvinylpyrrolidone*, General Aniline & Film Corp., New York, 1951.

3 Wohrle D M A, *Angew Chem Int Ed*, 44 (2005),7500.

4 Majhi P R, Moulik S P, Burke S E, Rodgres M & Palepu R, *J Colloid Interface Sci*, 235 (2001), 227.

5 Wu H D, Wu I D & Chang F C, *Polymer,* 42 (2001) 555.

6 Zhang Z, Zhang L, Wang S, Chen W & Lei Y, *Polymer,* 42 (2002) 8315.

7 Wada Y, Kobayashi T, Yamasaki H, Sakata T, Hasegawa N, Mori H & Tsukahara Y, *Polymer,* 48 (2007) 1441.

8 Zhang M, Breiner T, Mori H & Müller A H E, *Polymer,* 44 (2003) 1449.

9 Ghosh K & Maiti S N, *J Appl Polym Sci,* 60 (1996) 323.

10 Huang H H, Ni X P, Loy G L, *Langmuir,* 12 (1996) 909.

11 Carotenuto G, *Appl Organometal Chem,* 15 (2001) 344.

12 Kapoor S, *Langmuir,* 14 (1998) 1021.

13 Sarkar A, Kapoor S & Mukherjee T, *J Phys Chem,B* 109 (2005) 7698.

14 Hongshui Wang, Xueliang Qiao, Jianguo Chen, Xiaojian Wang & Shiyuan Ding, *Mater Chem & Phys,* 94 (2005) 449.

15 Shacklette W L, Wolf J F, Gould S & Baughman R H, *J Chem Phys,* 88 (1988) 3955.

16 Bhat N V, Nate M M, Bhat R M, Bhatt B C, *Indian J Pure & Appl Phys,* 45 (2007) 545.

17 Ahmed B, Raghuvansi S K, Srivastava S, Krishna A K, Wahab M A, *Indian J Pure & Appl Phys,* 50 (2012) 892.

18 Toth S, Fule M, Veres M, Pocsik I, Koos M, Toth A & Ujvari T, Bertoti I, *Thin Solid Films,* 497 (2006) 279.

19 Mott N F & Davies E A, *Electronic Processes in Non-Crystalline Materials*, Clarendon Press, Oxford, 1979.

20 Hong H-K, Park C-K & Gong M-S, *Bull Korean Chem Soc*, 31 (2010) 5.

21 Ravindran A, Singh A, Raichur A M, Ch&rasekaran N & Mukherjee A, *Colloids Surf B,* 76 (2010) 32.

22 Zheng M P, Gu M Y, Jin Y P & Jin G L, *Mater Res Bull*, 36 (2001) 853.

23 Huang W-Y & XU G-C, *J Coll Sci & Engg*, 16 (2010) 188.

24 Monti O L A, Fourkas J T & Nesbitt D J, *J Phys Chem B*, 108 (2004)1604.

25 Sivaiah K, Koramala N K, Naresh V & Srinivasa B, *Mater Sci Appl*, 2 (2011)1688.

26 Sivaiah K, Rudramadevi H B, Buddhudu S, Bhaskar K G & Varadarajulu A, *Indian J Pure & Appl Phys,* 48 (2010) 658.

27 Jin M, Zhang X, Nishimoto S, Liu Z, Tryk D A, Murakami T & Fujishima A, *Nanotech* 18 (2007) 075605.