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*Research Article*

# Effect of Nano ZnO on the Optical Properties of Poly(vinyl chloride) Films

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Optical properties of pure and doped poly(vinyl chloride) (PVC) films, prepared by using casting technique, with different nanosize zinc oxide (ZnO) concentrations (1–20) wt% have been studied. Parameters such as extinction coefficient, refractive index, real and imaginary parts, Urbach energy, optical conductivity, infinitely high frequency dielectric constant, and average refractive index were studied by using the absorbance and transmittance measurement from computerized UV-visible spectrophotometer (Shimadzu UV-1601 PC) in the spectral range 200–800 nm. This study reveals that the optical properties of PVC are affected by the doping of ZnO where the absorption increases and transmission decreases as ZnO concentration increases. The extinction coefficient, refractive index, real and imaginary parts, infinitely high frequency dielectric constant, and average refractive index values were found to increase with increasing impurity percentage. The Urbach energy values are found to be decreasing with increasing ZnO concentration. The optical conductivity increased with photon energy after being doped and with the increase of ZnO concentration.

## 1. Introduction

A nanoparticle is the most fundamental component in the fabrication of a nanostructure; metallic nanoparticles have different physical and chemical properties from bulk metals (lower melting points, higher specific surface area, specific optical properties, mechanical strength, and specific magnetization) properties that might prove to be attractive in various industrial applications. The optical property is one of the fundamental attraction and characteristic of nanoparticle [1].

Science the introduction of metal nanoparticles in transparent polymer matrix, polymeric nanocomposites have attracted the attention of researches as advanced technological materials because of their unique optical, electronic, mechanical, and structural characteristics. These characteristics are obtained from the unique combination of the inherent characteristics of polymers and metal nanoparticles. The characteristics of these nanocomposite films can be manipulated by varying the polymer matrix, nanoparticles, and their composition. Polymer nanocomposites have been fabricated with different polymers and nanoparticles. The incorporation of the nanoparticles into polar polymers can induce significant changes in the ultimate properties of polymers and improve their properties [2].

Polymer material is widely being used in various devices as insulating material and for optoelectronic applications. This is due to their unique properties such as light weight, high flexibility, and ability to be fabricated at low temperature and low cost [3, 4]. Optical communications, including polymer optical fibers, optical waveguides, and optical connectors due to their ease of processing, relatively low cost, and mass production are compared to silica-based optical materials. They also have potential advantages for applications in optical storage systems, such as high thermal stability, low absorption loss, and the ability of refractive index changing upon exposure to light [5]. The electrical and optical properties of polymers have attracted much attention in view of their applications in optical devices with remarkable reflection, antireflection, interference, and polarization properties. In recent times, polyvinyl chloride (PVC) has received much attention and is being exploited as a polymer host. PVC is a commercially available, inexpensive polymer and is compatible with plasticizers such as dibutyl phthalate (DBP), dioctyl adipate (DOA), dioctyl phthalate (DOP), polycarbonate (PC), and ethylene carbonate (EC). Various PVC-based systems have been found to form electrolytes with conductivities ranging from $10^{-8}$ to $10^{-3}$ S·cm$^{-1}$ at room temperature. The electrical and optical properties of polymers can be suitably modified by the addition of dopants depending on their reactivity with the host matrix [6].

Recently, electrical conductivity of polyaniline doped PVC-PMMA polymer blends, Deshmukh et al. [7], electrical and thermal conductivity of systems based on epoxy resin (ER) and PVC filled with metal powders, Mamunya et al. [8], investigation on the influence of sodium zirconate nanoparticles on the structural characteristics and electrical properties of poly vinyl alcohol nanocomposite films, Chandrakala et al. [9], dielectric properties of carbon lack/PVC (cement) composites, Jasem and Hussain [10]. The optical absorption spectrum is one of the most important tools for understanding band structure, electronic properties, and optical constants (refractive and absorption indices) of pure and doped polymers [11].

Analysis of the absorption spectra in the lower energy part gives information about atomic vibrations, while the higher energy part of the spectrum gives knowledge about the electronic states in the atom. There are many researches on the optical properties of polyvinyl alcohol doped PVC-PVA thin films [12]. Electrical and optical properties of (PEMA/PVC) polymer blend electrolyte doped with $NaClO_4$ have been studied [13] and Yousif et al. studied the optical properties of pure and modified poly(vinyl chloride) containing 1,3,4,-thiadiazole and phthalyl groups [14]. The aim of this work is to investigate the optical properties of pure and doped PVC films with different concentration of nano ZnO.

## 2. Experiment

Poly(vinyl chloride) (PVC) is powder supplied by BDH, doped with nano ZnO at room temperature by using casting technique in this work. The PVC was dissolved in THF and heated gently in water bath to prevent thermal decomposition of polymer. The polymer was stirred using a magnetic stirrer until completely dissolved. Nano ZnO material with different weights (1, 5, 10, 15, and 20) wt% was added to the polymer solution and heated for a while until completely dissolved. The solution was poured into a clean glass plate and left to dry for 24 hr to remove any residual solvent. The thickness of the produced films was 20 $\mu$m and measurements by using electronic Digital caliper. Optical absorbance and transmittance spectra were recorded in the wavelength range 200–800 nm using computerized UV-visible spectrophotometer (Shimadzu UV-1601 PC). The light sources are halogen lamp and socket-deuterium lamp.

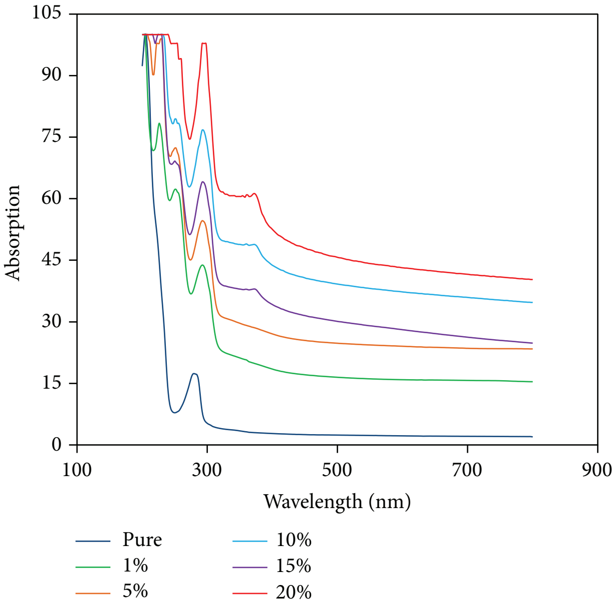

Figure 1: Absorption spectra of all PVC samples.

## 3. Results and Discussion

The UV-VIS absorbance spectra in the region 200–800 nm for doped and undoped films are shown in Figure 1. It is clear from the figure that the absorption spectra for all films decreased with increasing wavelength, while for the doped films of samples (1, 5, 10, 15, and 20%), the absorption increased with increasing doping concentration of ZnO. This is agreement with the values reported by earlier workers [15–17], in accordance with Beer′s Law. The absorption is proportional to the number of absorbing molecules [18]. Formation of new peaks for the samples after doping and also broadening of those peaks with increasing ZnO indicate a considerable interaction between PVC and ZnO [17].

The optical transmission spectra of the PVC thin films with different concentrations of nano ZnO are shown in Figure 2. The measurements were performed in the wavelength range of 200–800 nm.

This figure shows that the transmittance intensity increases with the increasing of the wavelength, and as the concentration of doped material nano ZnO increases, the transmittance decreases. The reason for this behavior is that the increases of concentration of ZnO lead to increases the localized state density which reduces the transmittance values. The transmission spectrum increases and it is approximately constant at 71%, 57%, 55%, 42%, and 37% for the concentrations 1, 5, 10, 15, and 20%, respectively. It is noticed that the composite films after doped have new peaks where appear in the short wavelengths, So higher transmission values in the higher wavelengths of the spectrum.

The dependence of the extinction coefficient ($k$) on the wavelength in the range 200–800 nm of pure and doped samples is shown in Figure 3. It is clear that the extinction coefficient for pure PVC sample shows a decrease in values of the all wavelengths (200–800) nm, while it increases extinction

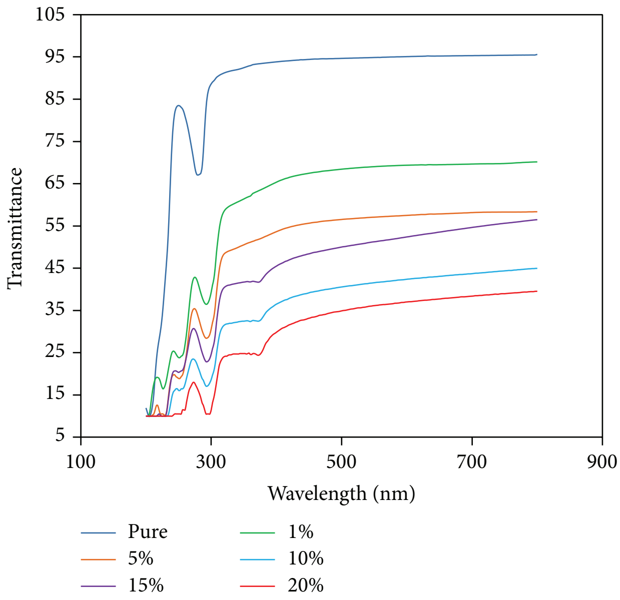

Figure 2: Transmission spectra of all PVC samples.

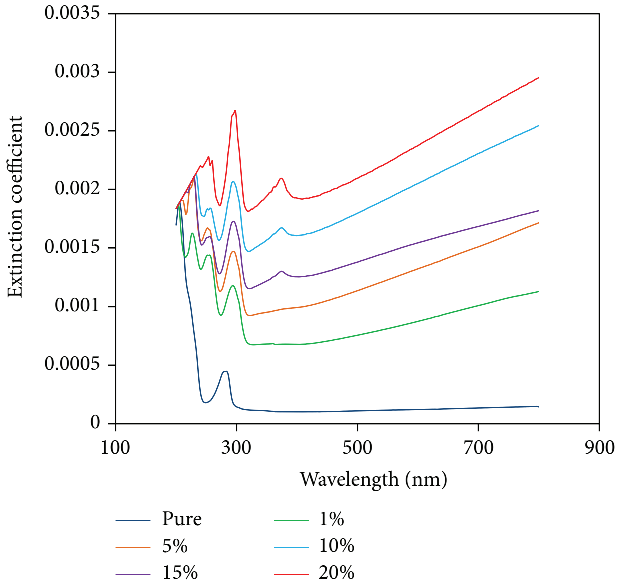

Figure 3: Variation of the extinction coefficient as a function of wavelength.

coefficient after doping the samples (1, 5, 10, 15, and 20%), in the wavelength from 300 nm to 800 nm. Extinction coefficient was increased for PVC films with increasing doping concentration; this is due to the increase in absorption coefficient, where the extinction coefficient depends on the absorption coefficient by the following equation [19, 20]:

$$k = \frac{\alpha\lambda}{4\pi}, \tag{1}$$

where $\alpha$ is the absorption coefficient.

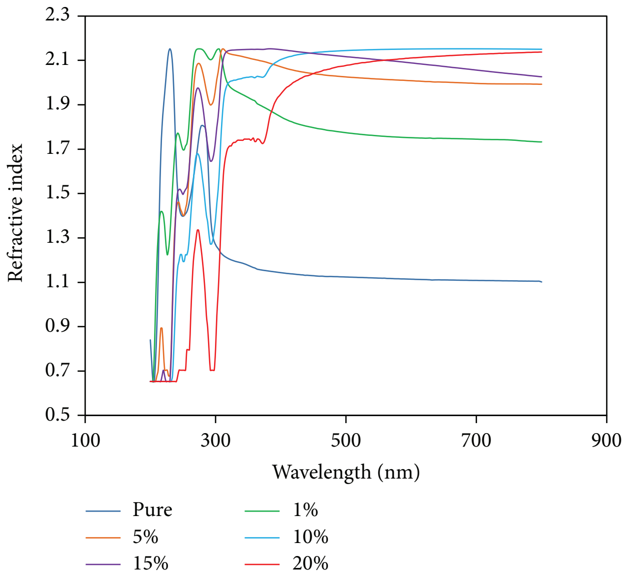

Figure 4: Variation of the refractive index as a function of wavelength.

Formation of new peaks for all samples after the doping and broadening of those peaks with increasing ZnO is an indication of change in the molecular structure (degradation, polymer fragments, or free radicals) of PVC and/or PVC/ZnO film samples by doping [17].

The refractive index ($n$) is a fundamental optical property of polymers that is directly related to other optical, electrical, and magnetic properties, and also of interest to those studying the physical, chemical, and molecular properties of polymers by optical techniques [21]. Refractive index was determined from the absolute values of the absorbance and transmittance of the investigated films using the following formula:

$$n = \left[\frac{1+R}{1-R}\right] + \left[\frac{4R}{(1-R)^2} - k^2\right]^{1/2}, \tag{2}$$

where $R$ is the optical reflectance. Plots in Figure 4 represent the dispersion in the refractive index for the doped polymers films in the investigated range of wavelengths. Inspection of Figure 4 indicates for all compositions that the refractive index decreases with increasing wavelength for samples pure, 1, 5, and 10% but samples 15 and 20% increase with wavelength. The figure shows that the refractive index increases as a result of an increase in the percentage of ZnO; this behavior can be attributed to the increasing of the packing density as a result of filler content.

The real $\varepsilon_r$ and imaginary $\varepsilon_i$ parts of the dielectric constant are related to the ($n$) and ($k$) values. The real and imaginary values were calculated using the following equations [22]:

$$\varepsilon_r = n^2 - k^2, \tag{3}$$

$$\varepsilon_i = 2nk. \tag{4}$$

The dependence of the real part on the wavelength is shown in Figure 5 for pure sample and with impurity.

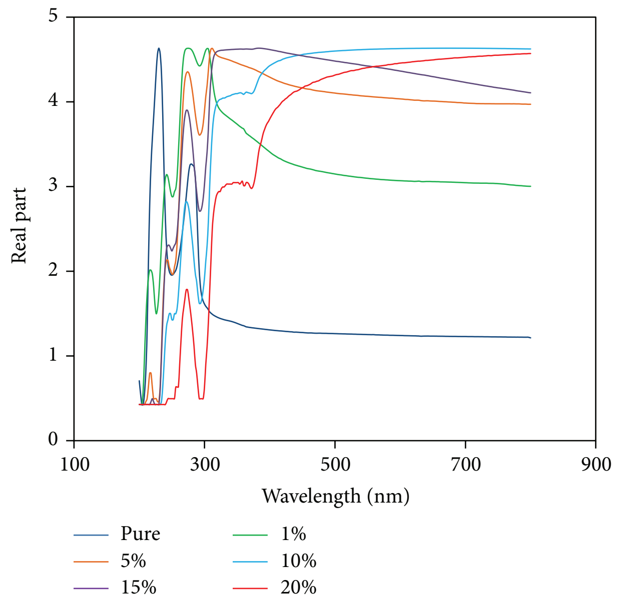

FIGURE 5: Variation of the real part of dielectric constant as a function of wavelength.

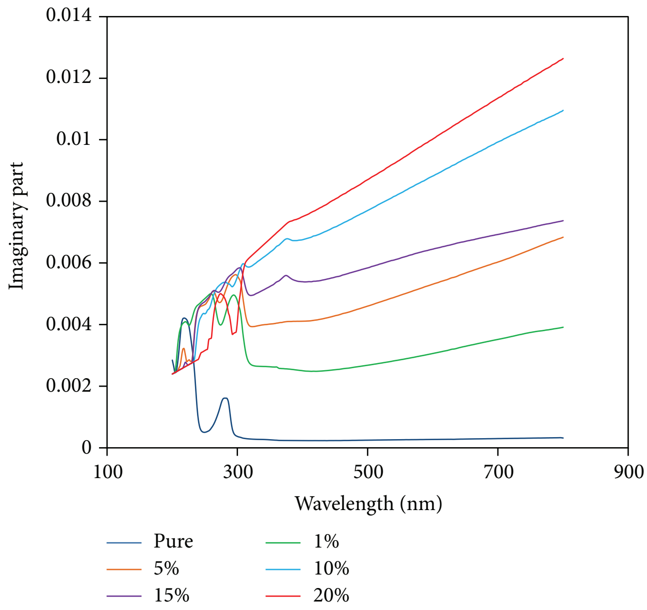

FIGURE 6: Variation of the imaginary part of dielectric constant as a function of wavelength.

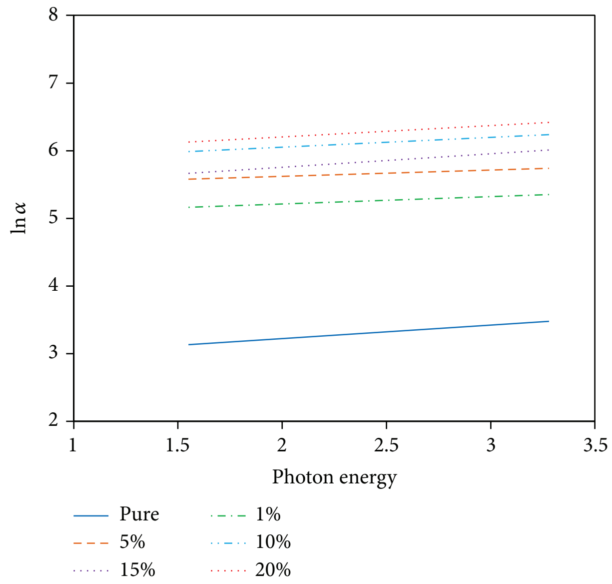

FIGURE 7: Variation of the Urbach plot of (ln $\alpha$) as a function of photon energy.

Observe from this figure that the real part depends on refractive index by (3) because the effect of extinction coefficient is very small may be canceling [23]. The real part are increase after doped for all samples with increasing wavelength and with impurity concentration, moving the curves vertex to higher wavelengths were happened with increasing impurity percentage may be attributed to related real part of dielectric constant with refractive index by equation (3) [23].

The imaginary part of dielectric constant as a function of wavelength is shown in Figure 6. It is clear that the imaginary part depends on extinction coefficient by (4) because the refractive index is very small [23, 24].

Pure PVC sample values is very few change up to 300 nm to 800 nm. After adding nano ZnO impurity for samples 1, 5, 10, 15, and 20%, the imaginary part increases for all wavelengths up to 200 nm to 800 nm and with increasing impurity percentage. New peaks appear which indicate that the samples have the no same structure. Hence, the change in the doped percentage gave change in the chemical composition of the polymer [17].

The absorption spectra clarify an extending tail for lower photon energies below the band edge, which can be described by [25]

$$\alpha = \alpha_{\circ} \exp\left(\frac{E}{E_u}\right), \tag{5}$$

where $E_u$ is the energy of Urbach corresponding to the width of the band tails of localized states in the band gap. The values of $E_u$ were calculated as the reciprocal gradient of the linear portion of the plot. Moreover, Figure 7 shows the plot of (ln $\alpha$) versus photon energy $E$ (eV) for all samples before and after being doped. Table 1 summarizes the values of optical parameter $E_u$ for different impurity concentration.

Figure 8 represents the variation between optical conductivity $\sigma$ and photon energy for all samples. The behavior of pure sample is different from the doping films (1, 5, 10, 15,and 20%) where optical conductivity of it slightly increases in low photon energies and hence high increases where happened in the beyond energies but after doping the optical conductivity were increasing with photon energy this behavior is resemble absorption coefficient because the depending on it.

Observe increasing in the optical conductivity with impurity percentage cases to moving curves vertex to low photon energies and new peaks appear in these samples.

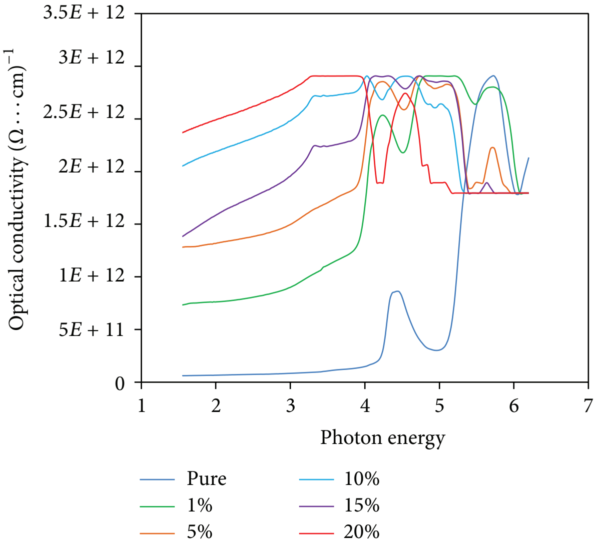

Figure 8: The optical conductivity as a function of photon energy.

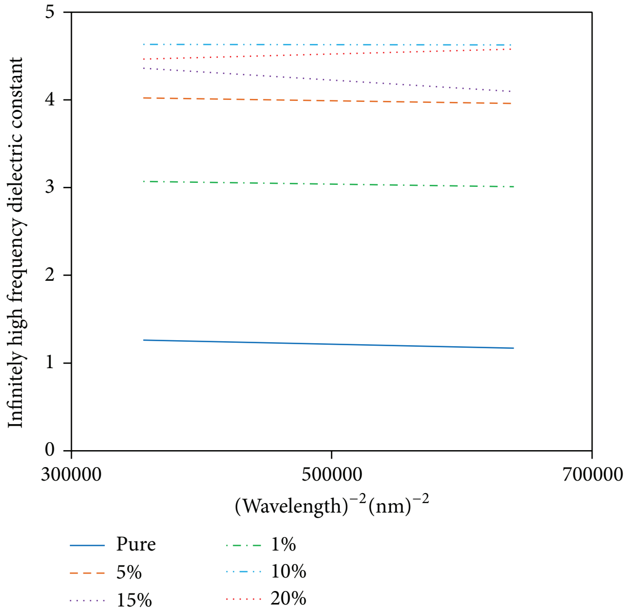

Figure 9: Dielectric constant as a function of square wavelength.

Analysis of the obtained data of refractive index can be used to obtain the infinitely high frequency dielectric constant $\varepsilon'_\infty$. The dielectric constant $\varepsilon'$ versus $\lambda^2$ plots are shown in Figure 9; values of the infinitely high frequency dielectric constant $\varepsilon'_\infty$ are determined from the extrapolation of these plots to $\lambda^2 = 0$ and are listed in Table 1 as a function of film composition. The compositional dependence of the nonlinear refractive index and dielectric constant is observed similar to the amorphous materials. The values of average refractive index are calculated from optical constant for all the wavelengths. The average value of refractive index shows the dependence on ZnO concentration. As shown in this figure, the infinitely high frequency dielectric constant and average refractive index increase for all samples after being doping. Also these values increase with the increasing of ZnO concentration [11].

Table 1: The values of optical parameters for different concentrations.

| Wt% | $E_u$ | $\varepsilon'_\infty$ | $n$ |
|---|---|---|---|
| Pure | 0.2011 | 1.2638 | 1.1241 |
| 1 | 0.1072 | 3.1482 | 1.7743 |
| 5 | 0.0914 | 4.1028 | 2.0255 |
| 10 | 0.1453 | 4.6396 | 2.1539 |
| 15 | 0.2004 | 4.6905 | 2.1657 |
| 20 | 0.1677 | 4.3221 | 2.0789 |

## 4. Conclusions

The results indicate that nanosize zinc oxide ZnO can effectively dope PVC and enhance its optical properties. The presence of ZnO leads to an increase in the absorption and to a decrease in the transmission as ZnO concentration increases. The extinction coefficient, refractive index, real and imaginary partes, optical conductivity, infinitely high frequency dielectric constant, and average refractive index values show dependence on ZnO concentration where they increase after being doped and with the increase of ZnO concentration. The Urbach energy decreased with increasing impurity concentration.

## Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

## Acknowledgment

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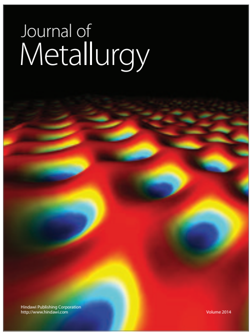
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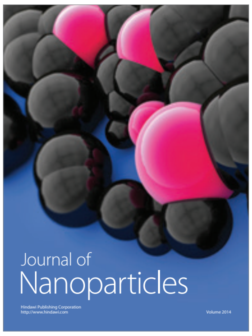
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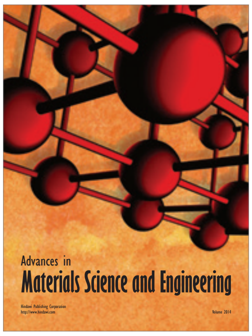
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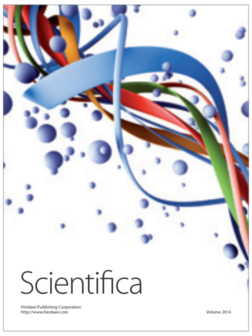
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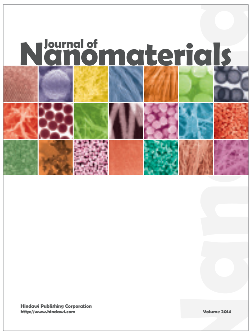
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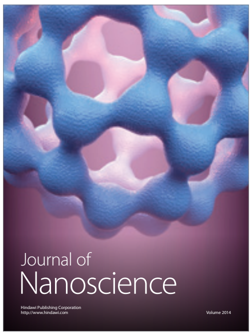
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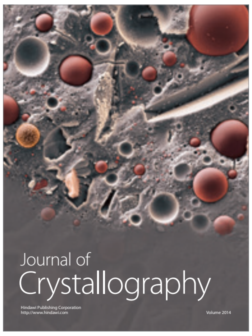
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