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Comparative Analysis of ZnO Quantum Dots Synthesized on PVA and PVP Capping Matrix

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Polymer capping matrix plays an important role in the synthesis of quantum dots via chemical methods. In this article, polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) polymers are used as capping matrix for the synthesis of quantum dots. Quantum dots of zinc oxide are directly synthesized from ZnO powder by thermal quenching methods on PVA and PVP capping matrix, and standard characterization techniques are utilized to characterize the samples. Thereafter, comparative analysis for the properties of ZnO quantum dots for PVA and PVP is presented.

Полімерна покривна матриця відіграє важливу роль у синтезі квантових точок хемічними методами. У даній статті полімери полівінілового спирту та полівінілпіролідону використовуються як покривна матриця для синтези квантових точок. Квантові точки ZnO безпосередньо синтезуються з порошку оксиду Цинку методами термічного гартування на покривній матриці з полівінілового спирту та полівінілпіролідону, а стандартні методи характеризації використовуються для характеристики зразків. Після цього представлено порівняльну аналізу властивостей квантових точок ZnO на матриці з полівінілового спирту та полівінілпіролідону.

Key words: quantum dots, quenching, polyvinyl alcohol, polyvinyl pyrrolidone, nanotechnology.

Ключові слова: квантові точки, гартування, полівінілалкоголь, полівінілпіролідон, нанотехнологія.

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1. INTRODUCTION

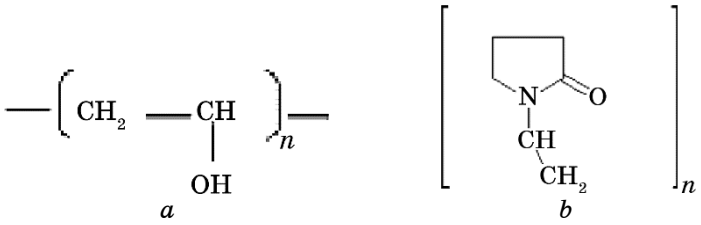
In recent times, quantum dots (QDs) find their use in a wide variety of applications in photonics, sensors, photovoltaics, and biomedical applications [1–3].

Various methods are available to synthesize quantum dots such as molecular beam epitaxy (MBE), electron beam lithography, RF sputtering, *etc.* [4, 5]. Most of these methods require sophisticated instruments [6]. On the other hand, the chemical synthesis method is considered a more economical and straightforward method of quantum dot synthesis [7, 17]. One of the vital requirements for the chemical synthesis of quantum dots is the proper capping matrix or capping solution [8]. The quantum dots are produced in the interstitial gaps of the capping matrix in a controlled manner. The capping matrix function is to restrict the size of QDs, but itself does not take part in the reaction [9]. Two of the most commonly used capping layer materials are polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP). Table 1 indicates the physical properties, and Fig. 1 shows the polymer structures of both the PVA and PVP capping materials, respectively [10].

Both PVA and PVP are noncorrosive and easily soluble in water at room temperature. In addition, the size of the particle can be modulated by regulating the reaction time, polymer concentration

TABLE 1. Physical properties of PVA and PVP.

Physical properties	PVA	PVP
Melting point, °C	200	180
Specific gravity	1.30	2.3
Thermal conductivity, W/(m·K)	2.0	1
Specific heat, J/(gm·K)	1.66	0.7
Resistivity, Ohm·cm	$(3.1–3.38)\cdot10^7$	$5\cdot10^7$
pH	Neutral or slightly acidic	3–8
Dielectric constant	2.0	7



a *b*

Fig. 1. Structures of polymers: (*a*) PVA and (*b*) PVP.

or temperature. This article aims to analyse the physical, crystallographic, and optical properties of common quantum dots synthesized on both polymer matrices.

For this purpose, ZnO quantum dots have been synthesized using the quenching method (Fig. 2) [11]. Quenching is a chemical method for synthesizing quantum dots directly from the bulk powder of the material. The bulk material in powdered form is sintered, for a long time, in a thermal furnace at an extreme temperature as high as 1000°C. After heating, the sample is immediately dropped into the polymer-capping matrix in an ice-cold condition. As a result of a sudden cooling of the material immediately after being treated at a very high temperature, it causes fragmentation in the material. Due to this fragmentation of bulk material, quantum dot nanoparticles of the material are produced. These particles having their size reduced to nanodimension enter into the interstitial gaps of the polymer matrix during the reaction and, as a result, produce stable and well-shaped quantum dots of the material.

Thus, one can easily conclude that the polymer-capping matrix plays a vital role in the quantum-dots' chemical synthesis process. The quenching-method main advantage is that the size of the quantum dot can be controlled by varying the sintering temperature, heating period, and temperature of the polymer matrix during quenching [12]. It is a straightforward method and, as the nanoparticles are obtained due to the fragmentation of pure bulk powder, hence, high-purity quantum dots can be obtained. This is not possible in the case of normal chemical route synthesis techniques. In addition, the quenching method, like the usual chemical method, has an additional advantage that it is suitable for large-scale production of samples.

The reason for choosing ZnO for the synthesis is that ZnO is

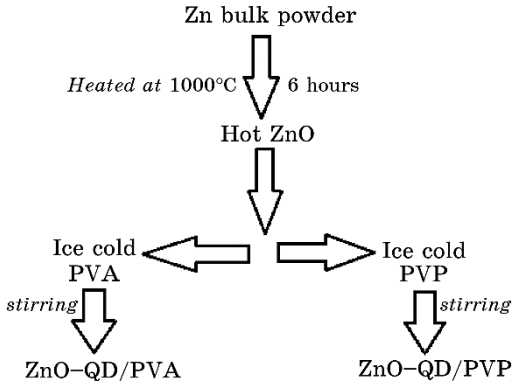


Fig. 2. Flow diagram of quenching process.

readily available in the powdered form [13].

This paper has been organized as follows. In Section 2, the synthesis of quantum dots used for this research work is described. Section 3 has the analysis and discussion of the model. Finally, Section 4 concludes the work and recommends the future aspects of the work.

2. EXPERIMENTAL

To prepare the PVA capping matrix solution, PVA (4% by weight) powder (99.9% pure, by E Merck) is taken and added into double distilled water with mild stirring and heating to form a vicious and transparent solution of PVA. Similarly, in another beaker, the PVP solution is prepared by adding PVP powder (99.9% pure, by E Merck) into double distilled water to form 4% aqueous solution by weight. The solutions are then kept in a freezer for six hours to make them ice cold.

Thereafter, to prepare the ZnO quantum dots by the chemical-synthesis quenching method, 2 gms of bulk ZnO powder are heated in a crucible inside the thermal furnace at 1000°C for about 6 hours. The white-hot powder ZnO is taken out, separated into two equal portions and immediately put into the ice-cold solution of PVA and PVP. The solution is then stirred continuously at about 170 rpm, for half about an hour, at normal room temperature. Both the solutions are then left undisturbed in a dark chamber for 6 hours for stabilization. After 6 hours, the solutions are cast into thin films on glass slides and dried by mild heating the glass slides at 40°C.

The synthesized samples have been tested by UV/Vis spectrophotometer (PerkinElmer Lambda 35 ultraviolet–visible (UV–Vis) spectrophotometer), x-ray diffraction spectrometer study (Bruker AXS, x-ray source: CuK_α), scanning electron microscopy (SEM), and high-resolution transmission microscopy.

3. RESULTS AND DISCUSSIONS

The UV–Visible absorption spectra for ZnO QDs in PVA and PVP polymer matrix are shown in Fig. 3. It is noted from the absorption plot that the absorption edge in the quantum dots are at 215 nm and 210 nm for ZnO:PVA and ZnO:PVP, respectively. The band edges in the UV–Vis absorption plot is determined by drawing tangent on the curve, which meets the x-axis at the corresponding value of absorption edge. From the absorption edge, the value of nano-band-gap, *i.e.*, E_{gn} is determined by the energy–wavelength relation

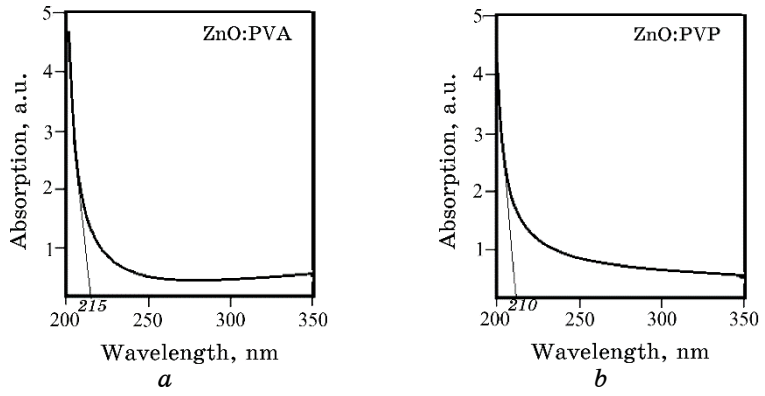


Fig. 3. Absorption spectroscopy of ZnO quantum dots in: (*a*) PVA capping layer, and (*b*) PVP capping layer.

($E = hc/\lambda$). Here, wavelength value is the corresponding absorption edge value of the sample as obtained from the UV–Vis absorption spectroscopy. For estimating particle size from absorption edge value in UV–Vis spectroscopy, we have utilized the theoretical hyperbolic band model (HBM), which is written as [16]:

$$R = \sqrt{\frac{2\pi^2 h^2 E_{gb}}{m^* \left(E_{gn}^2 - E_{gb}^2\right)}}, \tag{1}$$

where R is the quantum-dot radius, E_{gb} (of 3.20 eV) is the bulk band-gap of ZnO, E_{gn} is the quantum dot band-gap, h is Planck's constant, m^* (of $2.45 \cdot 10^{-31}$ kg) is the effective mass of electron for ZnO [15]. The data obtained from the absorption-spectroscopy study for ZnO quantum dots are shown in Table 2.

Figure 4 shows the XRD pattern for ZnO quantum dots in PVA and PVP. From x-ray diffraction of the synthesized samples, average diameter of particle is obtained by using the Debye–Scherrer formula [17, 18]:

$$D = \frac{0.9\lambda}{W\cos\theta}. \tag{2}$$

Here, D is the diameter or the size of the quantum dots to be estimated, λ is the wave-length of x-ray, which has a constant value of 0.1541 nm, θ (theta) is the glancing angle as seen in XRD in the x-axis, and W is known as the full width at half maxima, which is abbreviated as FWHM [19, 20]. Considering all the peaks in the XRD patterns in Fig. 4, *a*, *b* and calculating their glancing angle from the x-axis (2θ in degree), the average size of quantum dots is

TABLE 2. Data from UV–Vis absorption spectroscopy.

Sample	Absorption edge in quantum dot	Energy gap in quantum dot	Enhancement in band-gap in QD	Quantum dot size, D
(*a*) ZnO:PVA	215 nm	5.77 eV	2.63 eV	11 nm
(*b*) ZnO:PVP	210 nm	5.86 eV	2.69	10.2 nm

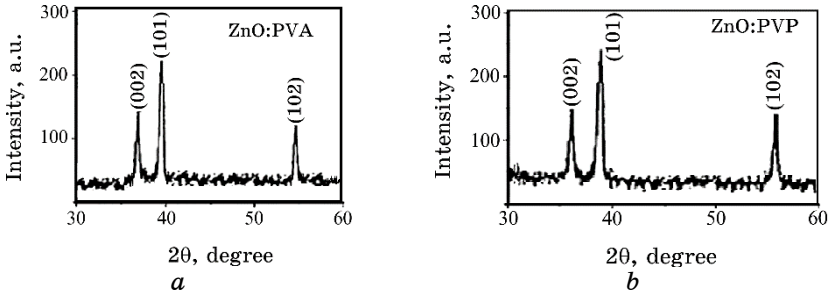


Fig. 4. XRD of ZnO quantum dots in: (*a*) PVA capping layer, and (*b*) PVP capping layer.

calculated. In both cases (ZnO:PVA and ZnO:PVP), the average crystallite size is of around 11 nm. Along with an estimation of size of the prepared quantum dots, the XRD pattern also gives an idea about the crystallographic structure of the sample. Further, analysing the XRD pattern by comparing it with the standard International Center Diffraction Data (ICCD) database, it has been found that ZnO quantum dots are having a wurtzite-type crystalline structure. The data for XRD study is shown in details in Table 3.

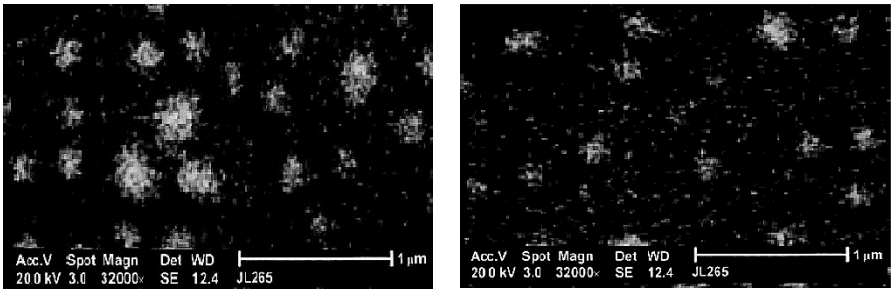
The scanning electron microscopy (SEM) images for the prepared ZnO quantum dots are shown in Fig. 5. The SEM provides an idea about the overall distribution and uniformity of the quantum dots formed in the polymer-matrix gaps [21, 22]. From the SEM in Fig. 5, it has been observed that, in case of ZnO:PVA (Fig. 4, *a*), the PVA polymer matrix has provided uniform gaps among the formed quantum dots. The quantum dots on PVA are very closely arranged to each other and uniformly distributed in an array on the capping layer.

Therefore, it can be stated that the quantum dots formed on PVA capping layer are of uniform size and orderly arranged close to one another.

From an analytical point of view, it can be stated that, as the quantum dots synthesized on PVA capping matrix are very closely distributed, hence, it is challenging to study the property of individual quantum dots in this case. Whereas in the PVP case, the

TABLE 3. Data from x-ray diffraction study.

Sample	XRD peaks (2θ)	Quantum dot size (diameter)
(*a*) ZnO:PVA	(002), (101), (102)	10.1 nm
(*b*) ZnO:PVP	(002), (101), (102)	9.4 nm



a *b*

Fig. 5. SEM images of ZnO quantum dots in: (*a*) PVA capping layer, and (*b*) PVP capping layer.

gapes in the PVP capping layer are well arranged and round. As a result, quantum dots synthesized on polymeric PVP are round in shape and adequately distributed on the matrix. In addition, for individual study of quantum dots, PVP is a better option as a capping polymer. In addition, the time taken in the synthesis of same quantum dots using PVA takes longer duration than that of PVP. Moreover, after weekly analysis of the samples under SEM, it is observed that the ZnO quantum dots on PVP are more stable compared to that of ZnO quantum dots on PVA capping layer.

The high-resolution transmission electron microscopy (HRTEM) images of the synthesized ZnO quantum dots in samples on PVA and PVP are shown in Fig. 6, *a*, *b*, respectively. The size of all quantum dots is of around 10–11 nm in both the cases. This is in close agreement with the size of ZnO quantum dots estimated from the absorption spectra from the XRD pattern. The HRTEM images also confirm the successful formation of quantum dots by quenching method.

4. CONCLUSIONS

The ZnO quantum dots have been successfully synthesized on PVA and PVP using the quenching method. The absorption characteristics of the prepared samples are studied using UV–Vis spectropho-

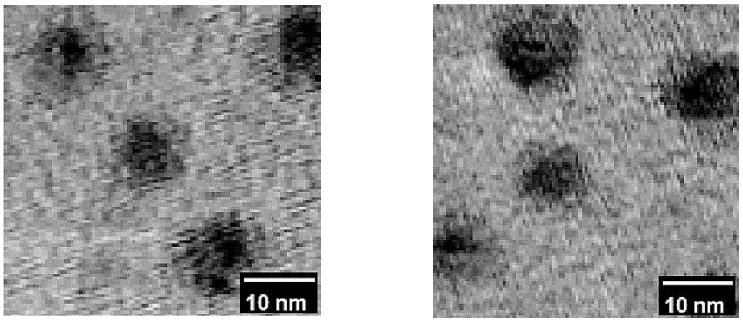


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Fig. 6. HRTEM images of ZnO quantum dots in: (*a*) PVA capping layer, and (*b*) PVP capping layer.

tometry, and the crystalline structure is studied by x-ray diffraction spectrometry. The overall distribution and uniformity of the ZnO quantum dots embedded in polymer capping layers of PVA and PVP are analysed by scanning electron microscopy.

The size and the successful formation of ZnO quantum dots are confirmed by high-resolution transmission microscopy. It has been observed that both PVA and PVP can be used for the preparation of quantum dots. However, the preparation of quantum dots on the PVA matrix takes longer time than that of PVP. The quantum dots embedded in polymeric capping layers of PVA and PVP matrix are uniformly arranged in the orderly manner of array. Quantum dots are observed to be very closely distributed in the PVA matrix, making it challenging to study the properties of individual quantum dots on the PVA capping layer compared to that of PVP. In addition, PVP polymer matrix is more stable than that of PVA.

These conclusions come in handy while using PVA or PVP polymers in the nanoparticles' synthesis [17, 23]. Although, in this case, the quantum dots prepared are of ZnO, and the synthesis technique utilized is quenching, the results can help material researchers in case they go for other chemical-synthesis methods. Polymer capping layers like PVA and PVP are common in most chemical synthesis methods [24]. Thus, depending on their requirement, one can choose the ideal capping solution between PVA and PVP.

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