Precursor- and Time-Dependent Morphological Evolution of ZnO Nanostructures for Comparative Photocatalytic Activity and Adsorption Dynamics with Methylene Blue Dye

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ABSTRACT: Diverse ZnO nanostructures were successfully fabricated at 700 °C by direct annealing of 1D Zn(II) coordination polymer precursors, namely, [Zn₂(bpta)₂(adc)₂]₆, [Zn₂(bpea)₂(adc)₂]₆, and [{Zn₆(bpta)₆(adc)₆·2H₂O}]₆. The effect of sacrificial ligands present in the precursors as well as a variation in the retention time (6–24 h) during their synthesis resulted in 0D nanospheres, 1D microrods, and 3D polyhedra (with a diamond-like structure) of ZnO. The as-synthesized ZnO nanostructures were characterized by field-emission scanning electron microscopy, transmission electron microscopy, X-ray diffractometry, diffuse reflectance spectroscopy, and Raman spectroscopy. The hexagonal crystal structure was confirmed for all the ZnO samples. A lattice spacing of 0.22 nm has been observed for nanospheres, whereas a lattice spacing of 0.26 nm has been observed for the polyhedra. Their Raman spectra confirm the wurtzite phase of ZnO. UV–vis spectra of ZnO nanostructures exhibit broad peaks in the range of 350–370 nm, and the band gap energies are found to be in the range of 3.02–3.20 eV. Based on the photoluminescence spectra photocatalytic activities of the as-synthesized ZnO nanostructures calcined for 12 h were tested with methylene blue (MB) as a contaminant in an aqueous solution. These results demonstrate that the photocatalytic efficiency of polyhedra is higher than those of nanospheres and microrods. The adsorption kinetics of MB dye by these nanostructures were studied by three different kinetic models—Elovich’s, intraparticle, and pseudo-second-order. The maximum rate of adsorption was observed with the intraparticle diffusion model.

INTRODUCTION

Nanostructured semiconductor oxides have drawn a great deal of attention owing to their interesting optical and electrical properties, which makes their potential use in the field of optoelectronics, sensing, photovoltaics, and catalysis. However, designing and fabricating nanostructured oxides for their potential use in photocatalysis has always been an area of interest. There are several semiconductor oxides such as ZnO, SnO₂, TiO₂, and ZrO₂, which are found to be efficient photocatalysts. These oxides can successfully oxidize the organic dye pollutants in waste water. Among these oxides, ZnO has been widely used as the most effective heterogeneous catalyst in photochemical reactions for solving the problems of waste water purification and combating the environmental pollution by degrading the harmful organic pollutants and dyes. This is due to its wide direct energy band gap of 3.3 eV and a large excitonic binding energy of 60 meV that are also responsible for other applications in solar cells, optics, LEDs, UV detectors, UV emitting devices, and biosensors. Thus, special emphasis has been given for the synthesis of ZnO to have a control over the size, shape, and composition. The need to develop the strategy for constructing ZnO nanostructures and understanding the underlying growth mechanism is highly desired.

Various synthetic routes like hydrothermal synthesis, sonochemical synthesis, thermal decomposition, chemical precipitation, ball milling, microemulsion synthesis, sol gel process, vapor phase synthesis, and the pulsed laser ablation technique have been applied for the preparation of ZnO nanomaterials. Nowadays, the solid-phase fabrication of metal oxides with unique sizes and morphologies via calcination of coordination polymers (CPs) under various conditions has become a suitable and convenient approach. In this approach, the CPs serve not only as starting materials but also as stabilizers of the formed nanomaterials. The simple calcination method provides a new paradigm in the synthesis of tailor-made metal oxide nanomaterials. The desired properties

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of nanomaterials (e.g., luminescence, ferromagnetism, and cytotoxicity) are dependent not only on the size but also on the appropriate morphology. Therefore, development of new efficient and cheap methods for the synthesis of nanomaterials with a desired size and morphology is very much required. In this regard, CPs serve as an important bridge between the synthetic chemistry and the materials science. This methodology has been used in the fabrication of various metal oxides, for example, PbO, ZnO, Fe₂O₃, CoO, CuO/Cu₂O, and Ti₃O₅. Although the use of CPs as precursors for the synthesis of ZnO has not been established thoroughly, few groups have reported the preparation of these oxides. For example, (a) Oh’s group synthesized the ZnO rings and hexagonal tubes by calcination of a CP consisting of hexagonal lumps, (b) Zhang and co-workers reported the synthesis of superhydrophobic ZnO utilizing a superhydrophobic Zn(II) CP, and (c) Morsi’s group also synthesized ZnO nanoparticles from a Zn(II) nitrite CP in oleic acid. The metal ions with a standard reduction potential of 0.27 V or higher such as Co, Ni, and Cu present in CPs form metal nanoparticles during calcination, whereas metal ions with a reduction potential lower than 0.27 V such as Mg, Al, Mn, Zn, or Cr present in CPs tend to form corresponding metal oxides. Thus, the direct calcination of a CP at a temperature of 700 °C, which is above its decomposition temperature, yields ZnO.

In the present work, we demonstrate the effective application of water-soluble CPs as the precursors for the fabrication of hydrophobic ZnO nanostructures via the simple calcination route. The advantages of these CPs as precursors are simplicity of processing, reproducibility, scalability, and long-range ordering to get metal oxides with varied morphologies. Herein, we report the synthesis of 0D nanospheres, 1D microrods, and 3D polyhedra of ZnO by direct calcination of three different 1D Zn(II) CPs, with a general formula of [Znₓ(bpta)₂(adc)ₓ]·xH₂O, (where bpta = N,N-bis(pyridinylmethyl)alkyl amine; adc = acetylene dicarboxylate; x = 0 or 2), at 700 °C. The three different ligands present in these CPs have a profound effect on the morphology of the obtained ZnO nanostructures as determined by the microscopic techniques and their photocatalytic activities. Furthermore, the three different kinetic theories (Elovich’s, intraparticle diffusion, and pseudo-second-order) were applied to model the experimental data for understanding the mechanism of sorption on the cationic methylene blue (MB) dye.

RESULTS AND DISCUSSION

Synthesis and Characterization. The as-synthesized ZnO samples were named ZnO-bpxa-t (where bpxa = bpma, bpea, bpta and t = 6, 12, 18, 24 h). The use of 1D Zn(II) CPs has yielded ZnO nanostructures with high crystallinity and purity. Zn(II) CPs were calcined for different time intervals (6, 12, 18, 24 h) in a tube furnace at 700 °C to get the ZnO nanostructures (Schemes 1–3), resulting in almost different morphologies in each case. The variation in morphology can be a result of some structural differences in the precursor polymers because of the change in the N-alkyl group from the methyl to ethyl to t-butyl group of the tridentate ligand in the CPs. Notably, the supramolecular interactions that are found in these CPs can be pointed out: moderate π–π interactions are present in [Znₓ(bpta)₂(adc)ₓ] and not in [Znₓ(bpma)₂(adc)ₓ] whereas two lattice water molecules in ([Znₓ(bpta)₂(adc)ₓ]·2H₂O) form a 2D supramolecular assembly by connecting two of its 1D CP chains. The formation of such nanostructures is remarkable without the use of any stabilizing agent. With a variation in the ligands of the precursors, these act as self-templating agents for the formation of different morphologies. Furthermore, the use of hydrothermal method followed by annealing of the same precursors provides different nanostructures as the mechanism of formation is different.

These are fully characterized by X-ray diffraction and microscopic and spectroscopic studies that are discussed in detail below. Figure 1 shows X-ray diffraction (XRD) patterns of the as-synthesized ZnO nanostructures with different retention times (6–24 h). All the peaks could be clearly indexed to the hexagonal wurtzite phase of ZnO, which matches well with the JCPS card no of 36–1451. It is clear that the other form of ZnO, the cubic zinc blende, which can be found as the nucleus in the initiation of some nanostructures but is rather unstable, has quickly been transformed into the thermodynamically more stable wurtzite form under high-temperature calcination. The scattering from the (100), (002), and (101) planes can be clearly observed. There is no other characteristic peak for any impurity. This indicates high crystallinity and purity of the as-synthesized ZnO samples. The estimated lattice parameters, interplanar spacing (d), and atomic packing parameters for the hexagonal ZnO nanoparticles are shown in Table S1.

Microscopic Studies. Figure 2 shows the scanning electron microscopy (SEM) images of nanoparticles emerged after the heat treatment of [Znₓ(bpma)₂(adc)ₓ] to 700 °C for 6 h of retention time. As a result of spheroidization process, the necks and grain boundaries started emerging between these particles. These particles continued to grow with a little variation in size up to 18 h of retention time to form nanospheres and eventually get assembled to produce nanorods (80 nm) after 24 h of retention time. In general, phase composition and properties of...
the resulting daughter metal oxide nanostructures depend on the crystal structure of the parent CP. For example, two CPs composed of the same building blocks, Co²⁺ and 1,4-BDC, have plate- or rodlike structure of the parent CP. For example, two CPs composed of the same building blocks, Co²⁺ and 1,4-BDC, have plate- or rodlike morphologies (p-MOF and r-MOF), respectively. Accordingly, plate- and rodlike Co₃O₄ nanomaterials (p-Co₃O₄ and r-Co₃O₄, respectively) prepared via pseudomorphic conversion retained the morphology of the parent CP. In another study, superhydrophobic Zn(II) CP particles with controllable shapes were synthesized. Zinc oxides obtained from calcination of these CPs retain superhydrophobicity. In contrast, our study shows the utilization of 1D CPs as precursors, which should result in producing 1D nanostructures, but 0D nanospheres, 1D microrods, and 3D polyhedra (with a diamond-like structure) were obtained. Further, in our study, the hydrophobic ZnO nanostructures have been obtained from the hydrophilic water-soluble 1D CPs. In the present work, a complete transformation in the dimensionality as well as solubility has been obtained, which is remarkable.

Furthermore, ZnO microrods were obtained with a change in precursor to [Zn₂(bpta)₂(adc)₂]·2H₂O following the same procedure. After 6 h of retention, etching started from the top end of the microrods to overall erode downwards toward the c-axis, as shown in Figure 3a. As a result of fast etching from the corners, the tips started emerging from the top ends of the microrods. With the increase in the retention time from 6 to 12 h, the length of the tip increased. When the retention time was further extended to 18 h, a decrease in the length of the microrods was observed; however, the diameters from the top and bottom ends of the rods changed very little. Finally, after 24 h of retention, the tips started disappearing to produce rods with hexagonal ends. Thus, it can be concluded that the shortening of microrods was observed as a result of retention, which happens to be the dominant process instead of growth (Figure 3b-d).

When [Zn₂(bpta)₂(adc)₂]·2H₂O, was calcined to 6 h, ZnO nanoparticles grew up to 50–70 nm and assembled into nanoscale polyhedra, as shown in Figure 4a. With the elongation in time from 12 to 24 h, these nanoparticles continued to grow to produce nanoscale polyhedra with a diamond-like structure (Figure 4b–d).

The formation of such nanostructure is remarkable without the use of a stabilizing agent. On the other hand, such a diamond-like structure of ZnO was obtained by refluxing the Zn(II) acetate precursor in tetraethylene glycol (TTEG) at 160 °C, where TTEG acts as a stabilizing agent. Based on the above results, the morphologies of nanostructures reported in this study are found to be precursor as well as time dependent (Table 1).

Figures 2f, g, 3f, g, and 4f, g show transmission electron microscopy (TEM) images of nanospheres (ZnO-bpma-12), microrods (ZnO-bpma-12), and polyhedra (ZnO-bpma-12) of ZnO nanostructures after 12 h of retention time. The nanostructures, microrods, and polyhedra are clearly visible in Figures 2f, 3f, and 4f. The high-resolution TEM (HRTEM) images (Figures 2e and 4e) show the distance of 0.22–0.26 nm between the lattice fringes of ZnO nanostructures coinciding with the distance between crystallographic planes of hexagonal wurtzite ZnO. The selected area electron diffraction (SAED) planes (100), (101), (001), and (0002), as shown in Figures 2h, 3b, and 4b, confirm the results of XRD patterns. These results indicate that different frameworks of CPs mature finally to different morphologies (Figure 5).

**Raman Spectroscopy.** The Raman scattering spectra of the as-prepared ZnO nanostructures are shown in Figure S1 with 785 nm laser light as an excitation source. The wurtzite-phase ZnO, which belongs to the space-group P6₃mc group theory, predicts the existence of the following optic modes: Γₜot = A₁, E₁, 2E₂, 2B₁. A₁ and E₁ are polar modes, whereas E₂ mode is a nonpolar mode. All are Raman-active modes except two B₁ modes, which are characterized as silent modes. The main dominant intense and sharp peak at around 435 cm⁻¹ is assigned to E₂ high mode of wurtzite ZnO, and the peak at 325 cm⁻¹ is associated with the second-order Raman spectrum originating from the zone-boundary phonons. No peak at around 584 cm⁻¹ was observed. This clearly indicates the absence of defects in the as-synthesized ZnO nanostructures.
Optical Properties. The room-temperature UV–visible absorption spectra of the as-synthesized ZnO nanostructures are shown in Figure S2. The absorption spectra showed a band around 380 nm corresponding to the formation of ZnO nanostructures. At this particular wavelength, a sharp decrease in the reflectance represents the uniform distribution of the particles in the nanostructures. The direct band gap energy ($E_g$) for the ZnO samples is determined from the graph of $h\nu$ versus $(\alpha h\nu)^2$ for the absorption coefficient $\alpha$, which is related to the band gap $E_g$ as $(\alpha h\nu)^2 = E_g(h\nu - E_g)^2$, where $h\nu$ is the photon energy, and $E_g$ is a constant. The extrapolation of the linear portion of the curve to absorption being equal to zero gives the

Table 1. Variation in the Morphology of ZnO Nanostructures Obtained in This Study

| time (h) | precursor: $[\text{Zn}_2(\text{bpma})_2(\text{adc})_2]_n$ | precursor: $[\text{Zn}_2(\text{bpea})_2(\text{adc})_2]_n$ | precursor: $[\text{Zn}_2(\text{bpta})_2(\text{adc})_2\cdot 2\text{H}_2\text{O}]_n$ |
|----------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| 6        | nanospheres (70–80 nm)                          | microrod                                        | polyhedra                                       |
|          |                                                 |                                                 | (60–70 nm)                                      |
| 12       | nanospheres (70–80 nm)                          | microrod                                        | polyhedra                                       |
|          |                                                 |                                                 | (65–70 nm)                                      |
| 18       | nanospheres (80–90 nm)                          | microrod                                        | polyhedra                                       |
|          |                                                 |                                                 | (80–90 nm)                                      |
| 24       | nanorods                                        | microrod                                        | polyhedra                                       |
|          |                                                 |                                                 | (80–90 nm)                                      |

Figure 2. FESEM images of (a) ZnO-bpma-6, (b) ZnO-bpma-12, (c) ZnO-bpma-18, (d) ZnO-bpma-24; (e) HRTEM image, (f,g) TEM images, and (h) SAED pattern of ZnO-bpta-12.

Figure 3. FESEM images of (a) ZnO-bpea-6, (b) ZnO-bpea-12, (c) ZnO-bpea-18, (d) ZnO-bpea-24; (e–g) TEM images and (h) SAED pattern of ZnO-bpea-12.

Figure 4. FESEM images of (a) ZnO-bpta-6, (b) ZnO-bpta-12, (c) ZnO-bpta-18, (d) ZnO-bpta-24; (e) HRTEM image, (f,g) TEM images, and (h) SAED pattern of ZnO-bpta-12.
value of band gap energy $E_g$. The inset in Figure S2 shows the band gap energies of the ZnO nanostructures. The band gap values of these nanostructures are given in Table S2. The average particle sizes of these nanostructures can be calculated from the absorption spectra by using the method proposed by Meulenkamp:

$$\frac{1240}{\lambda_{1/2}} = a + \frac{b}{D^2} - \frac{c}{D} \tag{1}$$

where $a = 3.301$, $b = 294.0$, and $c = -1.09$, $\lambda_{1/2}$ (nm) is the wavelength at which absorption becomes half of that of the shoulder, and $D$ (Å) is the diameter of the particle. The particle sizes of the as-synthesized ZnO nanostructures are given in Table S3.

**Photoluminescence Studies.** As a result of quantum confinement, the band gap energy of the materials increases, which can be clearly observed from the photoluminescence spectra for such materials. Further, the photocatalytic performance of the as-synthesized ZnO nanostructures is closely associated with the surface defects. The surface defects or the surface conditions can be effectively studied by measuring their optical properties. Figure 6a–c shows the photoluminescence spectrum of ZnO samples with an excitation wavelength of 320 nm at room temperature. All the samples showed a strong and broad emission band at around 395 nm, which corresponds to a near-band gap excitonic emission originating from the radiative recombination of excitons, whereas the emission band at around 508 nm in some of the nanostructures originates from deep-level transition in the surface defects. This emission is caused by the radiative recombination of charge carriers because of the oxygen vacancies and the interstitials of O and Zn atoms. High crystal quality can be observed in some of the nanostructures where only the UV emission is centered around 398 nm. Energy level diagrams for ZnO nanostructures are shown in Figure S3.

**Photocatalytic Activity.** The MB dye was used as a contaminant in aqueous solution to study the photocatalytic activity of the as-synthesized ZnO nanostructures calcined for 12 h. Owing to the absorption in the visible region, MB has been extensively used as an indicator to verify the photocatalytic activities of the nanostructures. The characteristic absorption peak at 663 nm for MB is used to monitor the photocatalytic activities of the nanostructures. In this study, an aqueous solution of MB with a catalytic amount of ZnO sample is first kept in the dark for 30 min to achieve the absorption–desorption equilibrium, followed by an irradiation with UV light (Figure 7). With time evolution, the decolorization of MB was observed in terms of the change in intensity of $\lambda_{max}$. The percentage of decolorization was calculated as follows:

$$\% \text{ decolorization} = \frac{A_0 - A_t}{A_0} \times 100 \tag{2}$$

where $A_0$ is the initial absorbance, and $A_t$ is the absorbance after irradiation at various time intervals. The photodegradation of MB can be considered as a Langmuir–Hinshelwood first-order kinetics reaction, which can be expressed as: $\ln(C/C_0) = kt$, where $k$ is the reaction rate constant. A comparison of the adsorption behaviors of MB on the surface of ZnO samples is shown in Figure 8a. The decolorization of MB dye by ZnO nanostructures is shown in Figure 8b. The degradation ability and the rate constants of these nanostructures are shown in Table S4. It has been observed that polyhedra with a diamond-like structure (ZnO-bpta-12) displayed better efficiency in degrading the MB dye, followed by nanospheres (ZnO-bpma-12) and microrods (ZnO-bpea-12). In general, the degradation efficiency depends

![Figure 5. Different morphologies (nanospheres, microrods, and polyhedra with a diamond-like structure) obtained as a result of change in the precursor.](image)

![Figure 6. (a–c) Room-temperature photoluminescence spectra of the as-synthesized ZnO nanostructures.](image)
on many factors—surface area, particle, band gap, and so forth. The surface area for a given volume depends on the morphology of the particle. As a result, these different shaped nanostructures define the surface area for a given volume, which affects the photocatalytic activity. As a consequence of the isoperimetric inequality in all three dimensions for a nanosphere, it has the smaller surface area for a given volume. In contrast, polyhedra having a diamond-like structure with tiny spikes have larger surface area for a given volume. However, the rods with the size in micron range have smallest surface area for a given volume. Consequently, the photocatalytic degradation of MB follows the order of their surface areas: polyhedra with a diamond-like structure > nanospheres > microrods. A comparison of the degradation efficiencies of the as-synthesized ZnO nanostructures with similar materials reported in the literature is shown in Table S5.70−74 Although the rates are better in the literature reports, the present work shows a simple route to get variation in the dimensionality and solubility of the as-synthesized nanostructures using water-soluble 1D CPs, which is exceptional. We have also shown a correlation between the surface area of three different nanostructures and the degradation rates through this systematic study. It should be noted that MB-adsorbed nanomaterials can be reused and recycled easily by separating these from the reaction media by centrifugation and washing with ethanol. Thus, these are promising recyclable materials for environmental remediation.

**Adsorption Dynamics.** To identify the type of adsorption mechanism in order to determine the effectiveness of sorption of ZnO nanostructures onto the MB, three different models were studied to predict the adsorption kinetics75 of the as-synthesized ZnO nanostructures on MB. These kinetic models included Elovich’s, intraparticle diffusion, and pseudo-second-order.

**Elovich’s Equation.** It is used to describe the second-order kinetics, which involves the chemisorption process, but no specific mechanism for adsorbate−adsorbent can be proposed from the application of this equation. This model indicates how strong adsorbates are held on the surface of adsorbents.76,77 The linear form of the equation is proposed by Chien and Clayton,78 which can be expressed as follows

$$q_t = \frac{a_e}{b_e} \ln \left( \frac{t}{t_a} \right)$$

where $a_e$ is the initial adsorption rate (mg/g min), and the parameter $b_e$ is related to the extent of surface coverage and activation energy for chemisorption (g/mg). These constants can be obtained from the slope and intercept of the plot of $q_t$ versus ln($t$). The plots of the samples fitted by this equation are shown in Figures S4, S7, and S10. The coefficient of regression values clearly indicates that the data are fitting well into this model (Table 2).

**Intraparticle Diffusion Model.** This model describes that the rate of adsorption process is controlled by the speed of diffusion of adsorbate into the adsorbent.79 The initial rate of intraparticle diffusion is given by Weber and Morris80 and can be expressed as

$$q_t = k_d t^{1/2}$$

A linear plot of $q_t$ versus $t^{1/2}$, which passes through the origin, confirms the rate of adsorption controlled by this model. It is observed that other kinetic models may be operating when the

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**Figure 7.** Absorption spectra of MB after adsorption in (a) ZnO-bpma-12, (b) ZnO-bpea-12, and (c) ZnO-bpta-12 for 8 h under UV light.

**Figure 8.** (a) Comparison of photocatalytic degradation of MB over the as-synthesized ZnO catalysts, and (b) decolorization of MB by ZnO-bpma-12, ZnO-bpea-12, and ZnO-bpta-12 (labeled 1, 2, and 3).
The regression values compared. Figures S6, S9, and S12 show the plot does not pass through the origin. The plots of the samples fitted according to this model are shown in Figures S5, S8, and S11. The rate constant values and other fitting parameters are given in Table 3. From the correlation coefficients, it can be concluded that this model has a good agreement with the experimental data.

Table 3. Fitted Intraparticle Diffusion Kinetic Model Parameters for the Removal of MB

| sample        | rate constant, $k_2$ (mg/g min$^{-1/2}$) | intercept, $C$ | $R^2$  |
|---------------|-----------------------------------------|---------------|--------|
| ZnO-bpma-6    | 0.2075                                  | 0.1886        | 0.98983|
| ZnO-bpma-12   | 0.2367                                  | 0.5735        | 0.98335|
| ZnO-bpma-18   | 0.1963                                  | 0.2278        | 0.98587|
| ZnO-bpma-24   | 0.0740                                  | −0.1240       | 0.96110|
| ZnO-bpea-6    | 0.1033                                  | −0.5011       | 0.92722|
| ZnO-bpea-12   | 0.1179                                  | −0.5315       | 0.97061|
| ZnO-bpea-18   | 0.0894                                  | −0.3113       | 0.97081|
| ZnO-bpea-24   | 0.0880                                  | −0.6432       | 0.98671|
| ZnO-bpta-6    | 0.0496                                  | −0.0113       | 0.98950|
| ZnO-bpta-12   | 0.0590                                  | 0.9914        | 0.94946|
| ZnO-bpta-18   | 0.0687                                  | 0.1162        | 0.99412|
| ZnO-bpta-24   | 0.0603                                  | 0.8694        | 0.94961|

**Pseudo-Second-Order.** When the rate of sorption follows the second-order mechanism, the pseudo-second-order rate equation is represented by its linear form as shown below

$$\frac{t}{q_e} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$

where $k_2$ is the rate constant of pseudo-second-order adsorption (g/mg min), and $q_e$ (mg/g) is the amount of adsorbate retained at time ($t$). The initial adsorption rate, $h_i$ (mg/g min) is expressed as

$$h_i = k_2 q_e^2$$

If the plot of $t/q_e$ versus $t$ gives a linear relationship, the constants $k_2$ and $h_i$ can be determined from the intercept and slope of the line obtained from the plot. The surface adsorption involving chemisorption is the rate-limiting step for this process. The removal of the dye from the aqueous solution is because of the physicochemical interactions between the phases. Figures S6, S9, and S12 show the plot fitted using this model. The regression values confirm fitting of the data into this model, as shown in Table 4. Because the experimental data fit well into all the three kinetic models, it can be concluded that the adsorption of the dye by ZnO nanostructures occurs simultaneously by all of them, but the rate of adsorption is maximum in the intraparticle diffusion model.

### EXPERIMENTAL SECTION

**Materials and Methods.** All chemicals for synthesis were purchased commercially and used as received without further purification. All reactions were carried out under aerobic conditions. All CPs used in this study were prepared in gram quantities following the literature method.

**Physical Measurements.** Powder X-ray diffraction was carried out with a Rigaku Ultima IV diffractometer that was equipped with a 3 kW sealed tube with Cu Kα X-ray radiation (generator power settings: 40 kV and 40 mA) and a DTex Ultra detector choosing the option for the Bragg Brentano geometry (2.5° primary and secondary solar slits and 0.5° divergence slit with 10 mm height limit slit). Each properly ground sample was placed on a glass sample holder that was placed on the sample stage for data collection between 2θ values of 5°–80° with a scanning speed of 2° per min. For the morphology and chemical composition of the as-synthesized samples, data were collected.
and analyzed by field-emission SEM (FESEM, JEOL, 15 kV) and energy-dispersive X-ray spectroscopy (EDX, HORIBA EX-250, 15 kV) associated with FESEM. For TEM of the as-synthesized samples, an FEI Tecnai G2 F20 instrument equipped with a field emission gun operated at 200 kV was used; in each case, a copper grid was appropriately loaded using 1 mg of sample (well dispersed in 10 mL of ethanol with the help of a sonicator for 20 min). Solid-state diffuse reflectance spectra were recorded using a Cary 5000 UV–vis–NIR spectrophotometer by Agilent Technology with a KBr solid-state holder. Solid-state fluorescence spectra were obtained using a HORIBA Fluorolog 3 spectrophotometer. Each data set was analyzed with FluorEssence software. Photocatalytic experiments were carried out using a spectrolite 8 W UV lamp.

**Preparation of ZnO Nanostructures.** For the synthesis of ZnO nanostructures, a conventional horizontal tube furnace composed of an alumina tube, a rotary pump system, a gas supply, and a control system was used. About 0.05 mmol of the source material, that is, Zn(H) polymers ([Zn_{n}(bpma)_{2}(ad)_{2}]_{n} (39 mg), [Zn_{2}(bpma)_{2}(ad)_{2}]_{n} (40 mg), and ([Zn_{4}(bpta)(ad)c)_{2}·2H_{2}O]_{n} (45 mg) were taken in silica crucibles and loaded on an alumina boat and positioned at the center of the tube to get the maximum temperature. The temperature of the source material was set at 700 °C, and the heating was maintained at the rate of 3 °C/min. After attaining this temperature, it was maintained for different times 6, 12, 18, and 24 h. The furnace was then allowed to cool with the same rate. The white powders were collected in each case.

**Photocatalytic Measurements.** The cationic dye MB was chosen to examine the photocatalytic performance of the as-synthesized nanostructures. A spectrolite 8 W UV lamp (λ = 365 nm) was used as the light source. The as-synthesized nanostructures (5 mg) were dispersed into 10 mL of a 0.94 mM solution of MB (30 mg in 100 mL water) and vigorously stirred in the dark for 30 min to reach the adsorption–desorption equilibrium between the samples and MB at room temperature. During illumination under an UV lamp, the aliquots of about 2 mL were collected and centrifuged at fixed time intervals. The concentration of MB was analyzed at given intervals by a Cary 60 UV–vis spectrophotometer.

**Adsorption Kinetics.** To study the kinetics of adsorption, the experimental data were fitted into suitable rate expressions to estimate the possible reaction mechanisms and the rates of adsorption of the ZnO nanostructures on the surface of MB. Thus, it becomes important to model the adsorption rates to analyze the adsorption dynamics and to establish the time dependence of these adsorption systems. Several mechanistic models have been studied to describe the adsorption kinetics effectively such as film diffusion, intraparticle diffusion, pseudo kinetic model, Elovich’s model, film solid model, and the film pore model. In the present study, an extensive analysis on three kinetic models (pseudo-second-order model, Elovich’s model, and intraparticle diffusion model) was made to have a better understanding of the adsorption kinetics.

**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c01555.

Lattice parameters and band gap values of the as-synthesized ZnO nanostructures, calculated particle sizes of the as-synthesized ZnO nanostructures using Meulenkamp’s equation, percent decolorization and rate constant values of the as-synthesized ZnO nanostructures calcined for 12 hours, comparison of percentage degradation efficiency of MB dye by the ZnO nanostructures with literature values, Raman spectra of ZnO nanostructures, Tauc plots of the as-synthesized ZnO nanostructures, energy level diagram of the as-synthesized ZnO nanostructures, and Linear fit of kinetic models (PDF)

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**Notes**

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