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Synthesis of Some Functional Oxides and Their Composites Using Sol-Gel Method

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Abstract

Two main approaches for nanomaterials fabrication are the top-down and the bottom-up methods. The first is limited to mechanical grinding, thermal evaporation, ion sputtering, arc discharge, pulsed laser ablation, and other physical and chemical vapor deposition. These routes are costly, consume higher energy, and require complex technology such as ultrahigh vacuum. The bottom-up methods refer to the production of complex nanostructured materials from atoms and molecules. This approach is relatively simple and low in cost. However, it requires a good knowledge of the optical properties of the particles and their modifications when the particles are integrated with nanostructures. One of the widest bottom-up methods is the sol-gel. It involves a solution or sol (single-phase liquid) that undergoes a sol-gel transition (stable suspension of colloidal particles). In this chapter, we throw light on the history of sol-gel, its advantages, and limitations, operating this method for the production of different types of nanomaterials in the form of powders or thin films. In addition, some applications of the sol-gel-derived nanosized materials will be discussed.

Keywords: sol-gel preparation, metal oxide nanomaterials, characterization, oxides, sol-gel chemistry

1. Introduction

Nanosized material, a material with at least one dimension limited to ~ 100 nm (A nanometer is 10^{-9} of a meter.), displays unique and unexpected physicochemical properties. This behavior of nanomaterials arises from the large surface area to volume ratio and the quantum confinement effect that can be defined as the reduction of the band structure of the material into discrete quantum levels and the emerging of new energies for the electrons, resulting from the limited size of its particle, also known as the “size-effect.” **Figure 1** shows that the surface atoms/volume ratio increases exponentially with decreasing particle size. Increasing the surface of the material increases its reactivity and photoelectrochemical performance. The accumulation of information on nanosized materials resulted in or emerged two branches, “Nanoscience” and “Nanotechnology.” The former focuses on the preparation and

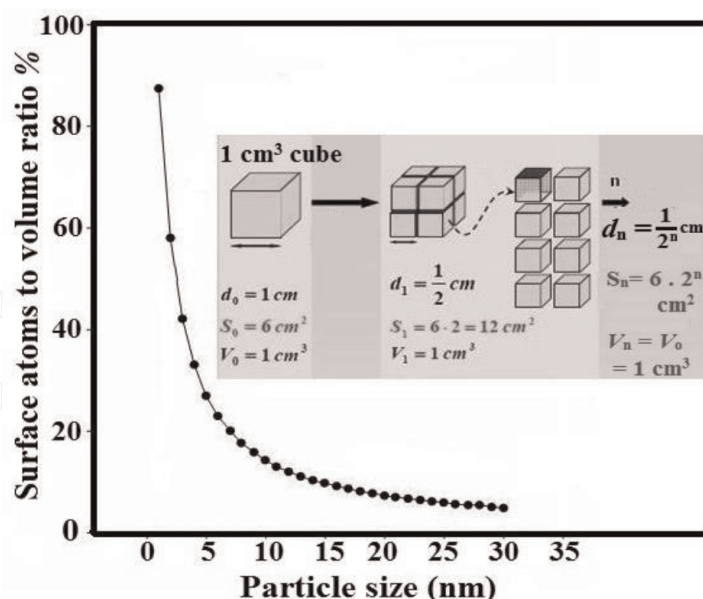


Figure 1.

The surface atoms/volume ratio (the determined surface-to-bulk atomic ratio) [1].

characterization of the nanomaterials and the fundamental study of their properties, whereas the latter is related to designing and using structures and devices based on these nanosized materials in different applications [2, 3].

The literature survey revealed that the physical and chemical properties of nanosized materials as well as the particles' morphology (0D, 1D, 2D, ...), also depend on the preparation method and preparative parameters and conditions. With the continuous headway of nanotechnology, there are several methods or techniques for preparing nanosized materials which can be classified into two main branches; top-down and bottom-up; the top-down methods are based on breaking down large pieces/particles of the material to convert it to the required nanostructures. The "bottom-up" methods are based on assembling single atoms/molecules (in solutions or gas phase) into larger nanostructures. We will discuss the details of one of the bottom-up methods in this chapter, named the sol-gel.

2. Sol-gel chemistry

As a phenomenon, the sol-gel transition was discovered and explored by Ebelmen in 1846 by observing the slow transformation of silicic esters, in the presence of moisture, to hydrated silica and the spontaneous gelation when the alkoxide was placed in contact with the atmosphere [4]. However, the interest in the sol-gel method began in 1980 and received a continuous and increased interest exponentially until today, and we expect a growing interest during the current decade, as shown in **Figure 2**.

A sol is defined as a colloidal system in which the dispersion medium is a liquid, and the dispersed phase is a polymerized molecule or fine particles, where the particle/molecular size should be in the range of 1 nm – 1 μm . A gel is a continuous solid network that supports the continuous liquid phase [5]. In the typical sol-gel process, consecutive steps are the sol formation through hydrolysis, the sol-gel transition (gel state), the gel drying, and conversion into a calcined material, as shown in **Figure 3**. The chelating agent binds tightly with the metal ions to prevent the formation of

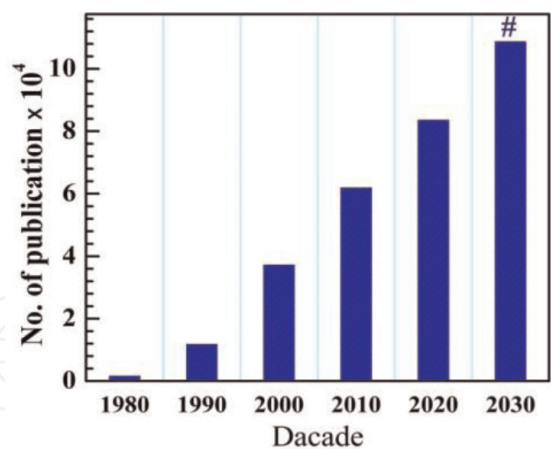


Figure 2.
Number of publications/decade utilizing the sol-gel route (Scopus database), # is the expected number [Scopus database].

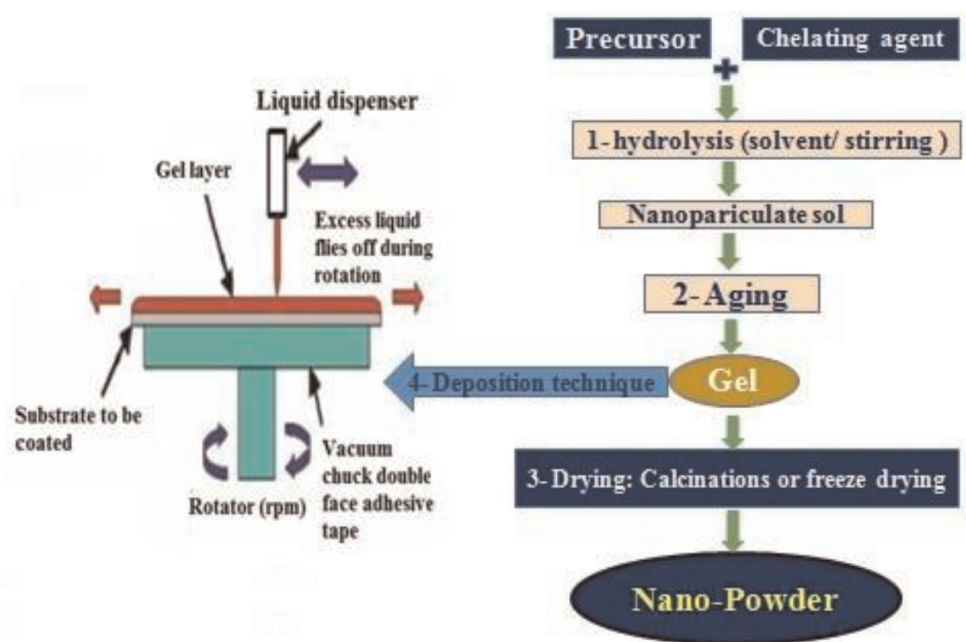


Figure 3.
Steps of sol-gel chemistry for powder and thin film formation [6, 7].

aggregations. The sol-gel chemistry begins with mixing the precursor (acetate, nitrate, or chloride) with the solvent. If water is the solvent, the sol-gel is hydrolytic but named nonhydrolytic sol-gel in the case of using an organic solvent such as ethanol [6]. The solution prepared by the sol-gel chemistry is used cooperatively with coating techniques such as spray, dip, and spin coating. For thin film deposition, the chelating agent has the role of stabilizer to prevent the metal ions to be precipitated or agglomerated. The spin-coated films will form in nanoparticulate layers, as will be discussed.

According to Brinker and others, the sol-gel method is a technology where the solution containing the precursor solid materials evolves gradually to form a networked gel comprising both the liquid and solid phases. The precursors react with each other in the common solvent to form a colloidal suspension (sol). This sol undergoes a hydrolysis reaction that could be represented as $M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH$ and condensation reaction: $M(OH)_n \rightarrow MO_{0.5n} + (0.5n)H_2O$ to form

a continuous liquid network (gel) [4, 7]. Once the gel is formed, it can be coated and dried to form thin films, as will be discussed, or be further dried, and densified at higher temperatures to fine powder, depending on the application [5], see **Figure 3**.

The sol-gel approach became one of the key technologies of the twenty-first century owing to low-energy consumption, reproducibility, eco-friendly, simplicity, low-cost, and pollution-free. In addition, it allows the combination of inorganic/organic materials in a single-phase and yields an organic/inorganic hybrid coating which attracted great attention owing to their high compatibility, good adhesion to the substrate, and corrosion resistance. Moreover, the sol-gel technology is represented in low-temperature requirements, repeatability, and controllability. In addition, it is possible to tune the intrinsic properties and the elemental chemical composition of the material. The final product of the sol-gel reaction can be controlled by precursors, pH, processing time, and molar ratios between the reacting agents. Löbmann revealed that the sol-gel route could yield various topologies; porous $\lambda/4$ films, dense interference layers, and arrays of antireflective structures (called moth-eye). These topologies can be used for antireflective coatings for architectural glazing, the display industry, solar energy conversion, and ophthalmic lenses [8]. Controlling the structure of sol-gel prepared film could yield highly selective gas sensors [9]. Chen et al. [10] studied the effect of pH value (1–10) on the corrosion protection ability of the sol-gel coatings. The highest condensation degree occurred at pH 4, resulting in a compact and stable 3D sol-gel network of high crosslinking density, and this provided highly effective corrosion protection.

It was also found that the photocatalytic properties of the sol-gel prepared TiO_2 nanopowder depend mainly on the sol composition, where the addition of water, HCl, and diethanolamine as well as the type of alcohol as solvent (ethanol, propanol, and butanol) were found to greatly affect the photocatalytic activity of the powder toward bromophenol blue dye removal [11]. Luo et al. [12] studied some of the variables related to the sol-gel preparation of CaO as a high-performance sorbent and they concluded that the molar ratio of $\text{H}_2\text{O}:\text{Ca}^{2+}$ had a minor effect on the CO_2 sorption performance of the CaO, and the optimal molar ratio was 80:1. The optimal molar ratio of citric acid: calcium nitrate optimal molar ratio is 1:1, and adding an excess of citric acid led to more gaseous products. In addition, when the pH 3, the sol-gel structure was destroyed, and the optimal pH value was 2, where the best performance of CaO sorbent was achieved. A. C.-Soria et al. [13] fabricated Fe_3C /few-layered graphene core/shell nanoparticles, with potential magnetic properties, embedded in a carbon matrix by a modified two-step surfactant sol-gel method, where the hydrolysis, polycondensation, and drying took place in a one-pot. Hashjin et al. [14] tuned up the sol-gel technique for preparing high-durable superhydrophobic coatings. The prepared layers are useful for anti-icing, self-cleaning, and anti-bacterial applications, in the energy and photovoltaic devices, textile and coating industry, construction, and aerospace industry.

Sol-gel technique, among various solution methods, is found to be more suitable for metal oxide thin films and nanopowder. Controlling the conditions of preparation, nanoparticles of controlled shape/morphology, control stoichiometry, size, textural, surface characteristics, purity, and high quality can be obtained. Besides, uncomplicated ideas can be executed via this technique for more recent and advanced technological applications [6]. In the following section, some examples of the sol-gel derived nanostructures will be mentioned with their characterization and some related applications. The data presented here are based on our experimental results. It would be better to throw light on some selected materials that were prepared using the sol-gel method.

3. Sol-gel preparation of NiO, CdO, SnO₂, and PbO and their nanocomposites

3.1 Experimental (preparation and characterization techniques)

The precursor materials used for NiO, CdO, SnO₂, and PbO preparation were: NiCl₂·6H₂O of molecular weight ($M_W = 237.7$), supplied by Schorlau, Spin, Cd(NO₃)₂ $M_W = 236.42$, supplied by Nova Oleochem Limited, SnCl₂·2H₂O, $M_W = 225.63$, from Merck, and CH₃COO)₂Pb·3H₂O, $M_W = 279.33$, Adwik, Egypt, were used to prepare 0.7 M solutions by dissolving the required mass of each salt in 100 ml double-distilled water. To each solution, 8.825 g of oxalic acid (C₂H₂O₄), as a chelating agent, was added under stirring at 60°C for 1 h. The obtained solutions were maintained in an oven at 80–90°C for 20 h to evaporate the excess water above the precipitate. The solutions were then cooled to room temperature and aged for 24 at room temperature (RT). Finally, the four gel was calcined at 400°C for 2 h to obtain the nanopowders: NiO, CdO, SnO₂, and PbO nanoparticles (NP). The characterization of these nanometal oxides will be discussed.

The identifying of the crystalline phase and samples purity was done by recording XRD spectra using the PANalytical X'Pert PRO diffractometer, with Cu K_α radiation of wavelength $\lambda = 1.541 \text{ \AA}$, and scan in the range of $2\theta = 5.0\text{--}80^\circ$. High-resolution transmission electron microscopy (HR-TEM) of model JEM, 2100, Jeol, Japan, was used to check the particle size and morphology of the prepared materials. For polymer nanocomposite films, the surface morphology was evaluated using field emission-scanning electron microscopy FE-SEM (Carl ZEISS Sigma 500 VP). In addition, the UV-vis spectra in the wavelength range of 200–1600 nm were recorded on a Shimadzu spectrophotometer (UV-3600 UV-Vis-NIR) with an accuracy of $\pm 0.2 \text{ nm}$.

3.2 Results and discussion

The crystallite size and phase identification of NiO, CdO, SnO₂, and PbO were examined by XRD, shown in **Figure 4**, and the shape and particle morphology was studied by HR-TEM, as shown in **Figure 5**. **Figure 4** shows the XRD pattern of NiO; the sharp peaks indicate that a good crystallite material was grown by the sol-gel technique. The diffraction peaks at $2\theta = 37.14, 43.13, \text{ and } 62.89^\circ$ are indexed for the crystal planes (111), (200), and (220) of NiO of rhombohedral [*fcc* (face-centered cubic) with a lattice constant $a = 4.175 \text{ \AA}$], in agreement with JCPDS No. 44–1159. Scherrer's formula ($C_s = 0.9\lambda_{Cu}/\beta_{1/2} \times \cos \theta$) was utilized to calculate the crystallite size (C_s), where $\beta_{1/2}$ is the full width at half maximum intensity. Considering the main detected peaks, the average C_s was $\approx 28 \text{ nm}$.

In the XRD pattern of the sol-gel prepared CdO nanoparticles, all of the detected diffraction peaks are indexed to the cubic phase of CdO with a lattice parameter $a = 4.69483 \text{ \AA}$. The peaks at $2\theta \approx 33.07^\circ, 38.39^\circ, 55.38^\circ, 66^\circ, \text{ and } 69.38^\circ$ are assigned to the (110), (200), (220), (311), and (222) crystal plans, respectively, according to JCPDS file No. 75–0592. This confirms the formation of CdO with excellent crystallinity and high purity, as no secondary phases were observed in the pattern of the CdO nanoparticles. The C_s of the CdO nanoparticles were found to be in the range of 66.4–73.2 nm with an average of 70.18 nm. The pattern of SnO₂ is also shown in **Figure 4**, where all the diffraction peaks with Miller indices of (110), (101), (200), (211), (220), (310), (112), and (301) are of the tetragonal (rutile) crystalline phase of

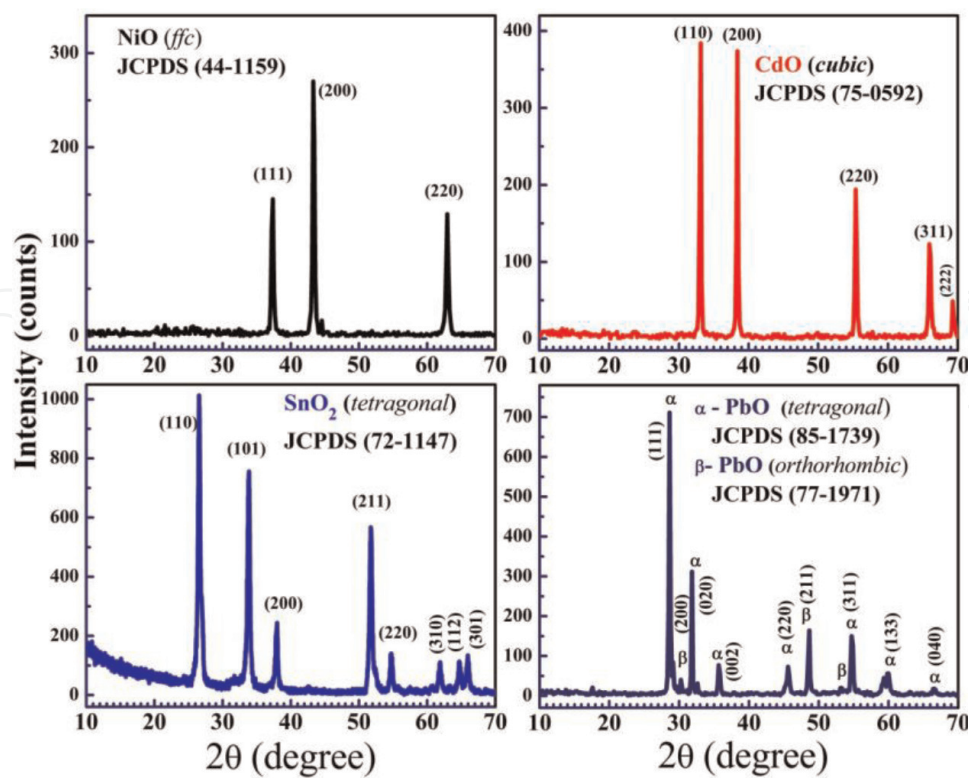


Figure 4.
(a-d) XRD patterns of the sol-gel-derived NiO, CdO, SnO₂, and PbO nanoparticles.

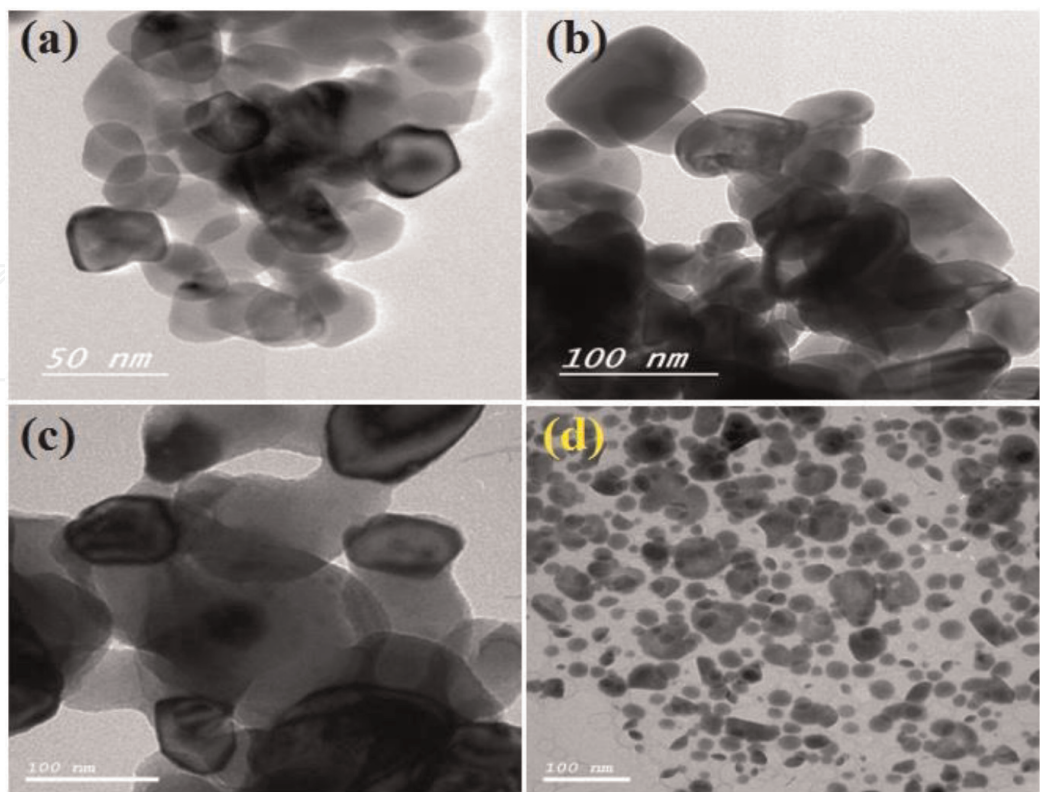


Figure 5.
HR-TEM of the sol-gel-derived NiO (a), CdO (b), SnO₂ (c), and PbO (d) nanoparticles.

SnO₂ according to JCPDS No. 72–1147. The (110) plane exhibits the highest intensity and presents the least surface energy and is the most thermodynamically and electrostatically stable [15]. The lattice parameters *a*, *b*, and *c* of the tetragonal SnO₂ phase are determined from the formula: $\frac{1}{d^2} = \frac{(h^2+k^2)}{a^2} + \frac{l^2}{c^2}$, and the calculated values were *a* = *b* = 4.473 Å and *c* = 3.189 Å. The *C_s* values are in the range of 17.93–47.06 nm with an average size of 30.2 nm. In the case of lead monoxide, the XRD pattern is a mixture of α- and β-PbO. The diffraction peaks of the orthorhombic β-PbO are at 2θ = 29.06°, 30.35°, 32.59°, and 53.17°, with *a* = 5.88 Å, *c* = 4.74 Å, according to JCPDS card No. 77–1971. The other peaks are assigned to the tetragonal α-PbO, with *a* = 3.97 Å, *c* = 5.024 Å, in agreement with JCPDS card No. 85–1739. The *C_s* of PbO is in the range of 24.4–113.4 nm with an average of 58.6 nm.

The HR-TEM image of NiO shows an average particle size of NiO in the range of 24.85–34.10 nm, which is smaller than that reported for NiO prepared from the thermal decomposition of Ni(OH)₂ at 600°C [16]. TEM image of the CdO shows that CdO nanoparticles are well-defined and their size is in the range of 52–116 nm with an average particle size of 72 nm. Besides, the image for the SnO₂ shows that SnO₂ grains are segregated together and form agglomerates or clusters of primary crystallites. Most of the observed particles are tetragonal in shape. The average particle size measured by HR-TEM is ~41 nm. Finally, the TEM image of the PbO formed as nanoparticles of sizes from tens of nm to <100 nm, with an average of about 59 nm, which is consistent with the XRD results.

Nickel oxide (NiO) is an interesting ceramic material with reasonable photostability and thermal stability, high melting at 1955°C, and a refractive index of ≈ 2.2. In addition, NiO is a *p*-type semiconductor with a wide optical bandgap (= 3.4–4 eV) [17, 18]. When the sol-gel prepared NiO was incorporated at 0.5 and 1.0 wt% into a polymer matrix composed of carboxymethyl cellulose–polyvinyl pyrrolidone (CMC–PVP) blend, the reflectivity and refractive index of the blend dramatically changed, as shown in **Figure 6**. For the pure blend, *R*% is in the range of 3–5 and decreases with increasing the incident wavelength. However, this behavior converted to a bell-like shape, and the *R*% increased to 6.5–13% after 1.0 wt% NiO doping. Similarly, the refractive index (*n*) value of the blend changed from 1.45 to 1.59 in the

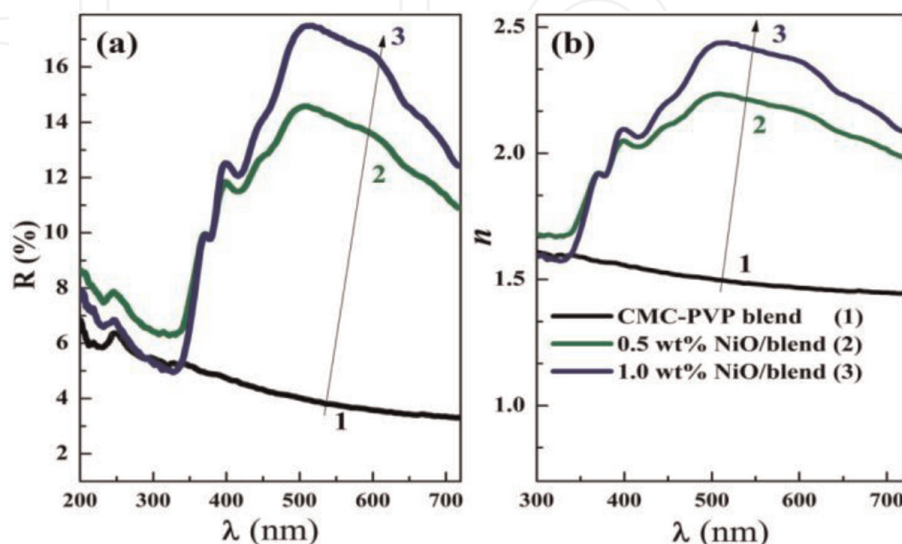


Figure 6.
 Influence of NiO on the reflection *R*% (a), and refractive index *n*, (b) of a polymer blend.

visible region and increased significantly to 2.233 after the NiO loading. This illustrates that NiO increased the packing density of the blend, and these nanoparticles act as scattering centers to increase the dispersion of light and increase the reflection and reflectivity of the matrix [19]. Therefore, NiO/blend are suitable material for coatings, lenses, and for engineering, and optoelectronic applications [20].

Cadmium oxide (CdO) is a promising II–VI compound that has *n*-type semiconductivity, resistivity in the order of 10^{-2} – 10^{-4} Ω cm [21], high optical transmittance in the visible region, and a refractive index of 2.49 [22]. The direct (indirect) band gap is in the range of 2.2–2.5 eV (1.36–1.98 eV) [23]. Therefore, CdO has been used for catalytic and sensing applications and in some optoelectronic devices [23]. The sol-gel prepared CdO when mixed with PVC polymer resulted in decreasing the transmittance of the polymer from 89% to the range of 70–84% and shrinking its band gap from 5.12 eV to 4.96 eV, as shown in **Figure 7**. This result may reflect the important applications of the CdO/PVC nanocomposites in optical and/or electrical devices [24].

Tin oxide (SnO_2) is also a transparent conducting oxide that exhibits outstanding electrical and optical properties. Its wide band gap (≈ 3.68 eV), high exciton binding energy (130 meV), high transmittance in the visible region of the spectra, high *n*-type conductivity (10^2 – 10^3 $\Omega^{-1}\cdot\text{cm}^{-1}$) at ambient temperature, nontoxicity, thermal stability, chemical sensitivity, and the low-cost makes SnO_2 the best choice for the biomedical applications, gas sensing, photo-catalysis, solar cells, and future optoelectronic devices [25, 26]. In this chapter, we have used the sol-gel prepared SnO_2 nanoparticles as nanofillers to modify the optical properties of a ternary blend composed of carboxymethyl cellulose–polyethylene glycol–polyvinyl alcohol (CMC–PEG–PVA). As shown in **Figure 8**. The E_g value of the pure blend and SnO_2 /CMC–PEG–PVA nanocomposite were calculated from the absorption spectra (*Abs.*) of the samples by using Tuac' relation: $(\alpha h\nu)^r = M(h\nu - E_g)$, where $h\nu$ is the energy of incident photons and $r = 1/2$ and 2 for the indirect and direct allowed transitions, respectively, and $\alpha = \frac{2.303 \text{ Abs.}}{\text{film thickness}}$ is the absorption coefficient.

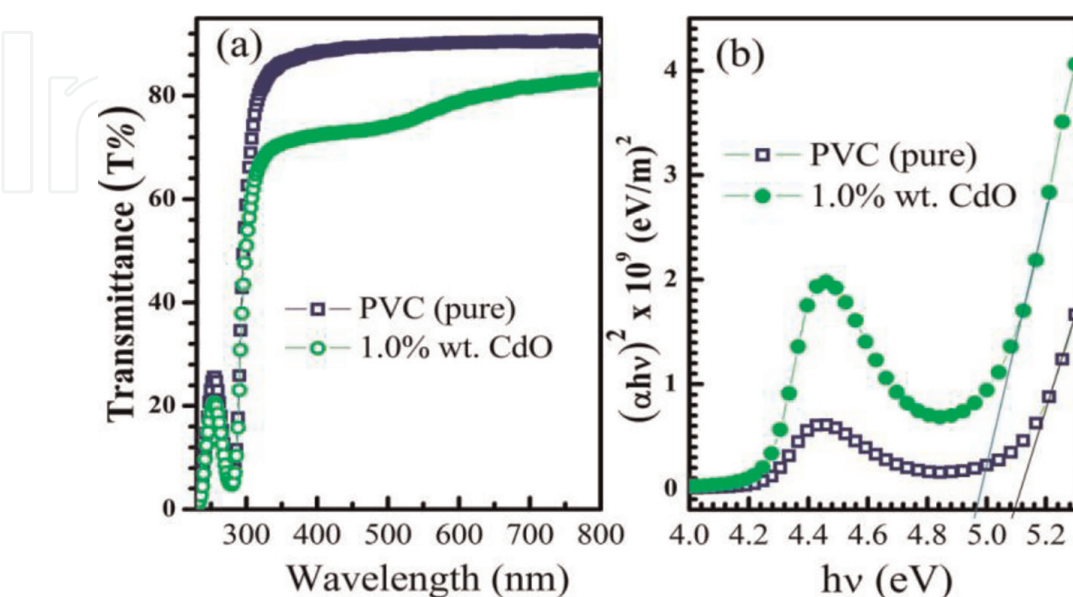


Figure 7. Effect of 1.0 wt% CdO on the transmittance (a), and optical gap (b) of PVC polymer.

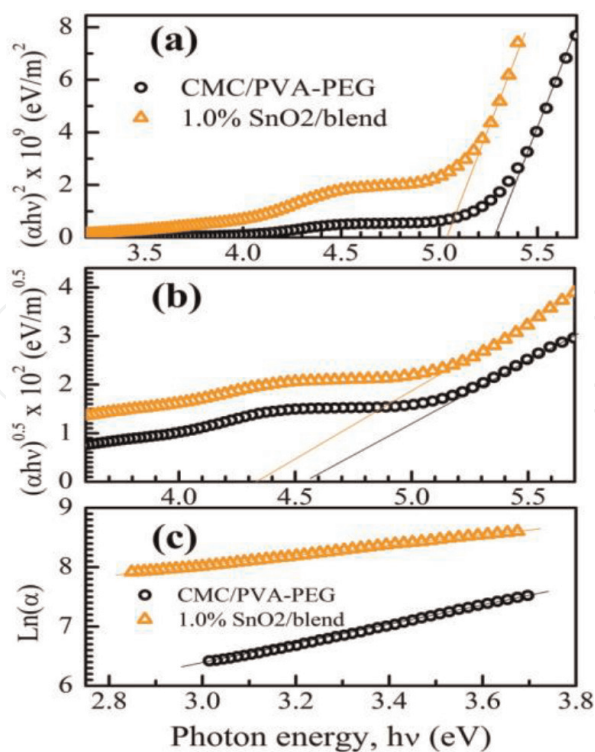


Figure 8. Influence of SnO₂ nanoparticles (at 1.0 wt% loading) on the direct (a) and indirect (b) optical gap and Urbach energy (c) of CMC-PEG-PVA ternary blend.

As shown in **Figure 8**, both the direct and indirect transitions for the polymeric films are possible. This is evidenced by the linear relationship of both $(\alpha h\nu)^2$ and $(\alpha h\nu)^{0.5}$ on $h\nu$ at higher photon energies. Extra-plotting the straight-line portions of the curves to zero absorption gives the E_g values: direct $E_g = 5.28$ and 5.04 eV and the indirect $E_g = 4.55$ and 4.20 eV for the pure blend and 1.0 wt% SnO₂/blend nanocomposite, respectively. Introducing the SnO₂ nanoparticles induce energy levels inside the band gap of the blend matrix, resulting in the shrinking of E_g . Similarly, doping with α -Fe₂O₃ nanorods at 1.0 wt% decreased E_g of PVA-PEG from 5.28 to 4.83 eV [27]. The Urbach energy (E_U), which is the width of the exponential absorption edge, can be calculated using the following equation [28]: $\alpha = \alpha_0 \exp\left[\frac{h\nu - E_c}{E_U}\right]$, where E_c and α_0 are constants. The dependence of $\ln(\alpha)$ on $h\nu$ for the films is shown in **Figure 8(c)**. The straight lines suggest that the absorption is according to the quadratic relation for inter-band transition, which satisfies the Urbach rule. The value of E_U is taken as the reciprocal of the slope of the lines ($E_U = (d(\ln\alpha)/d h\nu)^{-1}$), and its value was found to be 0.607 eV and 0.962 eV for pure and 1.0 wt% SnO₂ loaded film, respectively. Thus E_U changes inversely with E_g . Increasing the E_U is attributed to the disorder increase inside the material after SnO₂ nanoparticles incorporation, resulting in the tailing in the valence and conduction bands.

Lead oxides exist with a variety of oxidation states; α - and β -PbO, α - and β -PbO₂, Pb₂O₃, and Pb₃O₄ [29]. Among them, lead monoxide (PbO) is considered a transparent conducting oxide that has a high dielectric constant $\epsilon' = 25.9$ [30] and a direct transition band gap of 1.96 eV for α -PbO [29, 31]. It is in use in a variety of applications, such as paints, pastes for a new lead acid battery, pigments, gas sensors, network modifiers in luminescent glassy materials, and nanodevices [31, 32]. Moreover, it can be used to increase the dielectric contestant and ac conductivity of polymeric

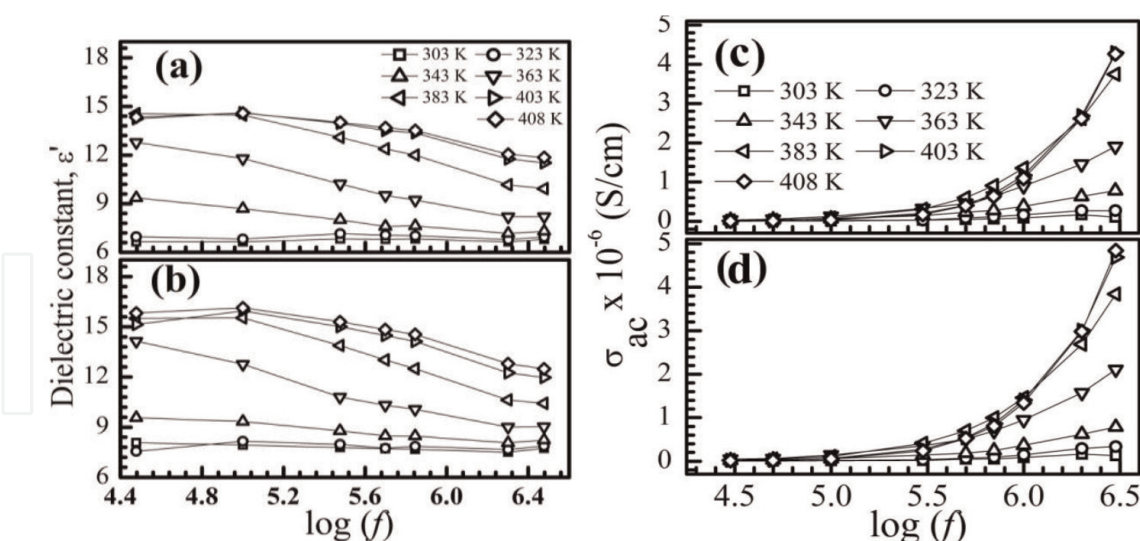


Figure 9. Dielectric constant (a, b) and ac conductivity (c, d) of pure PVC and 1.0 wt % PbO-doped PVC.

materials such as PVC, as shown in **Figure 9**. Incorporation of PbO nanoparticles increases the interfacial polarization due to the heterogeneous structure inside PbO/PVC nanocomposites. Many conductive three-dimensional networks could be formed throughout the nanocomposite, assisting the charge carriers to hop from conducting clusters to neighbors and therefore increases the conductivity of the material [33].

4. Preparation of nanosized hematite with different sizes and morphology

Controlling the morphology of the material at the nanosize is the key to broadening its industrial applications. Here we will describe tuning the microstructure and morphology of the nanosized hematite (α -Fe₂O₃) by varying the oxalic acid (chelating agent) molar ratio from 0.0 to 2.0 and the annealing temperature in the range 350–750°C. α -Fe₂O₃ is a direct band gap ($E_g = 2.0$ – 2.2 eV), an *n*-type semiconductor that can absorb about 40% of the solar spectrum. It has several advantages, such as its abundance, high thermal stability, nontoxic, high resistance to corrosion, melting point of 1350°C, and a high specific capacitance of 3623 F/g. Therefore, α -Fe₂O₃ is widely used in several technological fields, including rechargeable Li-ion batteries, recording devices, catalysis, biomedical, optical devices, solar cells, and gas sensors [34–37]. The literature survey displays that The α -Fe₂O₃ in the form of 0 D and 1D nanostructures have grown increasing interest. For example, α -Fe₂O₃ - δ nanoparticles showed enhanced electrochemical performance and cycling stability as anode materials for Li-ion batteries [38]. Moreover, hematite of plate-like morphology, displayed a significant hysteretic behavior at ambient temperature with saturation magnetization $M_S = 2.15$ emu/g and a coercivity $H_C = 1140$ Oe, remanent magnetization $M_r = 0.125$ emu/g [39].

4.1 The preparation and measurements

A nanopowder of α -Fe₂O₃ was prepared by a template-free sol-gel method as follows; 18.92 g of FeCl₃·6H₂O ($M_W = 270.3$), supplied by Nova Oleochem Limited, was dissolved in 100 ml double distilled by the magnetic stirring for 1.0 h. Different amounts of oxalic acid were added to the solution to maintain the molar ratios of

oxalic acid/ $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ at 0.0:1.0, 0.5:1.0, 1.0:1.0, and 2.0:1.0. These samples named $M = 0$, $M = 0.5$, $M = 1.0$, and $M = 2.0$, respectively. The solution aged for about 15 h at the ambient temperature, then the excess water was thermally evaporated at 95°C for 3 h. The samples were calcined at 550°C in the air for 2.0 h. The sample $M = 1.0$ was calcined at different temperatures in the range of $350\text{--}950^\circ\text{C}$, for 2 h. The crystal structural analysis and size and morphology of the prepared powders have been carried out by X-ray diffraction (using PANalytical's X'Pert PRO) and the HR-TEM (JEM 2100, Jeol).

4.2 Results and discussion

Figure 10 shows XRD patterns of the prepared materials ($M = 0\text{--}2.0$). All the diffraction peaks belong to the hexagonal structure of hematite according to JCPDS card no. 04-015-7029. No peaks related to any other FeO phases not detected. The strong peaks indicate the good crystallization of samples. The lattice parameters a and c and the volume $V = \frac{\sqrt{3}}{2}a^2c$ of the hexagonal cell are calculated from the following relation: $\frac{1}{d^2} = \frac{4}{3} \left(\frac{h^2 + k^2 + hk}{a^2} \right) + \frac{l^2}{c^2}$, where (hkl) is Miller's indices. Increasing M from 0.0 to 2.0 resulted in shifting the main peaks: (012), (104), and (110) to lower 2θ values, as shown in the inset of **Figure 10**.

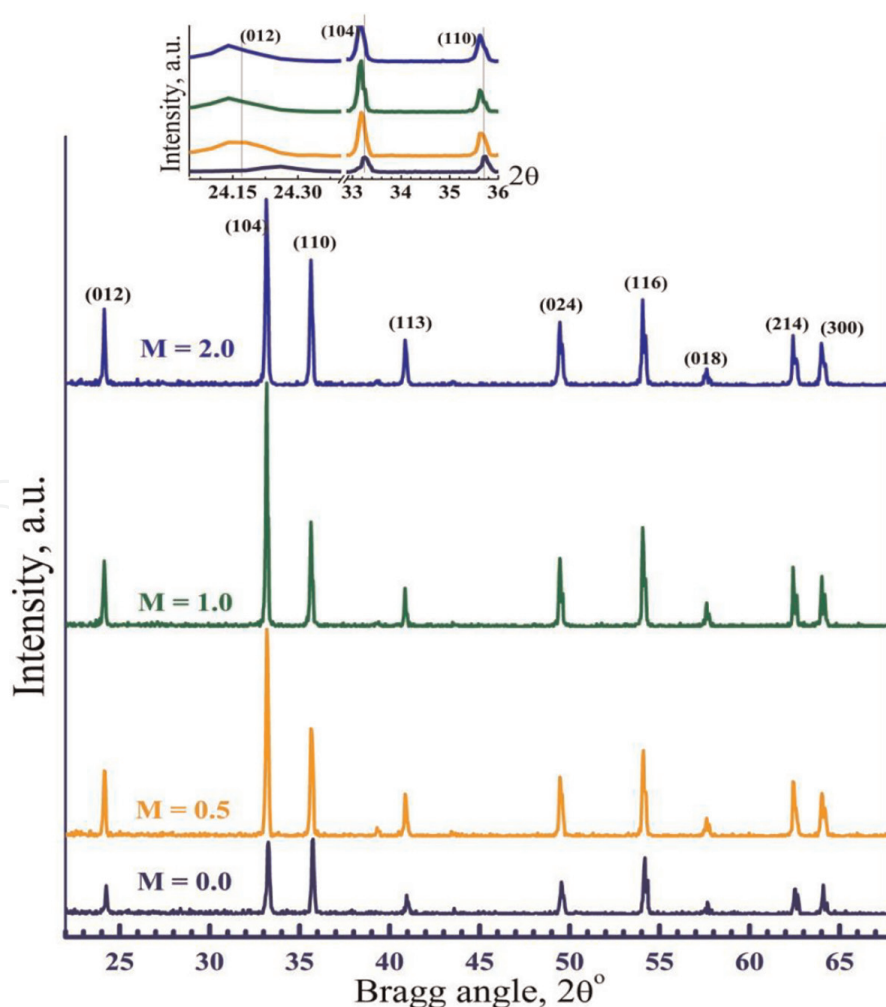


Figure 10.
 XRD patterns of the sol-gel prepared hematite at different oxalic/hematite ratios.

This indicates increasing the d -spacing values of the material, where Bragg's law states that $d = n\lambda/2 \sin\theta$. The V value is increased from $299.62 \text{ \AA}^3$ to $302.34 \text{ \AA}^3$ with an increasing M value from 0.0 to 2.0. The average C_s were calculated considering the main reflections: (012), (104), (110), and (116) reflections. C_s was decreased from 95.7 to 61.1 nm with increasing M , which illustrates the role of oxalic acid as a chelating agent to slow down the nucleation rate and encourage the hinder the particles' agglomerations.

Figure 11 shows the XRD patterns of $M = 1.0$ sample calcined at $350\text{--}750^\circ\text{C}$. At 350°C , the thermal energy delivered to the material is sufficient to remove all of the organic molecules and the full oxidation of Fe into Fe_2O_3 . Calcination temperatures higher than 350°C lead to an increase in the cell parameters and the diffraction peaks intensity. The C_s were increased from 51 to 73 nm., denoting the enhancement of the crystallinity with annealing. **Figure 12** shows the HR-TEM analysis of the sol-gel prepared hematite nanopowders at chelating agent/hematite molar ratios in the range of 0.0–2.0. As seen, the $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals aggregated more compactly at $M = 0.0$, a decrease of exposed surfaces of $\alpha\text{-Fe}_2\text{O}_3$ nanocrystals is expected. Increasing M to 1.0 changes the morphology of the $\alpha\text{-Fe}_2\text{O}_3$ structure to take the form of nanorods. However, increasing in M value to reach 2.0, these nanorods converted completely to nanoparticles. Therefore, the chelating agent ratio is a vital parameter in the nano synthesis process by sol-gel technique toward controlling the shape and morphology of $\alpha\text{-Fe}_2\text{O}_3$ nanostructures. **Figure 13** displays the morphology of the sample $M = 1.0$ after calcination at different temperatures ($350\text{--}750^\circ\text{C}$). The 350°C gives hematite nanopowder with nanorod/nanoneedle structure. The formation of the nanorods becomes clearer with increasing the calcination temperature to 750°C . The observed nanorods have average diameters of $\sim 11.38 \text{ nm}$ and different lengths. HR-TEM analysis illustrates that the shape/morphology of the obtained nanopowders is strongly influenced by the experimental conditions. Dissolving the $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ salt with oxalic acid at ambient temperature produces an iron oxalate ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) solution. Increasing M value from 0.0 to 2.0 may change the pH value of the solution. The crystal structure of the intermediate phase ($\text{FeC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$) [40], the pH value of the

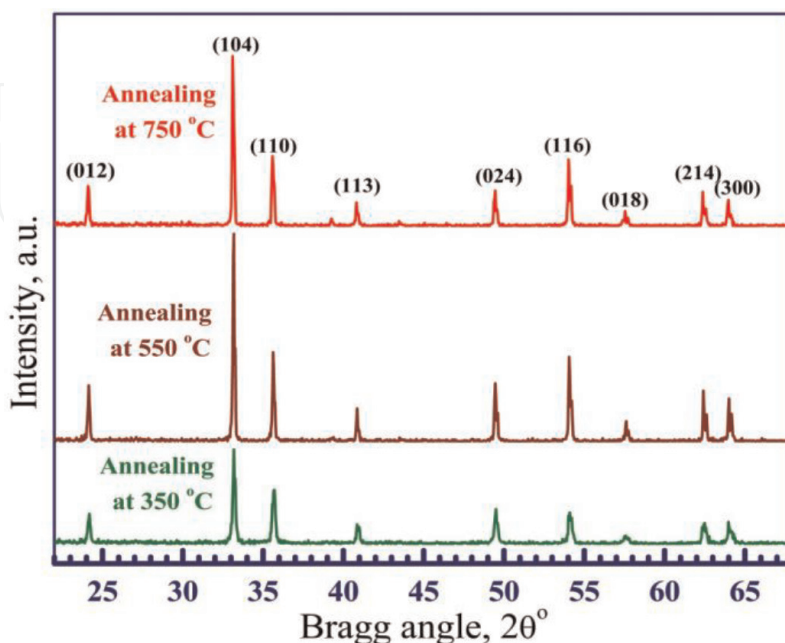


Figure 11. XRD patterns of the sol-gel prepared hematite at different calcination temperatures.

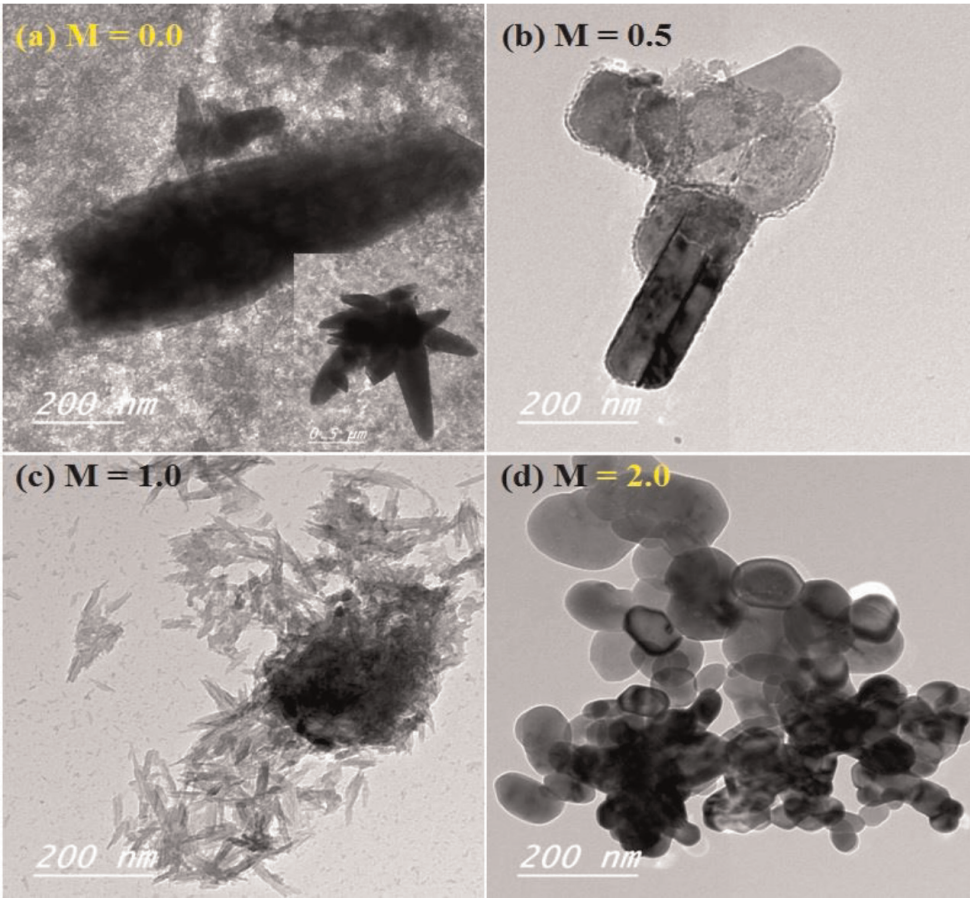


Figure 12.
(a-d) HR-TEM images for the sol-gel prepared hematite at different oxalic/hematite ratios.

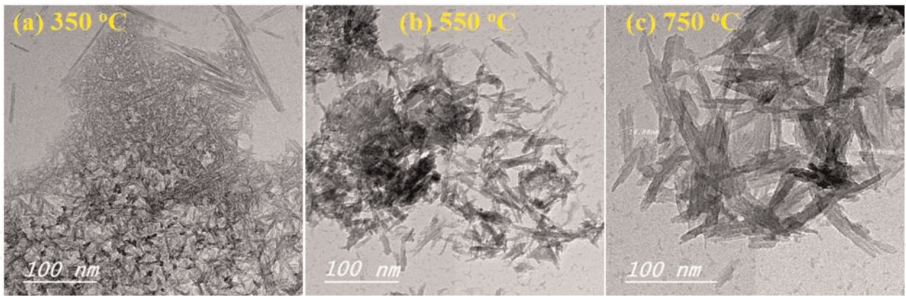


Figure 13.
(a-c) HR-TEM images for the sol-gel prepared hematite at different calcination temperatures.

solution, the aging time, and the calcination temperature and annealing rate may affect the shape/morphology of the obtained structure. Therefore, further investigations and studies on these parameters are required to understand the mechanism that leads to the growth of these different morphologies [41]. **Figure 14** depicts E-SEM of some prepared hexaferrites.

5. Ferrites and hexaferrites

The sol-gel method was also used to prepare different ceramics, for instance, as reported earlier [42, 43]. In which, M-type hexagonal ferrites $Ba_{1-x}Sr_xFe_{12}O_{19}$, where

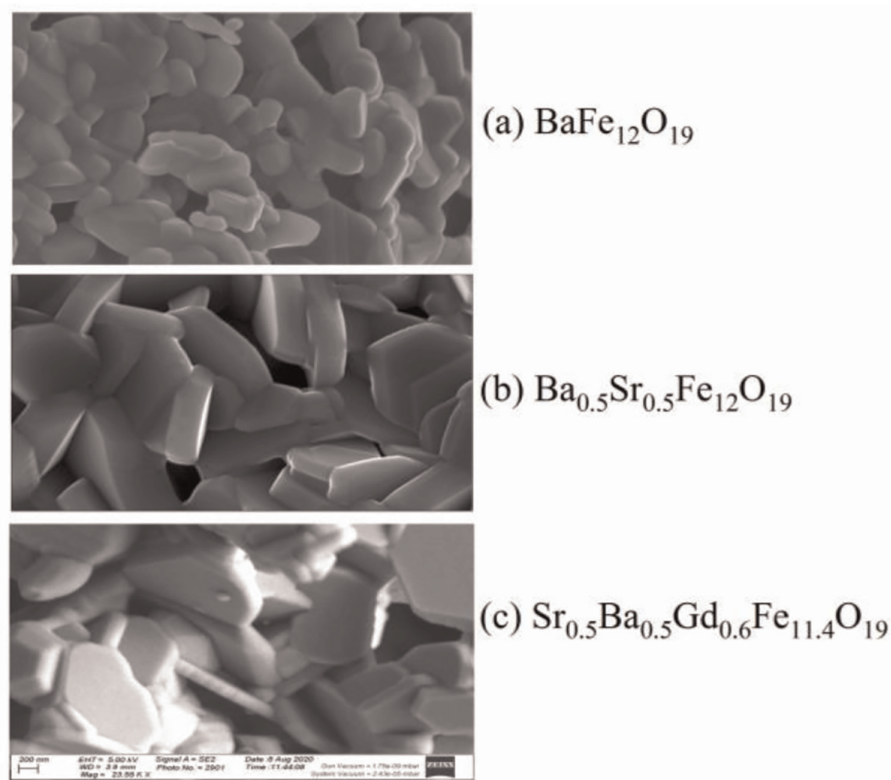


Figure 14.
(a-c) FE-SEM images of some prepared hexaferrites.

x ranged from 0 to 0.75, were synthesized [42]. The as-prepared ceramics were characterized by different techniques. The samples were single-phase based on the XRD and neutron diffractions. The average particle size of these hexaferrites was in the range of nanometers. Besides, the properties of the $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{RE}_{0.6}\text{Fe}_{11.4}\text{O}_{19}$, where $\text{RE} = \text{La}, \text{Yb}, \text{Sm}, \text{Gd}, \text{Er}, \text{Eu}, \text{and Dy}$ were reported [43]. It was emphasized that the quality of the samples was good based on the optimum use of the sol-gel method.

Figure 14 depicts the field emission-scanning electron microscope (FE-SEM) images of some prepared ceramic samples.

6. Rare earth oxides and titanium oxide-based perovskites

Lanthanum oxide (La_2O_3) is a rare earth sesquioxide that is optically active with a wide bandgap energy range of 4.3–5.4 eV. The ultrafine La_2O_3 NP has attractive properties for automobile exhaust-gas convectors, optical filters, and catalysis, as a strengthening agent in structural and ceramic materials, in high κ gate dielectric materials [44]. On the other hand, the Y_2O_3 is an interesting host material for solid-state lasers, high-temperature refractories (melting point of 2430°C), and infrared ceramics, owing to the distinctive $4f$ electronic configuration, corrosion resistivity, and thermal stability [45]. On the other hand, TiO_2 is a semiconductor with $E_g \approx 3.21$ eV. Owing to its odorless, high melting (1843°C) and boiling (2972°C) points and high transmittance in the visible region, TiO_2 is used for various applications such as paint, sunscreen, and antireflective coating, food coloring, photocatalyst, photovoltaic in solar cells, and optical filter [46, 47]. TiO_2 has two crystalline forms; anatase and rutile. The first form is more chemically reactive and favorable in the industry [48]. Moreover, titanium oxide-based perovskites, such as NaTiO_3 (sodium titanate),

attract increasing interest in PV cells and Li^+ batteries, as well as in biomedical and biochemical applications. This material has a band gap in the range of 2.2–2.5 eV and has a high cation-exchange capacity, thermal stability, and fast adsorption ability [49, 50].

6.1 Experimental

To prepare La_2O_3 nanoparticles (NP), 27.85 g of $\text{LaCl}_3 \cdot 7\text{H}_2\text{O}$ ($M_W = 371.37$, Schorlau) were dissolved in 100 ml of distilled water (DW), and about 9.5 g of oxalic acid was added, and the solution was stirred at 55–60°C for 1.0 h. This sol was held at 90°C for 20 h, then cooled to room temperature (RT) and aged for one day at RT. After that, it was calcined at about 500°C for 2.0 h. To prepare Y_2O_3 , about 9.6 g of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ($M_W = 383.01$ g/mol, supplied by PubChem USA) was dissolved in 50 ml distilled water by stirring 20 min. Then 3.15 g of oxalic acid was added to this solution, and the stirring continued for 6 h. The solution was held at 90°C to get rid of the excess water. The sol was turned to gel by aging for ~12 h at RT, and then calcined at 400°C to obtain the nanopowders. For TiO_2 preparation, 24 mL of $\text{Ti}[\text{OCH}(\text{CH}_3)_2]_4$ ($M_W = 284.22$, from Sigma) was added to 60 mL of 2-propanol under stirring for 30 min, and several water drops were added for the hydrolysis process, and the stirring continued for 6 h. The sol was aged for ~12 h at RT, and then calcined at 400°C to obtain the nanopowders. The TiO_2 was used to prepare NaTiO_3 nanofibers, where 2.0 g of TiO_2 powder was mixed with 200 ml NaOH solution (10 M) by sonication for 1 h. The white solution was poured into a Teflon-lined autoclave at 45–50°C for 24 h. The NaTiO_3 precipitate was then washed several times with double-distilled water and then dried at 100°C for 48 h.

6.2 Results and discussion

Figure 15(a) displays the XRD pattern of the sol-gel-prepared La_2O_3 . The sharp XRD peaks indicate the good crystallinity of the materials. The peaks at $2\theta = 13.17^\circ$, 26.48° , 29.57° , 40.11° , 46.40° , 51.55° , 54.66° , and 61.42° arise from the (001), (100), (011), (012), (110), (103), (112), and (202) crystal planes of La_2O_3 of hexagonal structure, consistent with the JCPDS no. 04–006-5083. The C_s was calculated considering the most intense peaks; the average value of C_s is ≈ 29.15 nm. The morphology was studied by the HR-TEM, as seen in the inset of the figure.

La_2O_3 has spherical NP morphology with a particle size of 30 nm, which is consistent with XRD results. Dal et al. [51] fabricated La_2O_3 NP of size 12.4 nm by sintering the La_2O_3 microparticles at 1250°C for 48 hrs with grinding for more than 3 hrs. This illustrates that our sol-gel process is low-cost in time and energy. **Figure 15(b)** displays the XRD peaks of the Y_2O_3 , which are indexed as (211), (222), (400), (411), (332), (431), (440), (532), (622), (444), (552), and (800), corresponding to yttria (Y_2O_3) of body-centered cubic structured, according to JCPDS 043–1036. No other phases are detected in this spectrum, indicating that all the $\text{Y}(\text{NO}_3)_3$ entirely transformed into Y_2O_3 of single-phase after calcination at 400°C. The crystallite size of Y_2O_3 is 24.7 nm. The inset of **Figure 15(b)** shows the powder morphology, where the particle sizes of Y_2O_3 look like nanosheets (Ns), which are allocated with each other to be bigger than the calculated crystallite size from XRD. Similarly, Y_2O_3 Np of $C_s = 8.7$ – 27.8 nm) was prepared by the Pechini sol-gel method, and particle size measured by FE-SEM was in the range of 40–50 nm [52].

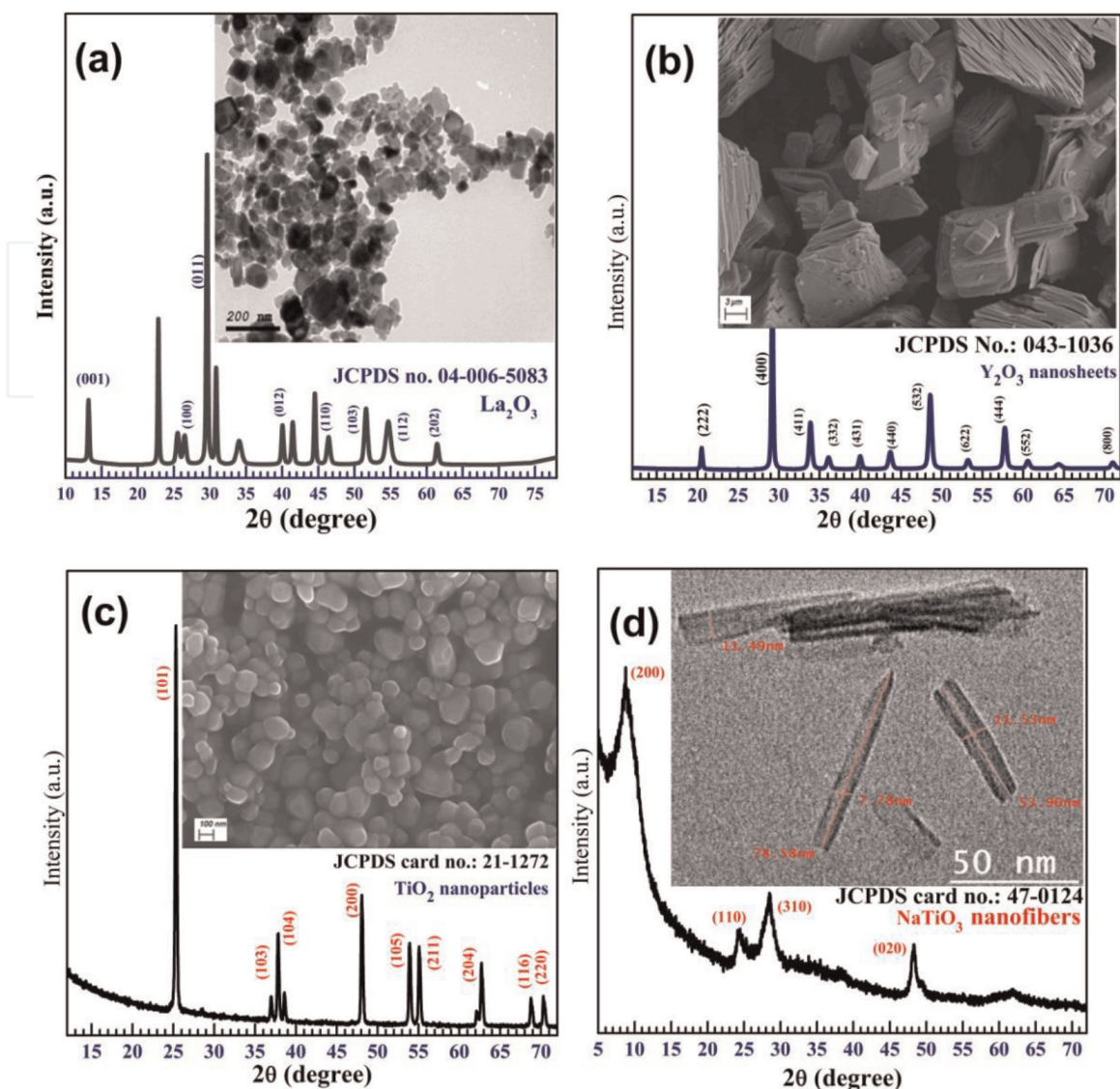


Figure 15. (a-d) XRD patterns of La_2O_3 , Y_2O_3 , TiO_2 , and NaTiO_3 . The insets show the HR-TEM analysis of each material.

The XRD pattern of TiO_2 , **Figure 15(c)**, consists of the following peaks; $2\theta = 25.32^\circ, 36.96^\circ, 37.78^\circ, 48.08^\circ, 53.9^\circ, 55.05^\circ, 62.68^\circ, 68.77^\circ, 70.26^\circ$, and 75.05° . These reflections correspond to Miller's indices of (101), (103), (004), (200), (105), (211), (204), (116), (220), and (215), respectively, as mentioned above their XRD peaks. This result confirms the formation of anatase TiO_2 of lattice parameter $a = 3.21 \text{ \AA}$, which is consistent with the JCPDS card no. 21-1272. In addition, the inset of this figure shows an FE-SEM image of the sol-gel prepared TiO_2 that shows nanoparticle morphology with an average particle size of 31.52 nm. This result is consistent with the estimated crystallite size by XRD. **Figure 15(d)** shows the XRD spectrum of the sol-gel/hydrothermally prepared NaTiO_3 . The peaks at $8.71^\circ, 24.25^\circ, 28.47^\circ$, and 48.37° are consistent with the JCPDS card no. 47-0124, confirming the high purity of the material [49]. The inset of this figure shows the HR-TEM image. NaTiO_3 displays nanofibers-like morphology, with diameters in the range of 7.7–21.5 nm and lengths up to $\sim 79 \text{ nm}$.

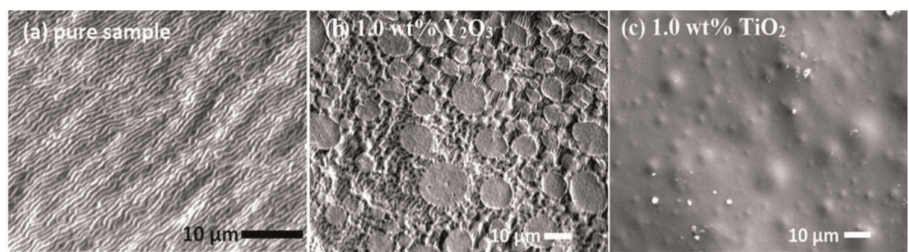


Figure 16.
(a-c) SEM images for PVAc/PMMA blended and the blend loaded with Y_2O_3 nanosheets and TiO_2 nanoparticles.

When Y_2O_3 or TiO_2 are introduced to PVAc/PMMA blend to make polymer nanocomposites, the morphology of this sol-gel prepared nanopowder did not change. **Figure 16(a–c)** shows the SEM image of PVAc/PMMA blend loaded with 1.0 wt% nanofillers. The un-doped blend surface exhibits a networked structure or wavy-like like the pool surface, **Figure 16(a)**. The fillers are distributed homogeneously and maintain their morphology, where Y_2O_3 distribute as nanosheets, **Figure 16(b)**, while TiO_2 is like small spheres of agglomerated particles, **Figure 16(c)**.

Moreover, differently prepared nanofillers were prepared to load with polymers and to get nanocomposites for suitable applications [24, 53–55]. The dielectric permittivity of poly(methyl methacrylate, PMMA, significantly increased while the dielectric loss remained almost low due to the doping with $\text{CuO}/\text{Co}_3\text{O}_4$ nanoparticles [53]. The semiconducting properties of poly(vinyl acetate)/poly(methyl methacrylate), P(VAc/MMA), were enhanced by adding TiO_2 nanoparticles and Y_2O_3 nanosheets to be used for some device applications [54]. The $\text{Zn}_{0.95}\text{N}_{0.05}\text{O}$ (ZNO) nanoparticles loaded with polyvinyl chloride (PVC) affected the optical as well as the dielectric properties of the pristine sample [55]. **Figure 17** represents the pronounced change in the absorbance of the polymeric materials by adding the ZNO and TiO_2 nanoparticles that were prepared using the sol-gel method.

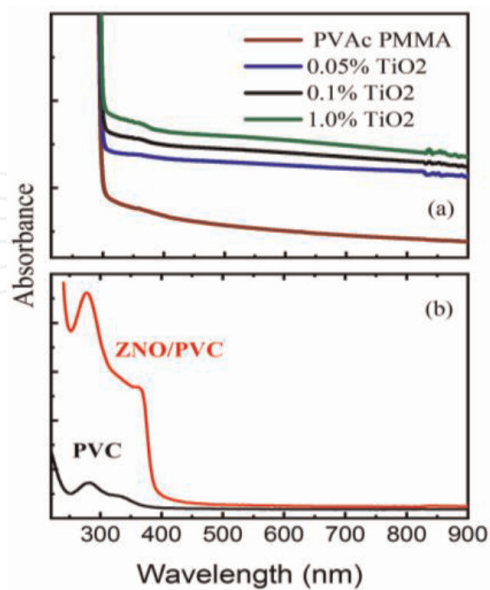


Figure 17.
The absorbance of PVAc/PMMA) loaded with TiO_2 nanoparticles (a), and PVC loaded with 5 wt.% ZNO nanoparticles (b).

7. Limitations exist for sol-Gel processing

- Sol-gel method process needs special attention at times of drying and aging.
- The reduction in the volume through the densification may cause shrinkage and cracking of the sample surface.
- Precursors used may be sensitive to moisture, and thus reduce the possibility of using the sol-gel materials on a large scale in optical coatings.
- The involved chemical reactions may yield undesired byproducts, which could affect the material's properties.
- The grade of the using precursors should be analytical in type to get pure materials.

8. Conclusion and outlook

The simplicity of the synthesizing process makes the sol-gel one of the most popular options in the coating industry and is projected to have a wide range of applications, with continued expansion. Recent progress in several applications was made by using the sol-gel technology, including the anti-reflection for solar cells, coating protection of aircraft, and cotton fabrics for flame retardant. In addition, the sol-gel process offers the possibility of large-area deposition, compared to vacuum-based-deposition processes, with the possible control of the microstructure and density of the films for improving the coloring efficiency and storage capacity of electrochromic films. Other advantages can be listed as:

- The low-temperature applied in all stages, except the densification, inhibits the thermal degradation of the material. Also, the development of amorphous, porous, and nanocrystalline materials is easily possible.
- Most of the precursors, solvents, and chelating agents are volatile, so the obtained materials are of high purity.
- Using the miscible precursors permits a homogeneous control over doping.
- The synthesis procedure requires only kind of chemical conditions.
- The easy casting of the materials into different shapes, such as monoliths, films, fibers, etc. However,
 1. More research on the effect of several preparative parameters in the sol-gel synthesis on the final structure of products and their physicochemical properties should be carried out. These parameters (solution molarities and concentration, pH, temperature, aging and preannealing/annealing times, and drying conditions).
 2. Utilizing the sol-gel technology for CO₂ capture within the developed materials (carbon-capture materials) will be a promising research area for a safe environment.

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Declaration (conflict of interest)

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper. Therefore, there are no interests to declare toward any financial interests/ personal relationships that may be considered potential competing interests.

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