A wrinkled ZnO/MCM-41 nanocomposite: hydrothermal synthesis and characterization

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Abstract

ZnO/MCM-41 composites consisting of loose particles with an irregular, wrinkled surface and flower-like morphology were obtained by adding MCM-41 to a mixture of zinc nitrate hexahydrate and hexamethylenetetramine under hydrothermal conditions. The physical properties of this composite were determined by scanning electron microscopy (SEM), x-ray powder diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), and photoluminescence spectroscopy (PL). The XRD analysis showed the characteristic diffractogram corresponding to silica overlapped with ZnO peaks, with a reduction in the sharpness and peak intensity, which may be the result of spatial disorder and defects, combined with anisotropic preferential growth. The FTIR spectrum had the characteristic vibrations expected for a silica framework, containing adsorbed water molecules, nitrate ions, and Zn−O bonds. This novel structure may be of particular interest from both fundamental and applied perspectives. It can be advantageous for the adsorption and capture of small molecules. Therefore, it may improve the performance of some previously investigated uses for these ZnO/MCM-41 composites, such as photocatalysis and adsorbents for pollutants removal. To the best of our knowledge, this is the first time that wrinkled ZnO/MCM-41 nanocomposite obtained by a low-cost and easy method is reported.

1. Introduction

MCM-41 is a form of hierarchical hexagonal mesoporous silica, with mesopores ranging from 20 to 100 Å in diameter, presenting high surface area (~1000 m² g⁻¹) and pore volume (0.98 cm³ g⁻¹). These properties make MCM-41 a good host material for the inclusion of different types of metal or semiconductor nanoparticles. Several experimental approaches have been developed to prepare ZnO/MCM-41 composites in which the ZnO may be confined inside the channels as well as on the surface of a well-preserved mesoporous silica structure. Table 1 shows a summary of the main characteristics of several methodologies and the morphology used for the ZnO/MCM-41 nanocomposites reported in the last two decades [1–22]. These techniques require several steps, such as hydrothermal process combined with calcination process, as well as the use of dispersant agents (polyethylene glycol), stabilizers (ammonium hydroxide), surfactants (triethanolamine, TEA), and in some cases, the functionalization of the MCM-41 surface using salicylaldimine, triethoxyl-γ-ethylaminopropylsilane.
| References | Synthesis type/silica | Zinc source/other reactive | Stirring T(°C)/Time | Autoclave reactor T(°C)/Time | Calcination T°C | Time | Morphology (SEM) |
|------------|----------------------|-----------------------------|---------------------|-----------------------------|-----------------|------|------------------|
| [1]        | PS/M-MCM-41          | Zinc nitrate                | RT/2 h              | X                           | 500–700         | 4 h  |                  |
|            |                      | Toluene                     |                     | TEEDPS                      |                 |      |                  |
| [2]        | PS/10 g MCM-41       | Zinc nitrate                | RT/24 h             | X                           | 550             | 3 h  |                  |
|            |                      | THF                         |                     |                             |                 |      |                  |
| [3]        | PS/MCM-41            | Zinc nitrate                | X                   | 80–85/10 h                  | 110–500         | 2 h  |                  |
|            |                      | Urea                        |                     |                             |                 |      |                  |
| [4]        | PS/0.1 g MCM-41      | Zinc acetate                | 80/2 h              | X                           | 550             | 5 h  |                  |
|            |                      | Polyethylene glycol         |                     |                             |                 |      |                  |
|            |                      | Ammonium hydroxide          |                     |                             |                 |      |                  |
| [5]        | PS/0.5 g M-MCM-41    | Zinc nitrate                | 30/24 h             | X                           | 550             | 6 h  | Hexagonal        |
|            |                      | Salicyldamine               |                     |                             |                 |      |                  |
| [6]        | PS/0.9 g MCM-41      | Zinc acetate/zinc nitrate   | 80/7.5 h            | X                           | 550             | 6 h  | Spherical        |
|            |                      | Ethanol                     |                     |                             |                 |      |                  |
|            |                      | Ammonia                     |                     |                             |                 |      |                  |
| [7]        | PS/0.5 g MCM-41      | Zinc acetylacetonate        | 70/6 h              | X                           | 500             | 5 h  |                  |
|            |                      |                             |                     |                             |                 |      |                  |
| [8]        | PS/1 g Silica        | Zinc nitrate                | X                   |                             | 700             | 1 h  |                  |
|            |                      | Ethanol                     |                     |                             |                 |      |                  |
| [9]        | PS/MCM-41            | Zinc nitrate                | 100/12 h            | X                           | 250             | 2 h  | Agglomerate      |
|            |                      | Water                       |                     |                             |                 |      |                  |
| [10]       | PS/MCM-41            | Zinc nitrate                | X griding           | X                           | 540             | 5 h  |                  |
|            |                      | Water                       |                     |                             |                 |      |                  |
| [11]       | PS/0.5 g MCM-41      | Zinc acetate                | 70/2 h              | 80 °C/NR                    | 550             | 1 h  |                  |
|            |                      |                             |                     |                             |                 |      |                  |
| [12]       | PS/0.33 g MCM-41     | Zinc nitrate                | RT/1 h              | X                           | 400             | 3 h  | Spherical        |
|            |                      | Water                       |                     |                             |                 |      |                  |
| [13]       | PS/MCM-41            | Zinc acetylacetonate        | 70/6 h              | X                           | 550             | 5 h  |                  |
|            |                      | Ethanol                     |                     |                             |                 |      |                  |
| [14]       | IS/MCM-41            | Zinc acetate                | RT/30 min           | X                           | 550             | 12 h |                  |
|            |                      | Ethanol                     |                     |                             |                 |      |                  |
| [15]       | IS/MCM-41            | No specific                 | x                   | 100/48 h                    | 550             | 6 h  | Nanoplates       |
|            |                      | Sulfuric acid               |                     |                             |                 |      |                  |
| [16]       | PS/MCM-41            | Zinc acetate                | RT/24 h             | X                           | 380             | 4 h  |                  |
|            |                      | Water                       |                     |                             |                 |      |                  |
| [17]       | PS/silica            | Zinc acetate                | 60/5 days           | X                           | 550             | 3 h  |                  |
| [18]       | PS/M-MCM-41          | Zinc acetate                | x                   | X                           | 600             | 10 h |                  |
|            |                      |                             |                     |                             |                 |      |                  |
| [19]       | IS/MCM-41            | Zinc acetylacetonate        | 35/70 min           | 70/24 h                     | 550             | 5 h  |                  |
|            |                      | Sulfuric acid               |                     |                             |                 |      |                  |
|            |                      | Ethanol                     |                     |                             |                 |      |                  |
| [20]       | PS/1 g MCM-41        | Zinc acetate                | RT/2 h              | X                           | 4450            | 22 h | Hexagonal        |
|            |                      | Ethanol                     |                     |                             |                 |      |                  |
References | Synthesis type/ silica | Zinc source/ other reactive | Stirring T/(°C)/Time | Autoclave reactor T/(°C)/Time | Calcination T/°C | Time | Morphology (SEM)
--- | --- | --- | --- | --- | --- | --- | ---
[21] | PS/MCM-41 | Zinc acetate, Zinc nitrate, Water, Ethanol | RT/24 h | X | 3380 | 44 h | ___
[22] | PS/MCM-41 | ZnO, Chitosan, Hyaluronic acid, Polyethylene glycol | RT/12 h | X | x | x | Agglomerate
This work | PS/0.012 g MCM-41 | Zinc nitrate, HMT | x | 150/48 h | x | x | Wrinkled

(TEDPS), N-[3-(trimethoxysilyl)propyl]ethylenediamine (TPED) and toluene. Although no one of these works reports the wrinkled morphology for ZnO/MCM-41 composites, being only reported the hexagonal, spherical, nanoparticles, and agglomerated morphologies as typical for this system.

Furthermore, the wrinkled morphology has been reported and used widely only on ZnO, which can be used in different applications either in the powder form or combined with organic material when preparing ZnO thin-films by sol-gel on conducting polymers (PCDTBT:PC70BM and PEDOT:PSS) and elastomers, as well as on silicon through e-beam evaporation and vapor deposition sputtering techniques. Other authors have also made a combination of sol-gel and spin-coating techniques with annealing treatment for the preparation of wrinkled ZnO thin films. In addition, there are reports on the use of thermal dissipation annealing or spray pyrolysis methods for the preparation of ZnO on surfaces. It is important to notice that according to Wang and co-workers [23], ZnO with wrinkled morphology may show an improved photocatalytic performance, among other uses, due to its large specific surface area.

Since ZnO/MCM-41 nanocomposites have been investigated for applications such as catalysis, adsorbents for pollutants removal, optoelectronics, thermal control coatings, hydrogenation process, antibacterial bandages, gas desulfurization, and antibacterial coatings, it is worth to consider that ZnO/MCM-41 nanocomposite with the wrinkled morphology will enhance the large specific surface and stable inverted structure, which will may then increase its impact in some important applications like the ones mentioned above, especially as component in solar cells, reinforcement material, photocatalytic systems, chemical sensor, UV photodetector, tunable window device, among other uses.

In this work, a ZnO/MCM-41 composite with a different morphology was prepared. The physical properties of this composite were investigated by scanning electron microscopy (SEM), x-ray powder diffraction (XRD), Fourier Transform Infrared spectroscopy (FTIR), and photoluminescence spectroscopy (PL).

### 2. Experimental

ZnO/MCM-41 composite was prepared by adding commercial MCM-41 to an aqueous solution containing 3 ml of 40 mM zinc nitrate hexahydrate (Zn(NO₃)₂·6H₂O, 98%) and 3 ml of 40 mM hexamethylenetetramine (HMT, C₁₂H₂₄N₄, 99%). Next, the mixture was transferred into a Teflon-lined autoclave, where it was kept at 423 K for 48 h. Repetitions using 12, 24, or 36 mg of MCM-41 were run. All the chemicals were reagent grade, purchased from Sigma-Aldrich, and used as received. Deionized (DI) water (18.2 MΩ cm) was obtained from a Milli-Q system (Millipore). For comparison, ZnO nanowires were grown using the same reagents and heating temperature but without adding MCM-41 to the mixture.

XRD analysis was performed in an X SIEMENS D 5000 diffractometer (Cu Kα radiation, λ = 1.542 Å, tube current 40 mA, 40 kV operating voltage), scanning from 10° to 80° (2θ) with a step size of 0.01°, 3 s at each step. Fourier Transform Infrared (FTIR) analyses were performed using a Bruker spectrometer. The IR spectra were obtained in KBr pellets in the transmittance mode over 4000–400 cm⁻¹. The SEM images were acquired with a JEOL JSM 5900 scanning electron microscope operated at 10–20 kV.
3. Results and discussion

ZnO nanowires were obtained under the described hydrothermal conditions in the absence of MCM-41 as shown in figures 1(a) and 2(b). Similar results have been previously reported [35].

A mixture of agglomerates of submicron tetrapods and disordered nanowires oriented in several directions can be observed. Figure 1(c) shows an SEM image of pure MCM-41 nanoparticles. When pure, powdered MCM-41 was added to the mixture under the same hydrothermal conditions used to prepare the ZnO nanowires, the morphology of the obtained product completely changed. Figures 1(d) to (f) show some loose particles with irregular wrinkled surfaces and flower-like aggregates of roughly spherical particles. The thickness of the 'wrinkles' or 'petals' was estimated to be in the range of 50 to 100 nm from the SEM micrographs.

This wrinkled surface morphology with its folded and curved features was entirely different from other typical arrangements of flat ZnO nanosheets, such as interwoven, flower-like or solid spheres described in...
Zinc nitrate is a water-soluble salt. It is dissociated in the form of \( \text{Zn}^{2+} \) and \( \text{NO}_3^- \) ions in water. The concentration of \( \text{Zn}^{2+} \) and \( \text{OH}^- \) ions controls the formation of the soluble zinc-hydroxyl complex \([\text{Zn(OH)}]_{n}^{(2-n)}\), which under the alkaline conditions starts forming oligomers with interconnected \( \text{Zn}^-\text{O}^-\text{Zn}^+ \) bonds due to dehydration-condensation reactions, resulting in nucleation and, after growing enough, formation of ZnO nanoparticles [39, 40].

\[
\text{4OH}^- + \text{Zn}^{2+} \leftrightarrow [\text{Zn(OH)}]_{n}^{(2-n)} \quad \text{(3)}
\]

\[
[\text{Zn(OH)}]_{n}^{(2-n)} \xrightarrow{\Delta} \text{ZnO(s)} + \text{H}_2\text{O} \quad \text{(4)}
\]

The ZnO crystal is gradually constructed by the continuous dehydration reaction between the \( \text{OH}^- \) ions on the surface of the growing crystal and the \( \text{OH}^- \) ligands of the zinc-hydroxyl complexes [20].

We propose a mechanism of formation for the wrinkled ZnO/MCM-41 nanocomposite based on reports in the literature. We suggest that the MCM-41 surface could be acting as a template for the hydrothermal growth of ZnO, where the hydroxyl groups, in and outside of its porous structure, serve as anchoring points for the oriented attachment and assembly of ZnO nanoparticles.

The fast decomposition of HMT under hydrothermal conditions results in the supersaturation of hydroxyl ions (OH\(^-\)) [20]. Previous works have reported that under hydroxyl supersaturation conditions, the ZnO nanostructures can transform nanorods to nanosheets [23, 41] in flower-like arrangements [36, 37, 42]. We consider that the higher supersaturation promoted the primary direct nucleation of ZnO nanoparticles inside and outside of the mesoporous MCM-41. These nanoparticles act as seeds for preferential growth of hexagonal ZnO nanosheets, which self-organize into microspheres with the observed wrinkled morphology.

This proposed mechanism agrees with others already reported in the literature [23]. Moreover, XRD results show (figure 2) that the (103) plane of ZnO is the preferential direction of growth, which supports the proposed mechanism of formation. In the literature, it has been reported that the (103) is a preferential crystalline plane of growth for ZnO nanosheets [43]. In addition, it is reported that when microspheres providing high-energy sites favorable to secondary nucleation self-organize to form a spherical crystal by decreasing surface energy, the resulting aggregates consist of particles with a wrinkled surface, presenting the observed flower-like structures [42, 44].

As MCM-41 can be prepared presenting different morphologies (spheres, hexagonal rods, spirals, and gyroids) [45], the effect on the morphology and structure of novel ZnO/MCM-41 nanocomposites using different types of MCM-41 as templates is a topic for future investigations.

The XRD diffractogram in figure 2 shows the characteristic diffraction peaks of silica (a diffuse peak at 26°) superposed with ZnO peaks, not sharply defined. Its low angle XRD diffractogram (figure 2, left inset) does not show the characteristic (100) and (200) peaks commonly observed for MCM-41. The right inset in figure 2 shows, for comparison, the XRD diffractogram of the ZnO nanowires. The wide-angle diffractogram of the ZnO/MCM-41 nanocomposite presents a broad peak from 35° to 40°, which seems to be related with the corresponding peaks from the ZnO nanosheet (100), (002), and (101) planes and two peaks at 53° and 61°, approximately, probably related with the ZnO nanosheet (110) and (103) planes, respectively.

When a polycrystalline sample is irradiated with a monochromatic beam, only the crystals in the Bragg position diffract. It is assumed that, for every family of characteristic planes, a large number of grains diffract. The sample must be comprised of a vast number of crystals and, additionally, that these crystals have random orientations. Sometimes, this latter condition is difficult to meet if the sample has a preferential orientation or the grain size is inadequate. If there is a preferential orientation, a reduction in the number of peaks occurs.

This effect is well known in clays, and it is necessary to use specialized fragmentation methods to produce polycrystalline particles with a random orientation [46]. A reduction in the sharpness and quantity of peaks in the XRD diffractogram was previously reported by Samanta et al for flower-like bundles of ZnO nanosheets, as...
the ones here reported; they suggested that the HMT ligand induces a preferential growth along (002) direction [47]. As HMT was also used in this work, it can be argued that the XRD results may be a consequence of spatial disordering and defects, combined with some sort of preferential growth. Further work is necessary to clarify this issue.

Figure 3 depicts the infrared spectrum of the ZnO/MCM-41 composite, along with the corresponding spectra of the MCM-41 powder and the ZnO nanowires, for comparison. Adsorbed water molecules are responsible for the broad peaks at 3450 cm$^{-1}$ and 1632 cm$^{-1}$ [48], which were also observed in the spectra of the ZnO nanowires and MCM-41. The broad peak at 909 cm$^{-1}$ in the ZnO nanowires spectrum is also related to the stretching mode of the hydroxyl groups [49, 50]. The small peak at 1383 cm$^{-1}$ can be assigned to the nitrate ion as similar peaks in the range 1378 to 1388 cm$^{-1}$ have been reported in other works where zinc nitrate was also used as a source of Zn$^{2+}$ ions for the preparation of ZnO nanowires [51, 52]. The typical vibration band of nitrate is usually in the 1200 to 1500 cm$^{-1}$ range [53].

The well-known vibrational modes of Si–O bonds of the silica framework are responsible for the broad peak with a shoulder peak at 1100 cm$^{-1}$ [54] and the peaks at 806 cm$^{-1}$ and 462 cm$^{-1}$ [55]. In contrast, the origin of the peak at 663 cm$^{-1}$ is less clear. Weak bands and peaks in the 500 cm$^{-1}$ to 650 cm$^{-1}$ range have also been observed by other researchers and attributed to Zn–O stretching vibrations [51, 56, 57]. The fact that the ZnO nanowires spectrum also presented a peak in this range (580 cm$^{-1}$) supports this interpretation.

Figure 4 shows the PL spectrum of the ZnO/MCM-41 nanocomposite. It is known that various deep level defects, such as oxygen and zinc vacancies present in the ZnO nanostructure may account for the PL bands observed. Two emission bands are observed in the spectrum. The first band has Gaussian fits at 2.84, 2.97, and 3.06 eV assigned to the near band edge. In polycrystalline ZnO, an emission band centered at 2.95 eV (blue emission) has been ascribed to radiative transitions between interface traps located at ZnO–ZnO grain boundaries and the valence band [1, 58]. So, the peaks at 2.84 and 2.97 eV can be attributed to these traps. Furthermore, the emissions located in this region are generated by deep levels inside the bandgap. It has been reported that multiple emission bands are originated from various defect centers such as zinc vacancy (VZn), zinc interstitial (Zn$i$), oxygen vacancy (VO), oxygen interstitial (Oi), antisite oxygen (OZn) [59]. Oxygen vacancies at the interface between ZnO and SiO$_2$ may also contribute to the band (peak at 3.06 eV, 410 nm). A similar peak (at 3.08 eV, 403 nm) has been previously reported for ZnO-loaded MCM-41 and attributed to these vacancies [30].

The broad PL band ranging from 1.7 to 2.45 eV has been reported before for MCM-41 [60], ZnO nanosheets [54, 61], and ZnO nanoparticles [62], in particular, the band emission in the red region (1.88 eV) has been related to oxygen excess located in interstitial sites (Oi), while the yellow band located at 2.09 eV was assigned to interstitial sites (Zn$i$) below the conduction [63]. Our Gaussian fits have peaks very close to those reported by Kumar et al (1.83 eV and 2.05 eV [62]).
4. Conclusions

A simple modification of the hydrothermal synthesis of ZnO nanowires resulted in the formation of a ZnO/MCM-41 nanocomposite, presenting an unusual surface morphology consisting of wrinkled, flower-like aggregates. The XRD analysis showed the characteristic features associated with silica superposed vibrations with some ZnO peaks not sharply defined. The characteristic features associated with vibrations in Zn–O bonds and the silica framework were detected in the FTIR spectrum. The PL spectrum showed two bands: one in the blue-violet region, ascribed to interface traps at grain boundaries and oxygen vacancies at the ZnO/SiO$_2$ interface; and the other in the red-orange region, ascribed to oxygen-related defects.

A tentative explanation for the growth of these structures was presented: the MCM-41 acts as a template for ZnO growth, where the ZnO nanoparticles start nucleating inside and outside the MCM-41 mesoporous structure, followed by additional steps of particle growth and agglomeration. As it is possible to fabricate MCM-41 particles presenting different well-defined morphologies, it is suggested that ZnO/MCM-41 nanocomposites having other unusual morphologies might be produced by following an experimental approach similar to the one here reported. Further work on this idea is currently under process. Wrinkled ZnO/MCM-41 nanocomposites with novel morphologies could be obtained, presenting interesting physical properties for catalysis applications, adsorbents for pollutants removal, optoelectronics, and sensors, among other fields.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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