A new facile synthesis of ultra fine magnesium oxide nanowires and optical properties

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Abstract One-dimensional metal oxides nanowires like magnesium oxide (MgO) play an important role in several nanotechnological applications. MgO nanowires were synthesized for the first time via hydrothermal route using magnesium acetate and urea at 180 °C for 2 h. The synthesized MgO nanowires were characterized by means of X-ray diffraction (XRD), Fourier transformer Infrared spectroscopy (FTIR), field emission scanning electron microscopy (FESEM), energy dispersive X-ray spectroscopy (EDS), transmission scanning electron microscopy (TEM) and thermal gravimetric analysis (TGA). The obtained results indicated that the MgO nanowires show a predominant well-crystalline cubic face-centered with an average diameter of 10 nm and an average length of $40\,\mu m$. The optical band gap energy of the sample was found to be 3.45 eV. The sample indicates a broadband PL emission in UV region and exhibits a good photoluminescence behavior for photonic devices applications. It is evaluated that this novel synthetic method is very useful and serves as a facile, direct preparation mild chemical method giving mass production of one dimensional MgO nanowires.

Keywords A:nanostructures · B:chemical synthesis · D:optical properties

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1 Introduction

New physical phenomena arisen from the reduction of material dimensions to nanoscale have often lead to interesting applications [1, 2]. During the nanotechnology revolution of the past decade, one — dimensional (1D) nanostructures such as nanowires, nanotubes, nanorods and nanobelts have enjoyed prominent attention and success [3]. The intrinsic dimensions such as diameters of 10–100 nm and lengths of a few micrometers provide a structural devices that can be very small, which have improved performance, extremely reduced power consumption that makes them appealing for applications in biological devices, nanorobotics, security monitoring, and defense technology [4–9]. Such structures can have two quantum-confined dimensions (the radial directions) and one unconfined dimension (the axial direction). 1D nanostructures may have a unique density of electronic states, which result in different optical, electronic, and magnetic properties compared to their bulk, two-dimensional (quantum wells), or 0-dimensional (quantum dots) counterparts [10]. However, a variety of synthetic
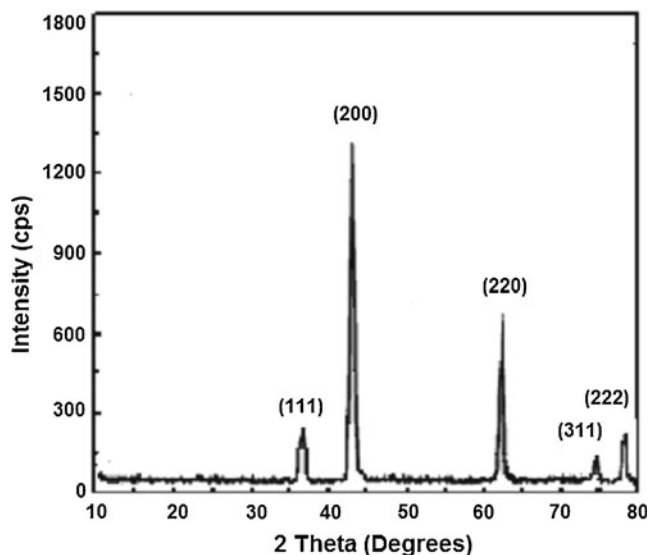
Fig. 1 X-ray pattern of the MgO nanowire network

many different synthetic methods provide nanoscale MgO including sol–gel [5, 6], spin coating sol–gel, dip coating sol gel, decomposition of various Mg salts, hydrothermal [7], laser ablation [8], chemical gas phase deposition [9], combustion aerosol synthesis [10], electron beam evaporation, aqueous wet chemical [11–15], and others.

To our knowledge, there are not yet any experimental results on the synthesis of MgO nanowires via hydrothermal method using magnesium acetate and urea. The scope of this paper is centered to synthesize of MgO nanowire with a facile and mild preparation method using magnesium acetate and urea via hydrothermal route at low reaction temperature. The microstructure and optical properties of the MgO nanowires were investigated in details.

2 Experimental details

2.1 Synthesis of MgO nanowires

All chemicals were analytical grade reagents and used without further purification. Magnesium oxide nanowires were synthesized by a single step hydrothermal technique. For preparation of the MgO nanowires, 6.44 g of magnesium acetate was dissolved in 75 ml distilled water and stirred for 30 min at room temperature. Then, 1.2 g urea in 25 ml water was added drop wise into this aqueous magnesium acetate solution under vigorous stirring for 30 min. Further, the above solution was loaded into a 100 mL Teflon-lined steel autoclave. Finally, the autoclave was sealed and maintained at 180 °C for 2 h. The autoclave was then allowed to cool down to room temperature naturally, until the reaction time was finished. The products were collected by centrifugation at 8000 rpm for 10 min, and washed with distilled water and then with ethanol to reduce the agglomeration, and later dried at 60 °C for 24 h. Finally, the white colored material was calcined at 450 °C for 2 h in an electrical oven.

strategies have been established to obtain 1D nanostructures by using templates [11], vapor-liquid–solid method [12], solution liquid–solid method [13], capping-agent-directed growth [14], intrinsically anisotropic growth without using any surfactants [15], etc. Magnesium oxide (MgO) is a very important wide-band gap insulator [2, 16], low weight [3], good chemical resistance [4, 17], high secondary electron emission [5], high thermal stability [6], non-toxicity [7] and has been attracting much attention due to it's a broad range of fundamental to industrial applications. Therefore, MgO is increasingly finding potential applications in a variety of fields, for example, the use in catalysis, glass industry, pharmaceutical, toxic waste remediation, as additives in refractory, paint, gas sensing and superconductor products, in the field of electronics, aerospace, automotive applications and biomedicine and in steel manufacturing because of its high corrosion-resistant behavior [3–10]. Generally,

Fig. 2 FESEM images of the MgO nanowires with various magnifications. (a) 5000× (b) 10000×
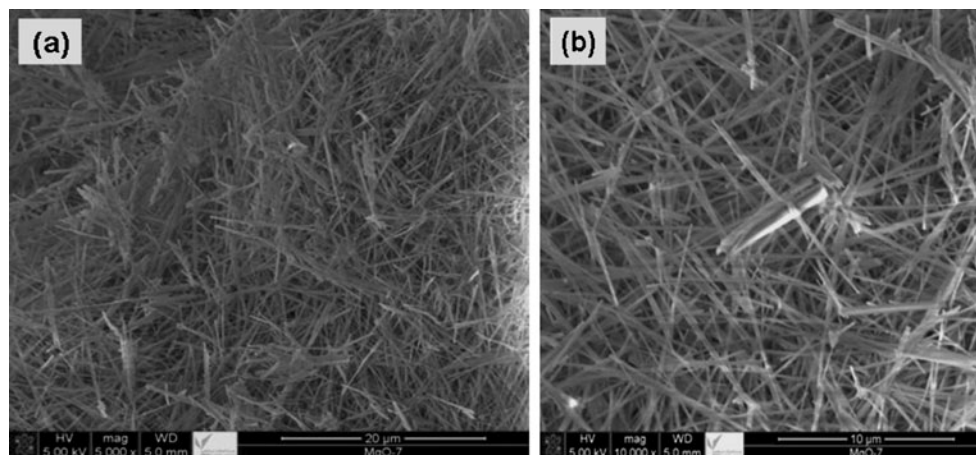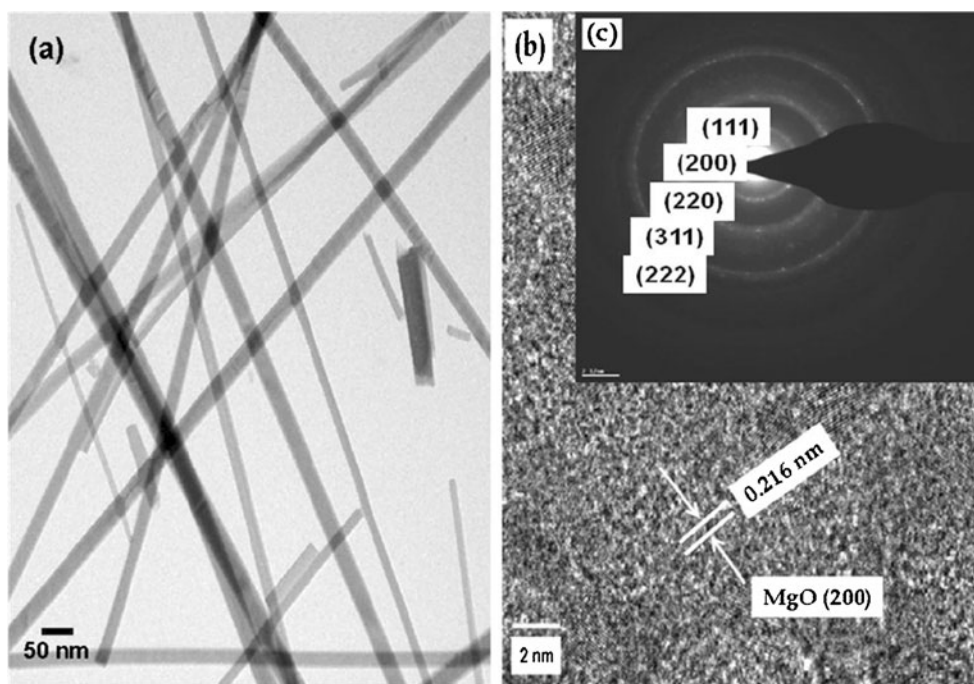
Fig. 3 (a) TEM image of the MgO nanowires, **(b)** HRTEM image of the MgO nanowires **(c)** SAED patterns of the MgO nanowires

### 2.2 Characterization techniques

X-ray measurements of the sample were performed using a Shimadzu XRD-6000 X-ray powder diffractometer using CuK_{α} radiation λ=0.15406 nm at 15 kV and 30 mA for the X-ray tube. The scanning rate was 5°/min to analyze the phase type and content. For each measurement, a complete 2θ scan was made between 10° and 80°. Field emission electron microscopy (FESEM) of the sample was carried out using a JEOL 2010 high-resolution transmission electron microscope operated at 100 kV. To study the chemical composition, the measure of the molar content of MgO was performed using an energy dispersion X-ray spectroscopy (EDS) attached to JEOL 2010 high-resolution transmission electron microscope. Transmission electron microscopy (HRTEM) of MgO nanowires was carried out using a JEOL 2010 high-resolution transmission electron micro scope operated at 200 kV. To prepare the TEM specimens, MgO nanowires were first dispersed in methanol and diluted, followed by placing a droplet of the solution onto a 400-mesh carbon-coated copper grid. Next, the grid was dried in desiccators for 5 h before imaging. Fourier transform infrared (FTIR) spectroscopy was performed using a Nicolet DTGS TEC detector spectrophotometer from 1500 to 400 cm^{-1} by the KBr pellet method. Thermo gravimetric analysis of MgO nanowires was investigated by nonisothermal thermogravimetric analysis (TGA) using Shimadzu differential scanning calorimeter DSC-60 with an accuracy of 60.1 K under air flow at a flow rate of 50 mlmin^{-1}. UV–VIS spectroscopy was measured at room temperature using 109 double-beam spectrophotometer (JASCO model V-570 UV–Vis–NIR) attached with a constant angle specular reflection. This measurement was carried out by preparing a suspension solution of magnesium oxide in ethanol under high power sonication for 10 min. Photoluminescence excitation was performed by 325 nm-HeCd laser at ambient conditions.

3 Results and discussion

X-ray is a reliable technique for investigating the nature of any crystalline material. Figure 1 shows X-ray diffraction spectra of the MgO nanowires with Miller planes of (111),
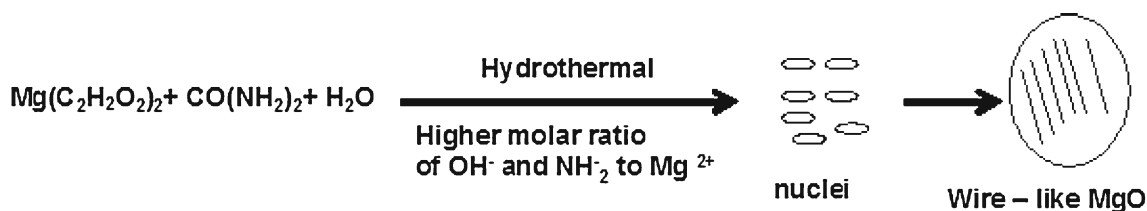
Scheme 1 The sequence of the chemical process for perpetrations of MgO nanowires

(200), (220), (311) and (222). The crystal structure of the sample is attributed to the single phase face centered cubic MgO, with the lattice constant of $a=0.42$ nm, which is in good agreement with the reported data (JCPDS card no. 87-0653). The sharp and intensive peaks further indicate that the MgO nanowires are well crystallized. The other phases were not observed. This indicates that the synthesized MgO nanowires have a high purity. The crystallite size for the synthesized MgO nanowires was calculated by Scherer's formula [5, 6]:

$$D = \frac{0.9\lambda}{\beta \cos\theta} \qquad (1)$$

where λ is the wavelength of the target used $(CuK_\alpha)=$ 0.15418 nm, β is the full width at half maxima of diffracted line in radian. Using the Scherer's equation, the diameter of synthesized MgO nanowires was found to be about 10 nm. The typical FESEM micrographs of the MgO nanowires with various magnifications are shown in Fig. 2(a) and (b). It is clear that the sample was consisted of uniform ultra fine MgO nanowire like structures with a high yield. The mean diameter of the MgO nanowire was determined to be about 10 nm and mean length is 18–20 μm. In order to confirm the chemical composition of the MgO nanowires, energy dispersive X-ray (EDS) analysis was performed. EDS spectra of the synthesized MgO nanowires indicate that there are a strong peaks for magnesium (Mg) and oxygen (O), which indicates the formation of purely MgO. The atomic ratio of Mg to O estimated from the EDS results was determined to be 1:2, which matches well with that of bulk MgO [1, 2].

The typical TEM image of the MgO nanowires is shown in Fig. 3(a). The diameter of the MgO nanowires was determined to be 10 nm and length from 18 to 20 μm. This result is in agreement with XRD and SEM results. Figure 3 (b) shows a HRTEM image taken from one of nanowires, which confirms the layer structure and good crystallinity of the MgO nanowires with a lattice spacing of 0.23 nm, in accordance with the (200) plane of cubic MgO. The growth direction of nanowires is supposed to be along the (100) direction. The urea as a combustion agent is the key factor for controlling of the morphology. This combustion agent acts as a catalysis to increase the chemical active sites [18, 19]. The mechanism of interaction of urea with magnesium acetate in hydrothermal cell is illustrated in Scheme 1.

The inset in Fig. 3(b) shows a selected area diffraction pattern (SAED) of MgO nanowire (Fig. 3(c)), indicating the polycrystal nature of cubic structure of MgO. This figure also shows a spotty ring pattern and the strong (200) and (220) diffraction arcs. However, the calculated interplanar spacing of (2 0 0) peak from SAED is 0.216 nm.

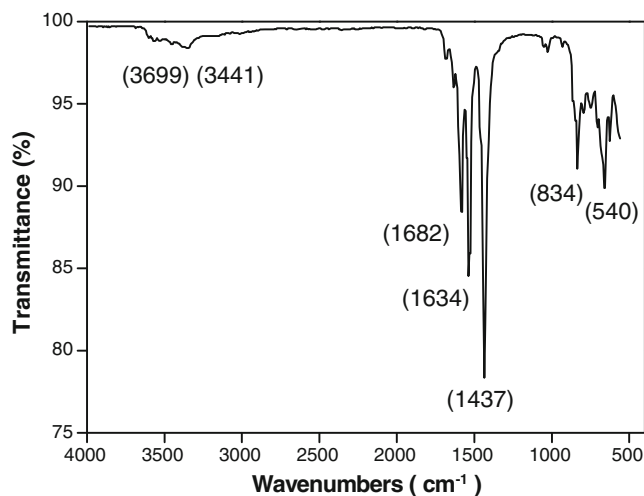FTIR spectra of the synthesized MgO nanowires are shown in Fig. 4. As seen in Fig. 4, two main bands are in

Fig. 4 FTIR spectra of the MgO nanowires

the range of 400–1000 cm^{-1}, in which, the high frequency band ($\nu1$) is in the range of 550–580 cm^{-1} and the low frequency band ($\nu2$) is the range of 410–450 cm^{-1} [8, 9]. Furthermore, in the FTIR spectrum of the MgO, the strong peak at around 540 cm^{-1} was assigned to the Mg–O stretching vibration. The bands in the range of 1437–1682 cm^{-1} were attributed to the –OH stretching mode in water. A broad band at 3441 cm^{-1} was attributed to surface adsorbed –OH groups. It is interesting to note that the 3441 cm^{-1} and 3699 cm^{-1} bands on the FTIR spectrum of the dried sample completely were disappeared after calcination at 450 °C, which is due to the formation of MgO [9]. The TGA spectrum of the synthesized MgO is shown in Fig. 5. It is seen that the first weight loss up to 300 °C is due to the removal of water and organic species. The second major weight loss was appeared in the temperature range of 300–625 °C related to decomposition of $Mg(OH)_2$ and crystallization of MgO particles. The observed total weight loss is 59 % which is in a good agreement with the calculated value 60 %.

The optical absorption edge of the sample is very useful route for clarification of optical transitions and electronic
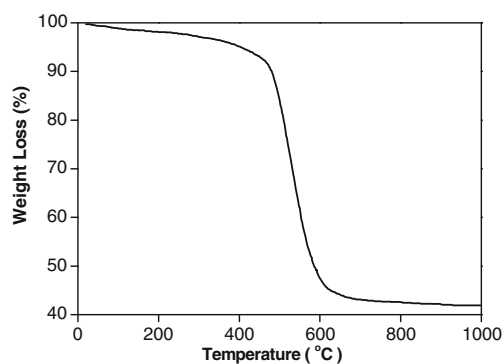

Fig. 5 TGA spectra of the MgO nanowires

band structure of the materials [1–4]. The UV–visible absorbance spectra of MgO nanowire at room temperature is shown in Fig. 6(a). An absorption peak in the UV regime with a wavelength of 227 nm can be associated to the band-to-band transition in the band gap region [1, 2].

The optical band gap of the sample can be determined by the following relation [4, 12]:

$$\alpha h\upsilon = \alpha_0 \left(h\upsilon - E_g\right)^n \qquad (2)$$

where constant n depend on the type of optical transitions in a semiconductor (the exponent $n=1/2$ for allowed direct transition, while $n=2$ for allowed indirect transition), α_0 is

a constant and E_g is the optical band gap energy. The optical band gap energy of the sample was determined from $(\alpha h\upsilon)^2$ vs. $(h\upsilon)$ plot, as shown in Fig. 6(b) and was found to be 3.45 eV. The PL emission spectra of the MgO nanowires are shown in Fig. 6(c). It is observed that there is a broad emission band at 336 nm. This is attributed to the defects generated from oxygen vacancies, Mg vacancies and interstitials entire MgO structural [16, 17]. This could induce the formation of new defect levels in the band gap zone of the MgO nanowires and thereby readily contribute to the luminescence [14, 15]. This makes the synthesized MgO nanowires are very useful in plasma display panel applications.

Fig. 6 (a) Absorbance spectra of the MgO nanowires, (b) Plot of $(\alpha h\upsilon)^2 - (h\upsilon)$ of the MgO nanowires (c) PL emission spectrum of the MgO nanowires
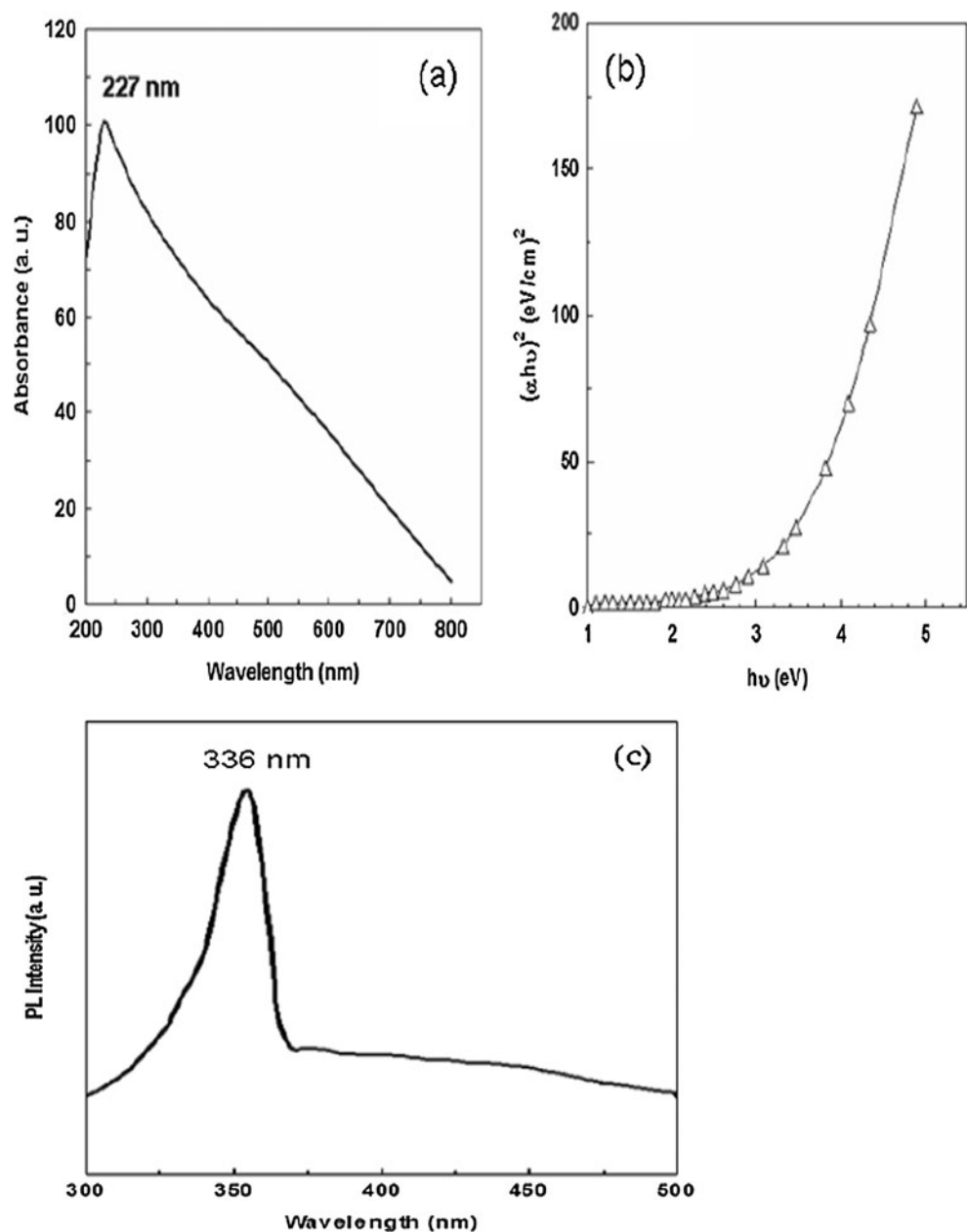
4 Conclusions

For the first time, large quantities of single crystalline cubic magnesium oxide nanowires were successfully synthesized using a simple mild chemical route. Ultrafine MgO cubic face-centered nanowires are obtained with a mean diameter of 10 nm and mean length of 18–20 μm. The UV–vis spectrum for MgO nanowires shows an enhanced absorption intensity in the low wavelength region and an optical energy gap of 3.45 eV determined from the absorption spectra. This wide band gap makes synthesized MgO nanowires have a potential application in optoelectronic nanodevices such as plasma display panels. PL emission peak appeared at 336 nm is attributed to new energy levels induced by defects or defect levels entire MgO structure. We believed that this new synthesis strategy may become a general mild chemical route for the fabrication of ultra fine nanowires for other metal oxides.

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