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Quantum Size Effect and very localized random laser in ZnO@mesoporous silica nanocomposite following a two-photon absorption process

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ABSTRACT

ZnO@mesoporous silica nanocomposite was prepared by the impregnation of a CMI-1 material in a Zn(NO₃)₂ solution followed by calcination under O₂. Intensive characterization was carried out by N₂ adsorption–desorption measurements, scanning and transmission electron microscopy. The optical properties of the ZnO@mesoporous silica nanocomposite were studied by photoluminescence spectroscopy. Quantum Size Effect was firstly demonstrated by subjecting the sample to a 254 nm excitation light, and was further confirmed by using a 680 nm excitation laser beam, which implies a two-photon absorption process. By focusing the 680 nm laser beam on different places in the sample, a very localized random laser effect, also induced by a two-photon absorption process, was detected.

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1. Introduction

In recent years, new nanostructured materials organized on the nanometric scale contribute greatly to the improvement of our everyday-life. Thanks to their exceptional properties, nanocompos-

ites are nowadays considered as the most innovative materials in optics [1], electronics [2] or even catalysis [3] and are found in many applications such as light-emitting diodes, screens, lasers or photochromic devices [4–6].

Nanocomposites can be defined as integrated chemical systems, structurally ordered with nanometric dimensions. The design of such systems requires the organization of the active components at the nanometric level while controlling their arrangement, their distribution and their properties inside a matrix. Zinc oxide, ZnO, is one of the most interesting binary semiconductor (3.37 eV [7])

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Table 1

N_2 adsorption–desorption measurements and chemical analysis by atomic absorption spectroscopy of CMI-1, CMI-blank materials and ZnO/CMI-1 mesoporous silica nanocomposite.

Sample	S_{BET} (m^2/g)	Pore diameter (nm)	ZnO loading (% wt.)
CMI-1	1020	3.0	0
CMI-blank	835	2.0	0
ZnO/CMI	505	2.3	35

with very important optical properties which can be used in short wavelength lasers, blue light-emitting diodes, UV detectors, gas sensors, etc. [3,8–12]. ZnO presents a high exciton binding energy (60 meV [13]) which makes excitons particularly stable even at high temperature (up to 550 K) in comparison with other wide bandgap semiconductor (25 meV for GaN) [14]. Mesoporous silica materials [15] are ideal candidates [16] for the encapsulation of semiconducting nanoparticles because of their high surface area, pore diameter ranging from 2.0 up to 50.0 nm, well-organized channels, internal reactive silanol (Si–OH) groups and good mechanical, thermal and hydrothermal stability. Another key feature is its transparency in the visible range [17] which allows to excite efficiently the ZnO particles included inside the matrix.

Usually, optoelectronic nanocomposites made of ZnO and mesoporous silica materials can produce random laser effect as far as no Quantum Size Effect (QSE) can be detected. Indeed, the production of lasing effect requires the presence of active ZnO nanoparticles close and large enough to allow the stimulated emission to be scattered and amplified through a mirrorless feedback mechanism. In most of the cases, this requirement is not encountered in ZnO@mesoporous silica nanocomposites showing strong QSE because, at very low ZnO loadings, ZnO particles are extremely small and highly dispersed within the silica network.

In this work, ZnO@mesoporous silica nanocomposite was prepared by the impregnation method. For the first time, Quantum Size Effect and random laser effect induced by one and two-photon absorption process were detected within the same sample.

2. Experimental

The mesoporous matrix CMI-1 was prepared using $C_{16}(EO)_{10}$ surfactant as a templating agent and TMOS as a silica source in a mild acid media as described in the literature [18]. In order to introduce ZnO nanoparticles inside the channels of the mesoporous material CMI-1, the direct impregnation method [19] was employed. 0.5 g of the CMI-1 sample was wetted in 20.0 ml of an aqueous zinc nitrate solution (1 M) for 2 h with stirring (300 rpm). After drying, the resultant material was calcined at 550 °C under flowing nitrogen for 12 h and then the atmosphere was switched to oxygen for a further 6 h.

Nitrogen adsorption–desorption isotherms were recorded at –196 °C over a broad relative pressure range from 0.01 to 0.995

with a volumetric adsorption analyzer (TRISTAR 3000, Micromeritics). The sample was degassed under vacuum for several hours at 320 °C prior to nitrogen adsorption. The pore diameter and the pore size distribution were determined by the BJH (Barret, Joyner, Halenda) method [20]. The morphologies of the synthesized mesoporous materials were studied using a Philips XL-20 scanning electron microscope (SEM); the sample was metallized prior to use. The transmission electron microscopy (TEM) micrographs were taken using a 100 kV Philips Tecnai microscope for which the TEM specimen were prepared by embedding the nanocomposite powder in an epoxy resin sectioned with an ultramicrotome. The thin films were supported on copper grids previously coated by carbon to improve stability and reduce the accumulation of charge. The photoluminescence (PL) was excited by an Hg lamp with the wavelength of 254 nm and detected by a cooled photomultiplier linked to a grating monochromator. Lasing effect was studied with an amplified Ti:Sapphire laser system (TSA, Spectra Physics) with a central wavelength of 680 nm (pulse duration 100 fs, repetition rate 1 kHz). The laser beam was focused onto the sample with spotsizes of ca. $3 \cdot 10^{-4} \text{ cm}^2$.

3. Results

The mesoporosity of both the CMI-1 silica mesoporous matrix and the ZnO/CMI nanocomposite has been evaluated by N_2 adsorption–desorption measurements. Their specific area and pore diameter values are summarized in Table 1. The specific area of CMI-1 sample is very high (1020 m^2/g) with a narrow pore size distribution centered at 3.0 nm which will guarantee a homogeneous environment for the growth of ZnO nanoparticles [17]. The sharp decrease in BET surface after the incorporation of ZnO is attributed to the presence of nanoparticles inside the channels of the mesoporous matrix. The pore size also decreased due to the partial filling of the mesopores.

In order to estimate the influence of the ZnO incorporation process on the textural properties of the CMI-1 mesoporous matrix, a reference material has been prepared by an impregnation without the ZnO precursor ($Zn(NO_3)_2$). The mesoporous material has been wetted in pure water during 20 min and was then calcined under O_2 at 550 °C for 6 h. The sample obtained was labeled CMI-blank. The reduction in specific area (835 m^2/g) and pore size (2.0 nm) suggests that the impregnation in water and calcination can modify the textural properties of the starting mesoporous matrix [21]. This means that the diminution of specific area observed after the incorporation of ZnO cannot be attributed entirely to the presence of ZnO nanoparticles inside the channels and that the quantity of ZnO cannot be deduced from the difference between specific areas. By atomic absorption spectroscopy, the estimated ZnO loading in the CMI-1 mesoporous material is 35% wt.

The morphology of the CMI-1 silica mesoporous material consists of spherical and gyroidal particles with dimensions

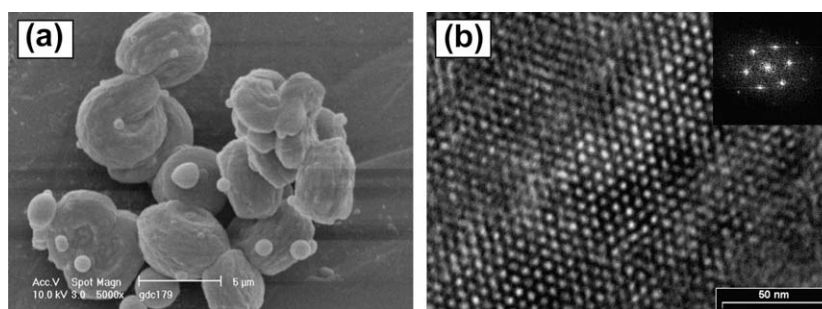


Fig. 1. Scanning (a) and transmission (b) electron microscopy images of the CMI-1 silica mesoporous material showing particles with diameters of 5–10 μm and the hexagonal organization of mesopores.

5–10 μm [18,22] (Fig. 1(a)) which are not modified after the incorporation of ZnO inside the matrix. It should be noted that no macroscopic ZnO particles have been observed by scanning electron microscopy. The organization of the mesochannels in a hexagonal symmetry, visualized by transmission electron microscopy (Fig. 1(b)) is important because it indicates that all the pores are very homogeneous and will present the same environment during the growth of the ZnO nanoparticles.

The optical properties of the ZnO/CMI nanocomposite have been studied by photoluminescent properties and the PL spectrum obtained under 254 nm (4.88 eV) excitation wavelength is presented in Fig. 2. The main contribution of this broad spectrum is a band at 3.41 eV, surrounded by two low-intensity bands around 3.0 and 4.0 eV. Their assignment will be discussed in details in the next section. Under IR excitation (680 nm, 1.82 eV), PL emission of the ZnO/CMI silica nanocomposite has been observed at 3.28 and 3.35 eV (Fig. 3(a)). This excitation wavelength was particularly appropriate because the structural defects of the silica matrix, which usually give luminescence in the range 3.0–4.3 eV, do not emit in this range under 1.82 eV incident photons. Aside from the emission of bulky particles (3.28 eV), the luminescence of

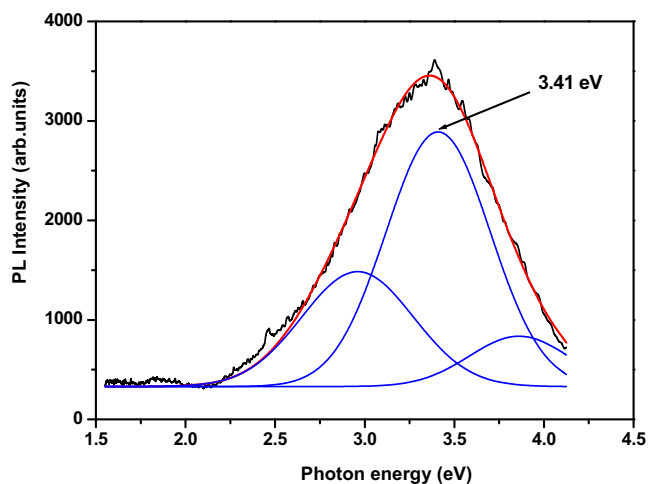


Fig. 2. Photoluminescence spectrum ($\lambda = 254$ nm, $E = 4.88$ eV) of ZnO/CMI nanocomposite with the Gaussian decomposition (reproduced from Ref. [28]).

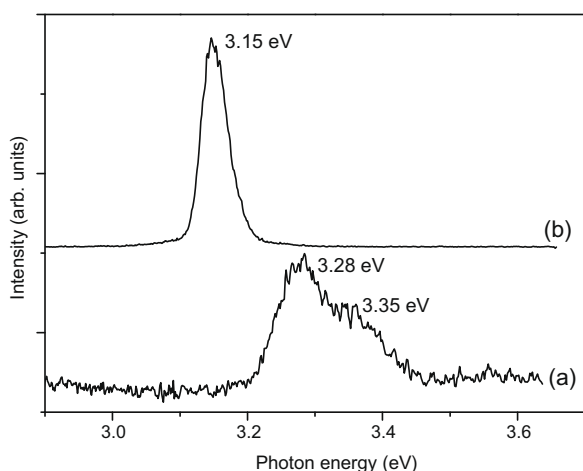


Fig. 3. Two-photon emission spectrum of ZnO/CMI nanocomposite excited by 1.82 eV photon energy (under $\lambda = 680$ nm) pumping fluence of 20 mJ/cm². These two spectra are from different regions of the same sample, measured under identical conditions.

ZnO nanoparticles embedded in the matrix is detected at 3.35 eV. By focusing the excitation source onto different places of the sample, we were able to detect a very strong and narrow signal at 3.15 eV (Fig. 3(b)) indicating the creation of random laser effect. In this particular case, the mechanism of lasing in a ZnO/CMI disordered powder implies a two-photon absorption process and a mirrorless feedback which allows the light to be amplified and to produce random stimulated emission.

4. Discussion

Due to the extremely small size of the ZnO nanoparticles confined inside the channels of the CMI-1 material, the ZnO/CMI nanocomposite is expected to present Quantum Size Effect (QSE) [23,24] which should cause a blue-shift of the PL emission band corresponding to ZnO. This effect has been reported in our previous work dealing with the incorporation of ZnO inside zeolitic materials [25,26] and the preparation of ZnO/CMI nanocomposites by the colloidal and reverse micelles methods [27]. As already published in our previous paper [28], the PL spectrum of the ZnO/CMI nanocomposite consists of one broad band in the range 2.5–4.0 eV (excitation at 254 nm, 4.88 eV) (Fig. 2). PL studies performed on pure CMI-1 mesoporous materials [17] allowed us to distinguish two main contributions, at 2.9 and 3.9 eV, which are generated by structural defects related to surface silanol groups. On this basis, the decomposition of the PL broad band gives three Gaussian curves, centered at 2.9, 3.4 and 3.9 eV. The bands at 2.9 and 3.9 eV correspond obviously to the silica matrix and the band at 3.4 eV (FWHM = 0.58 eV), can be attributed to the luminescence of ZnO nanoparticles confined in the mesochannels of the CMI-1 matrix. The blue-shift (120 meV) of this emission band compared to bulk ZnO (3.28 eV) confirmed the expected QSE. The size of the nanoparticles can be estimated through the well-known Brus equation [23]:

$$\Delta E = \frac{h^2}{8\mu R^2} - \frac{1.8e^2}{4\pi\epsilon_0\epsilon_\infty R},$$

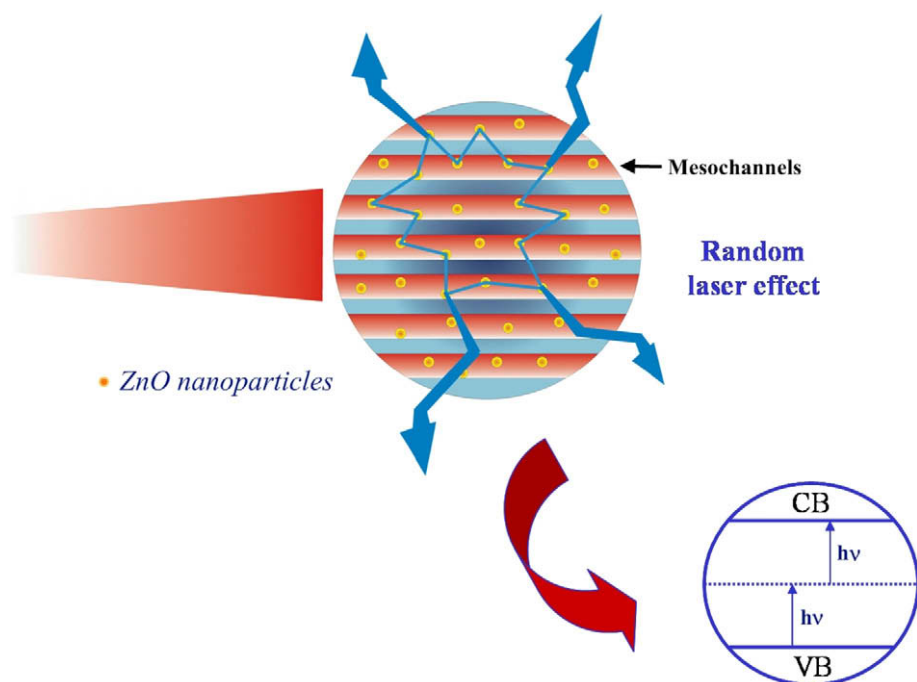
where μ is the effective mass of the exciton ($\mu = 0.18 m_e$, for ZnO), ϵ_∞ the high-frequency dielectric constant and R the diameter of the particle.

Assuming that the blue-shift is 120 meV and neglecting the second term of the equation which is not significant, this relation gives a diameter of ca. 4.0 nm, which fits quite well with the pore size of the silica matrix (3.0 nm), considering that all constant values have been obtained for macroscopic materials.

In order to eliminate the emission bands of the silica matrix, the ZnO/CMI nanocomposite was excited with a femtosecond laser beam at 680 nm (photon energy of 1.82 eV). The corresponding PL spectrum (Fig. 3(a)) presents two features: one emission band peaked at 3.28 eV and one shoulder centred at 3.35 eV. The photoluminescent contribution from the silica matrix disappeared effectively.

As the incident photon energy (1.82 eV) is too low to promote an electron from the valence band to the conduction band of ZnO (bandgap of 3.4 eV), the process of excitation which leads to the observation of two luminescence bands involves the simultaneous absorption of two photons [29,30]. Besides this two-photon absorption process through a virtual level, the excitation mechanism can also imply a two-step absorption through a defect level within the bandgap.

The presence of these two emission bands in the PL spectrum of ZnO/CMI nanocomposite suggests that two kinds of ZnO nanoparticles have been formed during the incorporation step. The luminescence at 3.28 eV is attributed to ZnO particles which are too large to show the expected QSE. They could have grown inside



Scheme 1. Schematic representation of random laser effect following a two-photon absorption process within ZnO@mesoporous silica nanocomposites. The random laser effect is based on the amplification of stimulated emission through a light scattering mechanism which involves the formation of a loop inside the matrix containing active ZnO nanoparticles.

the mesochannels and have altered somewhat the mesoporosity as observed by N_2 adsorption–desorption analysis. They could also have been formed outside the silica matrix but are too small to be observed by scanning electron microscopy. Due to the relative weak intensity of the signal, we believe that the first hypothesis is more probable. The emission band at 3.35 eV is blue-shifted in comparison with the emission of bulk ZnO and corresponds to the Gaussian curve peaked at 3.4 eV in the PL spectrum with excitation at 4.88 eV. This confirms that some ZnO nanoparticles have grown inside the pores of the CMI-1 matrix and that their dimension is small enough to present a significant QSE.

As already demonstrated in our previous experiments [31], random laser effect can be observed in ZnO/CMI nanocomposites which do not present any QSE. The random laser effect is based on the amplification of stimulated emission through a light scattering mechanism which involves the formation of a loop inside the matrix containing active ZnO nanoparticles [32–34]. The observation of QSE implies that extremely small ZnO nanoparticles have been formed and that they are highly dispersed inside the network of the silica matrix, which does not allow the formation of the required loop.

In the present case, the presence of the emission band at 3.28 eV indicates that some large ZnO particles have grown inside the matrix and that we could expect some random laser effect. By scanning the 680 nm wavelength excitation laser beam over the ZnO/CMI nanocomposite with the same pumping energy (20 mJ/cm^2), the transition from the spontaneous emission of ZnO to stimulated emission corresponding to random laser can be revealed in some very localized areas (Fig. 3(b)). The broad band ($\sim 100 \text{ meV}$) is converted to a much narrower peak (45 meV) and, due to the increased total carrier density as well as the presence of interparticle interactions which both result in bandgap renormalisation [35], its position is shifted towards lower energies (3.15 eV, spectral shift of 130 meV).

The behavior of the ZnO/CMI nanocomposite under IR excitation suggests that the sample is heterogeneous and contains some

places where extremely small and dispersed ZnO nanoparticles have been formed and some places where relatively large and adjacent ZnO particles have grown inside the mesochannels. At this point, it is important to insist that the excitation mechanism of ZnO implies a two-photon absorption process, which means that an incident IR excitation wavelength can be converted to UV emission and UV random laser (Scheme 1). This result opens new outlooks for the design of energy conversion devices, information storage materials, and biolabelling systems.

5. Conclusions

This paper presented the preparation of ZnO@mesoporous silica nanocomposite through the direct impregnation method with $Zn(NO_3)_2$ and O_2 as precursors for the growth of ZnO inside the mesopores of the silica matrix. PL spectroscopy revealed a strong Quantum Size Effect assigned to ZnO nanoparticles embedded in the CMI-1 matrix. At very localized places in the sample, an efficient random laser is observed coming from the amplification of stimulated emission of ZnO implying a two-photon absorption process. This observation is very important because random laser effect is usually not detected within nanocomposites showing strong QSE. In the present case, because of the heterogeneity of the sample, domains containing extremely small ZnO nanoparticles coexist simultaneously with domains containing ZnO particles large and close enough to produce random laser effect. The demonstration of both QSE and random laser effect within the same nanocomposite is of particular interest for the design of new optoelectronic devices such as light-emitting diodes and short wavelength lasers.

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