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Random laser action of ZnO@mesoporous silicas

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Abstract

ZnO@mesoporous silica nanocomposite was prepared by the impregnation method, and very efficient laser action was highlighted. As revealed by high-resolution transmission electron microscopy (HR-TEM), nanometric ZnO particles are confined inside the mesochannels of CMI-1 mesoporous silicas. Upon excitation at 3.6 eV of a femtosecond pulsed laser and at low pumping intensity, the ZnO@mesoporous silica showed a broad photoluminescence (PL) band corresponding to the excitonic recombination of ZnO. When the pumping intensity is increased up to a threshold (2.5 mJ cm^{-2}), the excitonic emission turns to stimulated emission through a mechanism which will be discussed. The same threshold value was obtained with another excitation source and nanocomposites with different ZnO loadings inside the CMI-1 mesoporous silica. These results allow a better understanding of the random laser effect in ZnO@mesoporous silica and, consequently, a model has been proposed to explain this phenomenon. Based on these new observations, many new applications can be considered since short-wavelength devices are required by industry to design new information storage supports.

1. Introduction

Short-wavelength devices have recently attracted great interest in the field of blue-laser technologies because of their capacity to enhance the storage of information on the surface. Other new and important applications have emerged in energy conversion, via wavelength conversion and also the design of photocatalysts active in the visible region. In order to target such devices, many scientists have focused their research on one of the most interesting binary II–VI semiconductors, zinc oxide, ZnO (band gap energy = 3.37 eV) [1]. The primary advantage lies with its high exciton binding energy [2] (60 meV) which allows the excitonic emission to be quite significant even at room temperature (25 meV). The recent observation of bulk lasing from epitaxially grown ZnO nanowire arrays represents a significant advance towards producing intense nanoscale sources of coherent light [3].

Yang *et al* reported a fascinating phenomenon that significant lasing occurs with undamaged single wires with high quality cavity end faces [4]. However, they also found that the clear lasing behaviour can be observed for only a few (out of several hundred) nanowires, elevated vertically by the vapour–liquid–solid (VLS) method on a sapphire substrate, even at very high peak excitation intensities ($>1 \text{ MW cm}^{-2}$) [5, 6]. Other light-emitting nanostructured systems based on ZnO are of great interest, and are hence providing many challenging areas of research. It is well known that one of the most promising properties of ZnO arises with reducing the particle size of the semiconductor to a few nanometres. This is due to the quantum size effect which results from an increase of the corresponding band gap value [7, 8]. The past few years have witnessed great advances in the preparation of nanoparticles (quantum dots) of various composition, size and shape. However, great challenges remain in the hierarchical integration of the nanoscaled units, for example, zero-dimensional nanoparticles or quantum dots, into functional and structured assemblies

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and ultimately into systems. Different chemical preparation techniques such as sol–gel, [9, 10] impregnation [11, 12] and molecular capping [13, 14] have been used for the dispersion of ZnO particles in inorganic [9–12] or polymeric [13, 14] matrices. However, the aggregation of ZnO particles remains unavoidable and the particle size is quite heterogeneous.

The discovery of highly ordered mesoporous materials [15] enables the control of nanoparticle size since the nanocrystallites are confined into the pore system, the size of which becomes tuneable. Inside the channels of the mesoporous matrix, the ZnO is confined in an ordered way along of the length of the mesoporous channels but all the ZnO nanoparticles could behave like a disordered powder in which it is possible to produce stimulated emission and some new and even unexpected phenomena. Silica matrices, owing to their optical transparency, are the best media for the incorporation of semiconductive nanoparticles [16] as they allow the complete exploration of the optical properties of encapsulated nanoparticles.

This work reports the significant random laser effects produced by ZnO nanoparticles confined inside the channels of a mesoporous silica CMI-1 material. The mechanism of lasing is based on the scattering of the light within the mesoporous matrix where active ZnO nanoparticles were introduced. The spontaneously emitted photons scatter from one particle to another and finally form a loop, thus contributing to a random laser phenomenon. The outcome of this specific study will have immediate and profound practical implications more generally in nanoscience and nanotechnology. Many new applications in the fields of biolabelling, information storage, conversion of long wavelength to short wavelength (i.e. energy conversion) and the realization of a new family of photocatalysts for the decomposition of air and water pollutants, which are active in the visible region, can be envisaged in light of this discovery. This work represents a significant advance toward producing intense nanoscale sources of coherent light.

2. Experimental details

2.1. Synthesis of the mesoporous matrix

The mesoporous matrix CMI-1 was prepared using C₁₆(EO)₁₀ as a surfactant templating agent and TMOS as a silica source in a mild acid media as described in the literature [17]. In order to integrate ZnO nanoparticles inside the channels of the mesoporous material CMI-1, the incipient wetness method [12] was employed. 0.5 g of the CMI-1 sample was wetted in 20.0 ml of an aqueous zinc nitrate solution 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. The amount of ZnO loaded in different samples is given in table 1, and the obtained samples were labelled ZnO-CMI-*X*% (*X* represents the loading).

2.2. Characterization

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

Table 1. Textural properties and ZnO loading of sample CMI-1 and nanocomposites ZnO-CMI-25% and ZnO-CMI-1%.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Pore diameter (nm)	ZnO loading (wt%)
CMI-1	1020	3.0	0
ZnO-CMI-25%	270	2.4	25
ZnO-CMI-1%	430	1.2	1

0.995 (p/po) with a volumetric adsorption analyser (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 [18]. 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 microscope (TEM) micrographs were taken using a 100 kV Philips Tecnaï microscope for which the TEM specimens 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 charges. High-resolution TEM images were recorded on a Jeol 200 CX microscope working at 200 kV. Typically a droplet of the sample suspended in ethanol was impregnated on a porous carbon grid for the observations. The lasing effect was studied with a femtosecond laser (pulse duration 100 fs, repetition rate 1 kHz) focused onto the sample with spotsize of about $3 \times 10^{-4} \text{cm}^2$.

3. Results and discussion

3.1. General features

Owing to the utilization of the neutral surfactant and the solvent extraction procedure used to remove these surfactant molecules, our preparation method yielded a matrix that was optically transparent with fewer defects than the ionic surfactant templated mesoporous silicas [16]. The introduction of ZnO nanoparticles in the channels of mesoporous CMI-1 was achieved by an incipient wetness method [12]. The general characteristics of both the silica matrix and the nanocomposites are summarized in table 1. The results indicated that the incorporation of ZnO nanoparticles in the channels of mesoporous silica did not influence the hexagonally organized structure and mesoporosity of the starting material. The sharp decrease in nitrogen adsorption, surface area and slight reduction of pore size suggested that a great number of ZnO nanoparticles were present inside the channels of the mesoporous material. For sample ZnO-CMI-1%, the pore size is significantly reduced, indicating that ZnO nanoparticles have probably grown inside the mesochannels but have not completely filled the pores, leading to an apparent pore diameter of 1.2 nm. It is noted that for the sample with 1 wt% of ZnO, the decrease in pore size is more important than for the sample with 25 wt% of ZnO. In fact, when preparing the sample with 25 wt% loading of ZnO, more Zn(NO₃)₂

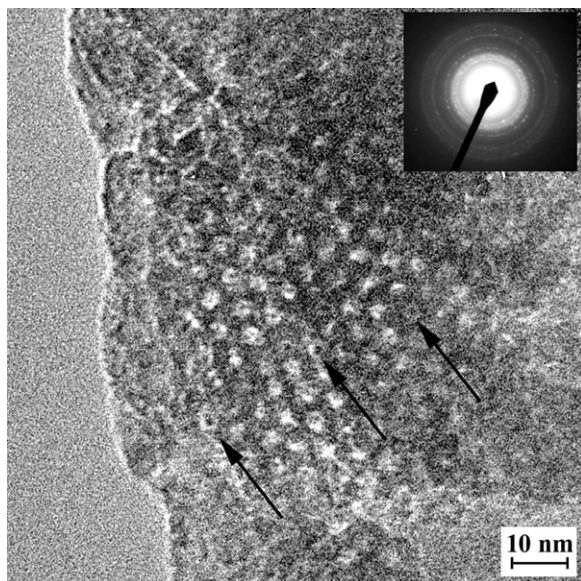


Figure 1. High-resolution TEM image of the channels of CMI-1 silica packed in a hexagonal lattice with ZnO nanoparticles confined inside some pores (the inset is the selected area electron diffraction pattern).

was used in the solution and the pH value of the solution (1.95) was lower. Due to some corrosion, the pore size is somehow enlarged. This phenomenon has been published by our group [19]. The pH value of the solution to prepare the sample with 1 wt% loading of ZnO decreases only slightly (from 6.5 of bidistilled water to 5.25) due to the low amount of $\text{Zn}(\text{NO}_3)_2$ added. No corrosion can be expected and no enlargement of pore size occurred during the impregnation process. The loading process will reduce the pore size whereas the acidic corrosion gives an enlargement of pore size. This antagonism leads to the observation that the decrease in pore size of the sample with 1 wt% of ZnO is more important than that in the sample with 25 wt% of ZnO. Despite this acidic impregnation process, all TEM and XRD results showed that the mesoporous structure of our samples remains unchanged.

High-resolution transmission electron microscopy was performed in order to confirm that the ZnO nanoparticles were confined inside the channels of the mesoporous silica CMI-1. Figure 1 shows unambiguously that the hexagonal arrangement of the channels of the starting mesoporous silica was maintained and that the ZnO nanoparticles were confined inside the channels. The ZnO nanoparticles (1–2 nm spherical in shape) can be seen in figure 1 as black dots which are located in the channels (see the black arrows). In this image, it is also observed that not all the channels were filled by the ZnO nanoparticles. Neither elongated particles nor nanowires, but only isolated ZnO nanoparticles were observed. Some bigger spherical nanoparticles were observed on the external surface of the mesoporous silica. The simultaneous presence of ZnO nanoparticles inside and outside the mesochannels could be very important in the production of a laser effect. In the inset, the selected area electron diffraction pattern shows a typical ‘ring’ pattern from polycrystalline nanoparticles with a sequence of the ring spacing characteristic of the hexagonal structure of ZnO.

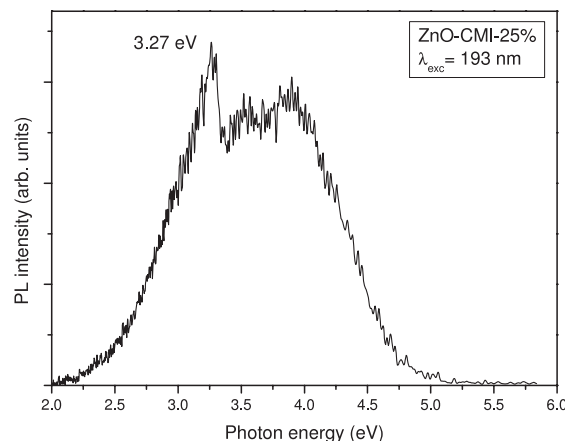


Figure 2. Photoluminescence spectrum of ZnO-CMI-25% nanocomposite excited by 6.4 eV photon energy.

3.2. Optical properties

The optical properties of the sample labelled ZnO-CMI-25% with a high loading of ZnO nanoparticles were first studied under 193 nm (6.4 eV) excitation coming from a nanosecond pulsed ArF laser. The photoluminescence (PL) was recorded in the spectrograph mode of an intensified-CCD device and a 235 nm (5.3 eV) cut-off filter was installed to eliminate the incident excitation wavelength. The PL spectrum, illustrated in figure 2, presents one broad band in the range 2.5–4.5 eV and one sharp peak centred at 3.27 eV. According to our previous studies of the PL properties of mesoporous silicas CMI-1 [16], the broad band can be assigned to structural defects related to silanol groups which have E' centres ($\equiv\text{Si}-$) produced after a dehydroxylation process via calcination. The narrow peak at 3.27 eV ($\lambda = 379$ nm) corresponds to the radiative recombination of ZnO excitons, which appeared to be in perfect accordance with the literature [1]. The quantum size effect (QSE) is usually reported in papers dealing with the preparation of ZnO nanoparticles [20–22]. Decreasing the size of semiconductors from bulk to a few nanometres, typically the Bohr radius, induces a broadening of the band gap which can be visualized by a blue-shift of the emission signal in the PL spectra [7, 8]. In our case, the position of the excitonic emission of ZnO at 3.27 eV suggests that no QSE is observed and that the ZnO nanoparticles size is larger than the Bohr radius. This deduction will be of great importance, as explained in the following section. Normally, the particle size depends on the amount of ZnO in the mesochannels and also on the dispersion of nanoparticles, which is related to the surface area and the mesopore size of mesoporous materials. It is evident that the QSE depends also on the interaction between ZnO and the surface of mesoporous silica.

Using another excitation source (340 nm (3.6 eV) of a femtosecond pulsed laser), the excitonic emission of ZnO in ZnO-CMI-25% nanocomposite (figure 3) was also detected. Because the energy of the incident light is smaller than the energy of the ArF laser (6.4 eV), the PL contribution of silica is only observed at 3.1 eV. When the intensity of the laser beam was increased up to 7.6 mJ cm^{-2} , the excitonic emission changed to stimulated emission, giving rise to a

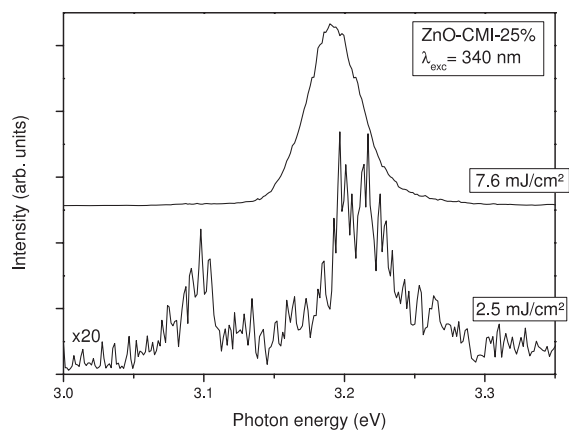


Figure 3. Emission spectrum of ZnO-CMI-25% nanocomposite excited by 3.6 eV photon energy under different pumping intensities.

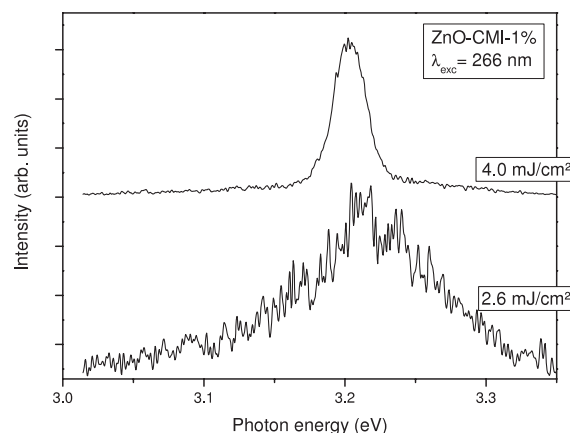
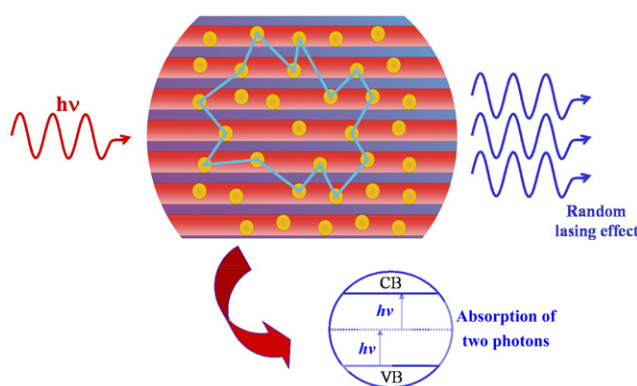


Figure 4. Emission spectrum of ZnO-CMI-1% nanocomposite excited by 4.7 eV photon energy under different pumping intensities.

very narrow (FWHM = 46 meV) and highly intense signal. The mechanism of lasing is based on light scattering within the mesoporous matrix where active ZnO nanoparticles were introduced. After excitation, the emitted photons scatter from one particle to another and finally form a loop, which guarantees the feedback of the light necessary to obtain stimulated emission. This phenomenon is called random lasing because the stimulated emission occurs in powdered materials and the amplification is carried out without mirrors such as in conventional lasers [23, 24]. This has been theoretically predicted by Letokhov [25], and the effects in ZnO have been extensively studied by Cao *et al* [26, 27]. One trivial condition is that enough active ZnO nanoparticles (25 wt%) are introduced in the silica network and are located close together in order to form an efficient loop for the amplification of the stimulated emission. The threshold pumping intensity, from which the spontaneous emission changes to stimulated emission, was observed to be 2.5 mJ cm^{-2} , which is very small compared to values obtained in epitaxially grown ZnO films [3, 4, 28].

A series of samples presenting significant QSE has been tested to check whether the random lasing effect can occur. No random lasing effect was observed with these samples. Indeed, the QSE occurs when the ZnO nanoparticles are very small, close to the Bohr radius, and highly dispersed, which does not allow the formation of the expected loop. However, it is important to note that there is no direct relationship between the QSE and random lasing.

To further confirm the low lasing threshold observed, another femtosecond laser was used to excite, at 266 nm (4.7 eV), the sample with a low loading amount of ZnO nanoparticles, labelled ZnO-CMI-1% (figure 4). When the laser beam intensity equals 2.6 mJ cm^{-2} , a broad band corresponding to the excitonic emission of ZnO is obtained. No defect bands related to the silica matrix can be observed in this range, probably because there is no absorbance process in this energy range. On increasing the incident beam light intensity up to 4.0 mJ cm^{-2} , the narrow peak (FWHM = 26 meV) assigned to stimulated emission occurring in ZnO nanoparticles dispersed in mesoporous SiO_2 is also present.



Scheme 1. Schematic representation of random lasing effect of ZnO nanoparticles embedded in the hexagonally arranged cylindrical channels of highly ordered mesoporous silica CMI-1.

(This figure is in colour only in the electronic version)

The threshold value is exactly the same as for sample ZnO-CMI-25%, which indicates that the pumping intensity needed for stimulated emission is independent of the quantity of active ZnO nanoparticles in the SiO_2 matrix (1 or 25 wt%). It has to be pointed out that it is quite easy to produce a random lasing effect in silica-based ZnO nanocomposites and that this phenomenon is of significant importance since short-wavelength devices are required by industry to design new information storage materials.

Moreover, as already published in our previous paper [29], the same phenomenon has been produced by using near-IR femtosecond excitation ($\lambda = 680 \text{ nm}$, $E = 1.8 \text{ eV}$). Since the incident energy is half of the band gap, a mechanism of two-photon random lasing was proposed. It is considered that the ZnO emission comes from the simultaneous absorption of two photons of 1.8 eV energy [30]. Although this mechanism was well detailed in our previous paper [29], scheme 1 can better illustrate this random laser action produced by one-photon or two-photon excitation processes. Regarding biological applications, this result opens new ways to monitor biological objects with spatial resolution. Indeed, the emission of ZnO nanoparticles produced after IR excitation comes only from

the focal point of the incident laser beam, in contrast to UV excitation, which induces emission produced by the whole excited volume. Assuming that ZnO nanoparticles can be grafted to biological objects, it is therefore possible to detect PL or a lasing effect originating from very localized areas in the sample.

4. Conclusions

The stimulated emission in disordered media such as ZnO nanoparticles introduced inside the channels of a highly ordered mesoporous material (CMI-1) has been described. The transition between spontaneous and stimulated emission was characterized by a threshold value which represents the minimum value of energy necessary to observe a lasing effect. Moreover, this lasing effect has been observed with ZnO nanoparticles, occurring after the absorption of two photons. A two-photon lasing effect can open exciting new avenues for designing devices for biolabelling, wavelength conversion, information storage using IR pumping pulses and the design and realization of new photocatalysts for the decomposition of air and water pollutants activated by visible light.

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