Photoacoustic spectroscopy investigation of zinc oxide/diatom frustules hybrid powders

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Abstract

ZnO nanoparticles were grown on porous surface of diatomite (DE) by a low temperature sol gel synthesis, starting from zinc acetate dihydrate solution in water/ethyl alcohol in presence of triethanolamine. Microstructural features of hybrid powders were investigated by field emission scanning electron microscopy.

Absorption and scattering characteristics of hybrid ZnO/DE powders in the UV-Vis range were inferred by photoacoustic spectroscopy and results were analyzed basing on Helander's theory. In particular we discussed in details the procedure to retrieve the absorption and scattering coefficients of the hybrid powders and we showed how from the scattering coefficient in the 300-450 nm range it is possible to obtain information on the size distribution of the ZnO nanospheres. By applying photoacoustic spectroscopy for different modulation frequencies we showed that is also possible to perform a size distribution depth profile of the ZnO aggregates, opening the way to interesting developments in this research field.

Keywords

Photoacoustics; Spectroscopy; Light Scattering; Light Absorption, Sol Gel Synthesis, Zinc Oxide Nanoparticles, Diatomite

1. Introduction

Diatoms are photosynthetic microorganisms colonising every aquatic environment. Diatoms are enclosed within cell walls called frustules made of hydrated amorphous silica

and exhibiting unique micro- and nano-porous architectures which contribute to high surface area.

Potential applications of diatom frustules are drug delivery [1,2] due to their biocompatibility, sensing and photovoltaic applications [3-5], thanks to their high specific surface area, light localization and/or light scattering capabilities [6,7].

Many examples of structure manipulation and/or chemical functionalization of diatom frustules with several materials (i.e. TiO_2, ZnO, MgO, zeolites, Au, MoS_2, polyaniline and organosilane) are reported in the literature for different applications [8]. ZnO is a highly investigated semiconductor due to its quantum confinement effect, the large exciton binding energy and the wide optical band gap which make it a suitable material for application in several optoelectronic devices. [9-11]. In addition, photocatalytic activity of ZnO nanoparticles may be enhanced by growth in porous silica media [12]. In this work, crystalline ZnO nanoparticles were grown by the sol gel technique on the porous surface of diatomite (DE), a fossil material composed of a mixture from frustules form different species. ZnO nanoparticles resulted homogeneously distributed on the frustules surface and inside the pores. Microstructural features of the hybrid powders were investigated by XRD and SEM analysis. The optical properties of DE and ZnO/DE hybrid powders were studied by the Photoacoustic Spectroscopy (PAS) in the UV/VIS range. PAS demonstrates that in the 300-450 nm range absorption and scattering coefficients of ZnO/DE increased with respect to ones measured on the bare diatomite substrate, showing that such hybrids powder can be used to capture the light more efficiently [13]. PAS shows also that as synthetized ZnO/DE powders are already effective in light absorption enhancement without the need of calcination treatments and that the light absorption increases with increasing zinc oxide nanoparticles.

2. Synthesis and microstructural features of ZnO/diatomite powders

ZnO nanoparticles were grown on DE powders by sol gel synthesis carried out at 80°C, starting from zinc acetate dihydrate solution in water/ethyl alcohol in presence of triethanolamine. Synthesis details are reported elsewhere [13]. XRD diffraction measurements (not shown here) revealed that ZnO nanoparticles were crystalline even without a calcination process. From analysis of SEM micrographs, obtained by a field emission scanning electron microscope (FE-SEM, Leo Supra 35), particles' size was in the range of 80-180 nm and ZnO nanoparticles were found homogeneously distributed on the frustules surface and inside the pores (see Fig,1). Pores with size ranging from 110 nm to 1.2 μm were observed on most of the frustules.

3. Optical properties by Photoacoustic Spectroscopy.

Photoacoustic Spectroscopy (PAS) [14,15] is an extremely versatile, non-destructive technique which allows the optical and thermal analysis of films [16,17], scattering materials [18,19], powders, gels, and recently nanomaterials [20,21], chiral materials [23,24], and metamaterials. It is a more suitable technique, if compared to conventional spectrophotometric ones, to measure the optical properties of nanomaterials and/or scattering media.

Some of the authors of this manuscript have already applied PAS to investigate powders, due to its versatility and easy applicability with respect to other non-destructive acoustic [24-27], thermal and photothermal techniques [28-32] which use sophisticated laboratory instruments. In our analysis we used the Rosencwaig-Gersho (RG) theory [14], which was developed for non-scattering samples, and substantially modified for scattering samples by Helander et al. [33] by using a diffusion equation for the photon distribution inside the sample.

In this paper PAS has been applied in the visible range for the measurement of the diatomite powder samples with or without zinc oxide nanospheres [13].

Concerning the experiment setup we use a PAS cell in a non-resonant configuration [34]. A Xe lamp is used as a pump light that passes through a monochromator allowing to do spectroscopy in the UV/VIS range 300−700 nm. The pump beam is modulated by a mechanical chopper at the frequency f, enters the PAS cell where it is selectively absorbed by the powder sample. The sample is heated and the induced thermal waves generate an acoustic signal in the cell eventually detected by a sensitive microphone with a low-noise preamplifier (Brüel & Kjær 4166 and 2660). The microphone linearity has been validated by using a set of neutral density filters (0.3, and 0.6) on the pump beam.

The pump beam spot on the sample has elliptical shape with sizes of 3mm x 1mm. Lateral heat diffusion is then negligible being the thermal diffusion length at 25Hz respectively of 45μm for diatomite and of 70μm for carbon glass. Accordingly the heat diffusion flows in the in depth direction according to 1D theory.

The measurements have been done according to the following procedure: first a calibration of the cell has been done by measuring PAS signal on a optically opaque carbon glass sample 1mm thick that is used as a reference signal; after that we measure the PAS signal of the ZnO/DE powders on a quartz plate: this signal is eventually normalized to the reference signal.

Clear differences between the normalized PAS signals for the hybrid powder ZnO/DE and for the pure Diatomite powder can be seen in Figs.2. In fact, PAS amplitude spectra (Fig.2a) are

very different for the pure Diatomite (●) and for the hybrid ZnO/DE at different modulation frequencies (○ at 9Hz, □ at 25Hz, ∇ at 81 Hz). The presence of dispersed nanospheres of ZnO increases the amplitude in the region where ZnO absorbs light (<450nm), while the signals merge together when ZnO becomes transparent (>450 nm). This phenomenon is also evident in the phase spectra (Fig.2b) across the opaque/transparent transition of ZnO.

The data analysis on the powders has been performed according to Helander' theory [35]. When a light source of intensity I_o is sent onto an optically thick scattering medium, the internal photon density, located at depth z, follows the equation

$$\rho(z) \propto I_o \left[\exp\left[-(\beta_a+\beta_s)z\right] + \frac{3}{1-3\beta_a/\beta_s} \cdot \left(\frac{1+\Delta}{1+\Delta\sqrt{3\beta_a/\beta_s}} \exp\left[-\sqrt{\frac{3\beta_a}{\beta_s}}(\beta_a+\beta_s)z \right] - \exp\left[-(\beta_a+\beta_s)z\right] \right) \right] \quad (1)$$

where β_a and β_s respectively are the absorption and scattering coefficients, and $\Delta = \frac{2}{3}(1+2r)$ depends on the reflection r at the sample surface of the light coming from the interior. If the light intensity is harmonically modulated in time, the absorbed photons at depth z generate thermal waves traveling towards the sample surface and contributing to the acoustic waves emitted from the surface layer. The PAS signal is eventually given by integrating the contributions over all the volume as follows:

$$S_{PAS} \propto \int_0^\infty \beta_a \cdot \rho(z) \cdot \exp\left[-(1+j)\frac{z}{\mu} \right] dz \quad (2)$$

where $\mu = \sqrt{D/\pi f}$ is the thermal diffusion length, f is the modulation frequency, and D is the sample thermal diffusivity.

PAS signal contains information on both absorption β_a and scattering β_s coefficients (see Eqs.(1) and (2)). If the other parameters are known (i.e. thermal diffusivity D, modulation frequency f, and internal reflection r), then PAS signal can be used to retrieve independently both β_a and β_s [13, 33]. As an example we show the details of the inverse procedure applied to the PAS signal measured on the hybrid powder ZnO/DE (see Figs.2) as summarized below:

i) we assume D=0.17 mm^2/s for the Diatomite thermal diffusivity, r=0.04 for the internal light reflection, and analyse the PAS signal at f=9Hz [13, 36-38].

ii) the PAS spectrum is normalized $S_{PAS}(\lambda)/S_{PAS}(\lambda_o)$ to the value at the reference wavelength λ_o where β_a and β_s are known. In particular we measured β_a =130 cm^{-1}, and β_s=120 cm^{-1} at λ_o=300 nm by using independent optical techniques.

iii) By using Eqs.(1) and (2) we calculate theoretically the amplitude ratio and the phase difference of $S_{PAS}(\lambda)/S_{PAS}(\lambda_o)$ as a function of β_a and β_s in the wide range of values 1-1000 cm^{-1}. The two contour plots are shown in Figs.3.

iv) In order to calculate the quantities β_a and β_s for example at λ=400nm and f=9Hz, first we find the experimental values of the normalized PAS amplitude A=0.25 (black spot in Fig.2a) and PAS phase shift Φ= -15° (black spot in Fig.2b). These experimental values are eventually inserted in the theoretical amplitude and phase charts in Fig.3a and Fig.3b so to estimate the quantities $\beta_a \approx 10\ cm^{-1}$ and $\beta_s \approx 320\ cm^{-1}$ from the intercept between the two contour levels at A=0.25 and Φ= -15° (see black spots in Fig.3a and Fig.3b)

This procedure has been repeated for the whole range of wavelengths allowing to calculate both the scattering and absorption spectra $\beta_a(\lambda)$ and $\beta_s(\lambda)$, fitting the experimental data in Figs.2 (see black cont. lines).

Figure 4 shows the scattering coefficient calculated for the DE powder (●) and for the hybrid powder ZnO/DE at different modulation frequencies (○ at 9Hz, □ at 25Hz, ∇ at 81 Hz). As expected, the scattering coefficient for ZnO/DE is higher than for DE due to the additional scattering of the ZnO nanospheres in the range of 300-500 nm.

In order to explain the experimental results we numerically calculate the scattering (Fig.5a) and the absorption (Fig.5b) cross sections of a single ZnO nanosphere as a function of wavelength for different diameters D of the ZnO sphere (80 nm , 130 nm, 180 nm) (the cross sections are all normalized to the geometrical sections $S=\pi D^2/4$). Figs.5 show also the theoretical expectation corresponding to the realistic case of an ensemble of ZnO nanospheres with diameters uniformly distributed in the range [80 nm ÷ 180 nm] (black solid line). In particular this last theoretical scattering cross section $\sigma_{sca}(\lambda)$ (see Fig.5a) can be used to fit the scattering coefficient $\beta_s(\lambda)$ found for ZnO/DE from the PAS signal at 25Hz (see symbols □ in Fig.4), thanks to the simple relationship $\beta_s(\lambda)=n\,\sigma_{sca}(\lambda)$ where $n=10^{11}\ cm^{-3}$ is the volume concentration of the ZnO spheres [13].

Further investigation on the sample with different modulation frequency of the light allows retrieving interesting information on vertical distribution of ZnO spheres diameters across the sample thickness. Indeed, the scattering spectrum $\beta_s(\lambda)$ found for ZnO/DE in Fig.4 depends on the modulation frequency; at 9Hz (○) (corresponding to a thermal diffusion length μ=75μm) one may observe a broad peak that is well fitted by ZnO nanospheres uniformly distributed in the wide range [80 nm ÷ 210 nm], at 25Hz (□) (μ=45μm) the peak is smaller and fitted by the uniform distribution [80 nm ÷ 180 nm], while at the frequency 81Hz (∇)

(μ=25μm) the narrow peak is shifted to the low wavelength corresponding to a uniform distribution in the range [80 nm ÷ 130 nm].

As the frequency decreases from 81Hz to 9Hz the thermal diffusion length μ increases from 25 μm to 75 μm. Then the sample volume under investigation becomes three times greater, and consequently the statistic on the ZnO spheres becomes more uniform with a homogeneous distribution of small and large spheres, while at higher frequencies the information is more related to thinner layers close to the sample surface. In these latter cases the concentration of smaller ZnO spheres diameters is higher with respect larger spheres. Thus, measurements in frequency put in evidence a non uniform distribution in depth of large diameter spheres that concentrate preferentially on the bottom of the quartz sample holder inside the photoacoustic cell for gravity effects.

From PAS signals it is also possible to determine the absorption spectrum (Fig.6). The differences between the $\beta_a(\lambda)$ determined for ZnO/DE at any modulation frequency (○, □, ∇) and for DE (●) are only in the region of 300 nm-450 nm due to the absorption of the ZnO nanospheres. All curves merge for λ>500 nm when ZnO becomes transparent and the absorption coefficient is substantially driven only by the DE contribution.

In order to compare the experiment in Fig.6 with the theoretical expectation in Figs.5, the absorption coefficient of the ZnO/DE powder is calculated as $\beta_a = n\,\sigma_{abs}(\lambda)+\beta_{DE}$, where $\sigma_{abs}(\lambda)$ is the ZnO absorption cross section of an ensamble of nanospheres ranging from 80 nm to 180 nm, and β_{DE} is the absorption contribution of the bare DE only (●). A good agreement between theory and experiment (black cont. line in Fig.6) is again obtained for $n=10^{11}$ cm^{-3}.

It is worth noting that Fig.6 couldn't highlight any relevant dependence with modulation frequency of the ZnO/DE absorption spectra. In fact, the quantity $\beta_a(\lambda)$ doesn't change from 9Hz (○), to 25Hz (□), till 81Hz (∇), because the shape of the absorption spectrum is rather insensitive to the particle sizes as shown theoretically in Fig.4b.

4. Conclusion

Crystalline zinc oxide nanoparticles were grown on diatomite powders by a low temperature sol gel synthesis. Microstructural features of ZnO/DE powders were investigated by SEM analysis. The optical properties of ZnO/DE hybrid powders and the grain size of ZnO nanoparticles were measured by Photoacoustic Spectroscopy, which allowed to perform a complete optical characterization and to discriminate between absorption and scattering of powder aggregates. Absorption and scattering coefficients of hybrid powders in the 300-450

nm range increased with respect to those measured on the bare diatomite, indicating that such hybrids are potential candidates for many photonic applications. Moreover Photoacoustic Spectroscopy at different modulation frequencies highlights the nonuniform distribution of the ZnO nanospheres in depth, allowing to retrieve a distribution depth profiling opening the way to interesting developments in this research field.

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Caption for figures

Figure 1. SEM micrographs of ZnO/DE powders as-dried,

Figures 2. Normalized PAS amplitude (a), and PAS phase (b) measured on DE powder as dried (●) and on a hybrid powder ZnO/DE at different modulation frequencies (○ at 9Hz, □ at 25Hz, ∇ at 81 Hz). Black lines are the best fit given by Eqs.(1) and (2).

Figures 3. Contour plot of the PAS normalized signal $S_{PAS}/S_{PAS}(\lambda_o)$ as a function of the absorption and scattering coefficients. The PAS signal is normalized to the reference wavelength λ_o=300 nm with β_a =130 cm^{-1}, and β_s=120 cm^{-1} at the frequency f=25Hz.
(a) amplitude ratio A; (b) phase difference Φ.

Figure 4. Calculated spectrum of the scattering coefficient from PAS Signal. (●) DE powder as dried; hybrid powder ZnO/DE at different modulation frequencies (○ at 9Hz, □ at 25Hz, ∇ at 81 Hz). Black lines are for the scattering coefficient corresponding to an ensemble of ZnO nanospheres with diameters uniformly distributed in the different ranges.

Figures 5. Cross sections of a single ZnO nanosphere normalized to its geometrical section $S=\pi D^2/4$. The calculated normalized scattering (a) and absorption (b) cross sections are shown as a function of wavelength. Dotted lines are for different diameter of the sphere (80

nm, 130 nm, 180 nm). The cont. line is for an ensemble with diameters uniformly distributed from 80 nm to 180 nm.

Figure 6. Calculated spectrum of the absorption coefficient from PAS Signal. (●) DE powder as dried; hybrid powder ZnO/DE at different modulation frequencies (○ at 9Hz, □ at 25Hz, ∇ at 81 Hz). Black line is for the scattering coefficient corresponding to an ensemble of ZnO nanospheres with diameters uniformly distributed in the range [80 nm - 180 nm].