CaWO₄@MPSiO₂ nanocomposite: synthesis and characterization

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The features of obtaining a nanocomposite consisting of the CaWO₄ core which is a scintillation nanocrystal and a mesoporous SiO₂ shell (CaWO₄@MPSiO₂) are considered. The results of the investigation of microscopic and optical parameters of CaWO₄@MPSiO₂ nanocomposite are presented. The mesoporous SiO₂ shell applied to the nanocrystal can be used both as a host for the photosensitizer, and set the necessary distance between the donor and the energy acceptor.

Keywords: Nanocomposite, CaWO₄, Mesoporous SiO₂, X-Ray Induced Photodynamic Therapy.

Рассмотрены особенности получения нанокомпозита, состоящего из ядра CaWO₄, представляющего собой сцинтилляционный нанокристалл, и мезопористой SiO₂ оболочкой (CaWO₄@MPSiO₂). Представлены результаты исследований микроскопических и оптических параметров нанокомпозита CaWO₄@MPSiO₂. Нанесенная на нанокристалл мезопористая оболочка может использоваться как в качестве хоста для фотосенсибилизатора, так и задавать необходимое расстояние между донором и акцептором энергии.

CaWO₄@MPSiO₂: синтез та характеристика. К.Губенюк, І.Беспалова, П.Максимчук, П.Матейченко, Р.Гринюк, С.Єфимова.

Розглянуті особливості отримання нанокомпозиту, що складається з ядра CaWO₄, який представляє собою сцинтилляційний нанокристал та мезопористої SiO₂ оболонки. Проведені результати досліджень мікроскопічних і оптичних параметрів нанокомпозиту CaWO₄ у мезопористій SiO₂ оболонці. Нанесена на нанокристал мезопориста оболонка може використовуватися як в якості хоста для фотосенсибілізатора, так і задавати необхідну відстань між донором і акцептором енергії.

1. Introduction

Photodynamic therapy (PDT) — method of local activation of the photosensitizer (PS) accumulated in the tumor by visible red light, which in the presence of tissue oxygen leads to the production of free radicals and reactive oxygen species (ROS) including singlet oxygen (¹O₂) due to electron or energy transfer from excited PS to oxy-
gen molecules and substrate [1, 2]. It is commonly accepted that singlet oxygen is the predominant cytotoxic agent produced during PDT [3, 4].

For deep cancer treatment, the light should be within the near infrared NIR range of 700–1100 nm, where most tissue chromophores, including oxyhemoglobin, deoxyhemoglobin, melanin, and fat, weakly absorb [5]. Unfortunately, most available PS has absorption bands at wavelengths shorter than 700 nm. Recently, to solve this problem and enhance the PDT treatment for deep cancers, a new concept has been proposed by Chen and co-authors [6]. This modern approach is based on the use of scintillation nanoparticles (ScNPs) as energy transducers, which transform X-ray to UV/visible photons, and act as an energy source for PS molecules to activate PDT [7–12]. One of the main advantages of X-ray-induced photodynamic therapy (X-PDT), unlike traditional PDT, is the absence of restrictions on the depth of the excitation light penetration into biological tissues [13]. A typical mechanism for energy transfer between ScNPs and PS is non-radiative (Forster) resonance energy transfer (FRET). In such systems scintillation NPs act as an excitation energy donor, whereas PS molecules as energy acceptors [14, 15]. To create efficient ScNPs — PS complexes, potential donor — acceptor pairs should meet one of the main requirements, mainly, overlapping the acceptor absorption spectrum with the donor luminescence one [16].

One of the most effective PS is Protoporphyrin IX [17]. The maximum of its absorption spectrum is in the range of 400–410 nm. Therefore, in order to ensure efficient energy transfer in the complex "ScNPs–PS", the nanoparticle should be characterized by intense X-ray luminescence in the same range. As one of the suitable candidates, one can consider nanoparticles of tungstates, in particular calcium tungstate (CaWO4). This is due to the good biological compatibility of this material [18], intensive luminescence of CaWO4 [19], and overlapping of its luminescence spectrum with the absorption spectrum of PS, as Protoporphyrin IX [17].

The second basic requirements for the realization of non-radiative excitation energy transfer from the ScNPs to the PS molecules is the distance between the energy donor (ScNPs) and the energy acceptor (PS molecules), which is governed by the FRET pair spectral overlap and is usually in the range of 1–10 nm [16]. There are currently various strategies for ScNPs binding with PS molecules, including physical PS loading, covalent conjugation, direct ScNPs surface coating and mesoporous silica coating loaded with PS [20].

In this paper, we report the synthesize and characterization of CaWO4@MPSiO2 nanocomposite, consisting of a CaWO4 ScNPs core and a mesoporous SiO2 shell, which can be used both as a host for the PS molecules and to set the required distance between ScNPs core and loaded PS.

2. Experimental

2.1. Materials

Calcium chloride (CaCl2, Khimlabreaktiv, Ukraine), ammonia water 25 mas. % (NH4OH, Khimlabreaktiv, Ukraine), citrate sodium crystalline hydrate (Na3Cit·5H2O, Khimlabreaktiv, Ukraine) were analytical reagents and used as received.

Tetraethyl orthosilicate (Si(OCH2CH3)4, TEOS, 98 %), cetyltrimethylammonium bromide (CH3(CH2)15N(Br)(CH3)3, CTAB, 95 %), sodium tungstate hydrate (Na2WO4·2H2O, 99 %) were purchased from Sigma-Aldrich (USA) and used as received.

2.2. Instrumentation and characterization

Synthesized CaWO4@MPSiO2 nanocomposite was characterized by scanning electron microscopy (SEM, JSM-6890LV, JEOL Company, USA), operated at 15 kV and Ultra-High Resolution Scanning Electron Microscopy (MAIA3 TESCAN, Czech Republic, EU), operated at 15 kV and transmission electron microscopy (TEM, JEM-2100F (JEOL Company, Japan)) operated at 200 kV, equipped with an Oxford CCD camera.

The X-ray diffraction pattern was measured with a PANalytical X’Pert Pro X-RAY diffractometer. The data were analyzed using the Program X’Pert HighScore Plus (Version 2.2e), which allowed comparisons with the ICCD X-ray diffraction pattern database (PDF Release-2, 2009).

Zeta-potential of the CaWO4@MPSiO2 nanocomposite was measured with a ZetaPALS analyzer (Brookhaven Instruments Corp., USA) operated in a phase analysis light scattering mode.

The photoluminescence and excitation spectra were recorded by means of automatic spectrofluorimeter based on the lattice monochromator MDR-23. The photomulti-
plier Hamamatsu R9110 operating in the photon counting mode had been used for luminescence spectra registration. The Xenon-lamp coupled with monochromator MDR-206 had been used as the photoluminescence excitation source.

The X-ray luminescence has been excited by an X-ray generator "REYS" (U = 25 kV, I = 37 μA), and registered using the MDR-23 grating monochromator with the Hamamatsu R9110 PMT in the photon counting mode.

All measurements were carried out at room temperature.

3. Results and discussion

3.1. Synthesis and characteristics of CaWO₄ nanoparticles

CaWO₄ amorphous nanoparticles were obtained by the colloidal method [21]. First, 10 mL of sodium citrate (C (Na₃C₆H₅O₇) = 0.225 M) was mixed with 10 mL of calcium chloride solution (C (CaCl₂) = 0.300 M). Then 10 mL of sodium tungstate (C (Na₂WO₄) = 0.45 M) was poured into the mixture under vigorous stirring. The resulting mixture was heated with constant stirring in a water bath to 65°C. The resulting slurry of amorphous calcium tungstate CaWO₄ was placed in a dialysis bag (molecular weight of 12,000 Da and 2.5 nm pore diameter) and the dialysis was conducted at room temperature for 5 h, changing the distilled water every hour to a value pH = 7.0. Then the suspension was evaporated on a water bath for powdered amorphous calcium tungstate CaWO₄. Obtained TEM images show CaWO₄ amorphous agglomerates of about 300 nm size (Fig. 1a), which are composed on CaWO₄ nanoparticles of about 10–20 nm size. These particles do not possess luminescence. To obtain required crystal structure and subsequently luminescent properties, amorphous CaWO₄ particles were coated with thin SiO₂ solid shell and annealed at high temperature.

For this purpose, 0.05 g amorphous CaWO₄ were treated with 20 mL ethanol under ultrasonication for 30 min. Then the particles were well dispersed in a mixture of 20 mL ethanol, deionized 10 mL water, and 0.5 mL concentrated ammonia solution. Then 0.03 mL TEOS was added dropwise to the solution. After being stirred for 4 h at room temperature, the products were separated, dried at 50°C overnight and annealing at 900°C for 2 h. As a result, the CaWO₄ nanocrystals were obtained (see Fig. 1b).

XRD analysis was used to study the crystal structures of the CaWO₄ nanoparticles. XRD pattern of the CaWO₄ nanocrystals exhibits the characteristic reflections of scheelite (Fig. 2).

3.2. Synthesis and characteristics of CaWO₄@MPSO₂ nanocomposite

To cover the obtained CaWO₄ nanocrystals with mesoporous silica layer, we use the procedure described in [22], where spheres with the Fe₃O₄ core with surface area 676 m²·g⁻¹ and total pore volume 0.46 cm³·g⁻¹ at a nanocomposite particle size of 500 nm were obtained.
Fig. 2. XRD analysis of CaWO₄ nanocrystals.

Fig. 3. SEM (a) and TEM (b) images of the CaWO₄@MPSiΟ₂ nanocomposite and SEM images of the blank SiΟ₂ (c).

For deposition of the mesoporous SiΟ₂ shell 0.02 g of CaWO₄@solid SiΟ₂ were redispersed in a mixed solution containing of 0.075 g CTAB, 20 mL deionized water, 0.30 mL concentrated ammonia solution and 15 mL ethanol. The resulting solution was stirred for 30 min. Then, 0.20 mL TEOS was added dropwise to the solution with vigorous stirring. After reaction for 4 h, the product was centrifuged, washed repeated with ethanol and distilled water.

Finally, the CTAB templating agents were removed using an acid extraction process: the synthesized CaWO₄@MPSiΟ₂ nanocomposite (residual sediment) were suspended in a solution of 25 mL ethanol and 1.25 mL HCl with a concentration 2 M. The suspension was vigorously stirred for 48 h, and the products were centrifuged, washed with ethanol and distilled water in sequence, and dried at 50°C for 2 h.

As a result, the obtained CaWO₄@MPSiΟ₂ nanocomposite of spherical shape with the average sphere diameter d ~ 500 nm and with a minimum spread in size is presented in Fig. 3a, b. Zeta-potential of the synthesized CaWO₄@MPSiΟ₂ nanocomposite is ±8.12±0.01 mV. The slight positive charge of the obtained nanospheres is governed by the residual of positively charged surfactant CTAB molecules using as a templating agent.

Also, we have prepared blank sample SiΟ₂ by the same procedure only without a scintillation core for comparison with CaWO₄@MPSiΟ₂ nanocomposite. Obtained SEM images show SiΟ₂ sphere (Fig. 3c).

XRD analysis showed that the obtained CaWO₄@MPSiΟ₂ nanocomposite consists of the CaWO₄ core, the solid SiΟ₂ shell, and the mesoporous SiΟ₂ shell. Roentgenogram showed reflexes from all phases (Fig. 4).

3.3 Optical properties of the CaWO₄@MPSiΟ₂ nanocomposite

Figure 5a shows the excitation and luminescence spectra of the obtained CaWO₄@MPSiΟ₂ nanocomposite. The excitation spectrum of the synthesized nanocomposite (Fig. 5a, curve 1) consists of the sin-
SINGLE BAND CENTERED AT ABOUT 250 NM. THIS BAND CORRESPONDS TO ELECTRON TRANSFER FROM 2p OXYGEN ORBITALS TO THE 5d TUNGSTEN ORBITALS.


IN SHOULDERED TO THE BLANK SiO$_2$ DO NOT POSSESS LUMINESCENCE IN THE SPECTRAL RANGE (FIG. 5A, CURVE 3).

FOR X-PDT APPLICATIONS, IT IS NECESSARY THAT THE CORE OF THE NANOCOMPOSITE BE CHARACTERIZED BY INTENSE X-RAY INDUCED LUMINESCENCE. THE LUMINESCENCE SPECTRUM OF THE INVESTIGATED CaWO$_4$@MPSiO$_2$ NANOCOMPOSITE UNDER X-RAY EXCITATION AT ROOM TEMPERATURE IS A BROAD BAND WITH A MAXIMUM AT 435 NM (FIG. 5B). THIS BAND IS ASSOCIATED WITH THE CaWO$_4$ HOST LATTICE. IT CORRESPONDS TO THE LUMINESCENCE OF THE CaWO$_4$@MPSiO$_2$ NANOCOMPOSITE UNDER X-RAY EXCITATION AT ROOM TEMPERATURE.

FIG. 5. PHOTOLUMINESCENCE PROPERTIES OF OBTAINED SAMPLES. (A) CURVE 1 — EXCITATION SPECTRUM FOR EMISSION $\lambda_{\text{exc}} = 440$ nm OF THE CaWO$_4$@MPSiO$_2$ NANOCOMPOSITE, CURVE 2 — EMISSION SPECTRUM OF THE CaWO$_4$@MPSiO$_2$ NANOCOMPOSITE UNDER EXCITATION $\lambda_{\text{exc}} = 260$ nm, CURVE 3 — EMISSION SPECTRUM OF THE BLANK SiO$_2$ UNDER EXCITATION $\lambda_{\text{exc}} = 260$ nm; EMISSION SPECTRUM OF THE CaWO$_4$@MPSiO$_2$ NANOCOMPOSITE UNDER X-RAY EXCITATION (B), $T = 293$ K.

4. CONCLUSIONS

CaWO$_4$@MPSiO$_2$ NANOCOMPOSITE WITH SIZE $d = 500$ NM WERE SYNTHESIZED AND CHARACTERIZED BY VARIOUS TECHNIQUES.
XRD analysis showed that the obtained CaWO₄@SiO₂ nanocomposite consists of the CaWO₄ core, the solid SiO₂ shell, and the mesoporous SiO₂ shell. Roentgenogram showed reflexes from all phases.

The photo- and X-ray-luminescence spectra of the resulting nanocomposite with maximum λ = 435 nm correspond to the luminescence of crystalline calcium tungstate.

Obtained nanocomposite can realize the necessary conditions for energy transfer from the X-ray-induced nanoparticle to the PS. The experimental results indicate high potential of the CaWO₄@MPSiO₂ nanocomposite as carriers for encapsulation of organic dye molecules, for instance, PS PPIX, used in PDT.

References