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Regular Article

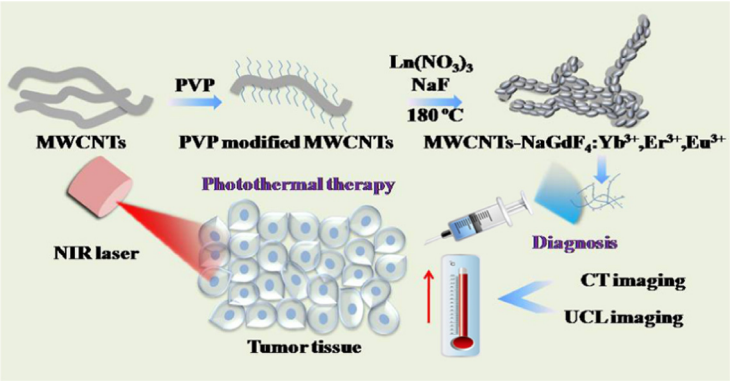
Integrating photoluminescence, magnetism and thermal conversion for potential photothermal therapy and dual-modal bioimaging

Jingting Sui, Guixia Liu *, Yan Song, Dan Li, Xiangting Dong, Jinxian Wang, Wensheng Yu

Key Laboratory of Applied Chemistry and Nanotechnology at University of Jilin Province, Changchun University of Science and Technology, Changchun 130022, China

GRAPHICAL ABSTRACT

The MWCNTs-$NaGdF_4$:Yb^{3+}, Er^{3+}, Eu^{3+} multifunctional nanocomposites with magnetic, luminescent and thermal conversion properties were fabricated by a facile hydrothermal method, the up-conversion luminescence imaging, X-ray computed tomography imaging and photothermal therapy of nanocomposites were investigated. The obtained nanocomposites would have promising applications in diagnosis and therapy of tumors.



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ABSTRACT

Multifunctional nanocomposites (NCs) incorporating magnetic, luminescent and photothermal conversion properties are endowed with potential application in many fields such as imaging, tumor detection, drug delivery and therapy. Here, multifunctional MWCNTs-$NaGdF_4$:Yb^{3+}, Er^{3+}, Eu^{3+} NCs, which offer the potential for integrated bioimaging and photothermal therapy (PTT) were fabricated by a facile hydrothermal method. The resulting sample exhibits uniform morphology, bright dual-modal luminescence and intrinsic paramagnetic properties. Under near-infrared laser excitation, NCs have excellent photothermal conversion properties. In addition, the MTT assay in HeLa cells shows that the NCs have good biocompatibility. Moreover, the up-conversion luminescence (UCL) imaging, X-ray computed tomography (CT) imaging and PTT in vitro of NCs were investigated. The results indicate that NCs can be used for dual-modal imaging-guided diagnose and PTT of cancer cells.

1. Introduction

The multifunctional nanomaterials have realized the combination of various components into one entity, which endows the nanoplatforms with distinct magnetic, thermal and luminescent

* Corresponding author.
E-mail address: liuguixia22@163.com (G. Liu).

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properties [1–5]. They have been considered as theranostic reagents integrated imaging modalities and therapeutic components to achieve the diagnosis and therapy of tumors [6]. There are many traditional therapeutic approaches for tumors such as radiotherapy and chemotherapy. However, these treatments have some side effects and toxicity [7,8]. Photothermal therapy (PTT) has attracted much attention due to its minimally invasive and highly effective [9–11]. It can provide accurate energy transfer to target tissues and high photothermal conversion efficiency. Various types of theranostic reagents combining PTT and multimodal imaging have been reported, including carbon materials [12,13], organic dyes [14,15], inorganic nanoparticles (NPs) [16], and noble metal NPs [17,18].

Compared with noble metals and organic dyes, multi-walled carbon nanotubes (MWCNTs) have the advantage of high chemical and thermal stability [19], inexpensive price and easy preparation, no damage of the surrounding healthy cells. Furthermore, they can effectively convert near-infrared reflection (NIR) to heat, so they can be suitable for photothermal conversion agents for PTT [20,21].

In order to achieve the diagnosis of tumor and detect the distribution and cumulative dose of photothermal agents at the tumor location, imaging techniques essential for tumor treatment [22]. Up-conversion luminescence (UCL) imaging and X-ray computed tomography (CT) imaging are two types important imaging techniques because UCL imaging has cellular level of sensitivity and resolution, large-scale biological activities monitoring [23,24], CT imaging possesses deep tissue penetration and specific 3D structure information [25]. Therefore, dual-modal imaging is required to integrate the advantages of different techniques into a single probe.

Lanthanide-doped up-conversion (UC) NPs have the potential to multimodal imaging [26,27]. Among all of host materials for lanthanide-doped nanocrystals, fluorides have considerable promise due to their unique properties such as high anionic conductivity and ionization degree, long life-times and low phonon energies [28–30]. Especially, $NaGdF_4$ displays excellent photostability and chemical stability [31]. Moreover, Gd^{3+} ions are paramagnetic at room temperature, which are ideal paramagnetic relaxation agents because of their intrinsic magnetic moment [32,33]. Therefore, $NaGdF_4$ can be used as a contrast agent for MRI. In addition, recent studies have indicated that elements with large atomic number can be used as ideal contrast agents [34]. Hence, Ln^{3+}-doped $NaGdF_4$ NPs are expected to possess UCL imaging and CT imaging, which will be used in multimodal imaging and multifunctional agents [35,36].

Most recently, CNTs-based multifunctional nanocomposites have been attracted much attention. For example, Wang et al. fabricated a novel polydopamine-encapsulated gadolinium-loaded MWCNTs (MWCNT-Gd@PDA) NCs by a solution oxidation method. The obtained NCs achieved dual-modality guided photothermal dissection of tumor metastasis [37]. Zhang et al. prepared PLA/MWCNTs composite nanofibers by electrospinning technique. The resulting samples can be used for chemo- and photothermal therapy [38]. As we all know, various MWCNTs surface modification strategies have been investigated, including an acid oxidation process [39] and addition of surfactants [40,41]. PVP is a water-soluble polymer, it can be used as surfactant to enhance the hydrophilicity of MWCNTs. In our group's previous work, PVP was added to synthesize MWCNTs-$NaGdF_4$:Yb^{3+}, Er^{3+}, Eu^{3+} NCs and MWCNTs-$NaGdF_4$:Yb^{3+}, Er^{3+} NCs by solution route [42,43]. The prepared samples exhibited bright luminescence, good magnetic and thermal properties. However, the synthetic procedures of the above mentioned NCs had inherent complex operation and severe conditions, involving non-aqueous solvent and vacuum environment, which limit their applications in commercialized production. Therefore, it is necessary to find a simple method to synthesize MWCNTs-based multifunctional NCs with excellent UC and CT imaging properties.

Herein, Yb^{3+}, Er^{3+} and Eu^{3+} co-doped $NaGdF_4$ dual-mode luminescence NPs modified on the surface of MWCNTs were synthesized by a facile hydrothermal method for the first time. Compared with other methods, hydrothermal route is nontoxic, environmentally friendly and simple procedure. The structure, morphology, dual-mode luminescence and magnetic properties of the as-prepared samples were discussed. Furthermore, the biocompatibility, photothermal conversion and UCL/CT dual-modal imaging of NCs were studied in detail.

2. Experimental sections

2.1. Materials

The rare earth oxides Ln_2O_3 (Ln = Gd, Yb, Er, Eu), nitric acid (HNO_3), polyvinylpyrrolidone (PVP, K = 30), ethanol and sodium fluoride (NaF) were purchased from Sinopharm Chemical Reagent Co., Ltd. MWCNTs (purity >95%) were purchased from Shenzhen Nanotech Port Co., Ltd. In this experiment, deionized (DI) water was used as solvent. All of these chemicals were analytical grade and used as received without further purification.

2.2. Synthesis of MWCNTs-$NaGdF_4$:Yb^{3+}, Er^{3+}, Eu^{3+} NCs

The MWCNTs-$NaGdF_4$:Yb^{3+}, Er^{3+}, Eu^{3+} NCs were synthesized by a facile hydrothermal method. Firstly, 0.05 mol L^{-1} $Yb(NO_3)_3$, $Er(NO_3)_3$, $Eu(NO_3)_3$ and 0.1 mol L^{-1} $Gd(NO_3)_3$ aqueous solutions were prepared by dissolving the corresponding rare earth oxides Gd_2O_3, Yb_2O_3, Er_2O_3, Eu_2O_3 in dilute HNO_3 solution under heating and agitation, the residual HNO_3 was removed by evaporation. Secondly, 7 mg MWCNT and 2 g PVP were added into 10 mL DI water under vigorous stirring to form homogeneous solution **A**. Subsequently, 2 mmol solution of $Gd(NO_3)_3$ (0.1 mol L^{-1}), $Yb(NO_3)_3$ (0.05 mol L^{-1}), $Er(NO_3)_3$ (0.05 mol L^{-1}) and $Eu(NO_3)_3$ (0.05 mol L^{-1}) with the molar ratio of 74:20:2:4 under vigorous stirring to form transparent solution **B**. Then solution **B** was introduced into solution **A** to form mixture solution **C**. Then, 5 mL of NaF (4.8 mol L^{-1}) was added dropwise into the above mixture solution again stirring for 30 min. After additional agitation for another 30 min, the mixture was transferred into a 50 mL stainless Teflon-lined autoclave and kept at 180 °C for 24 h. When the autoclave was cooled to room temperature, the resulting gray precipitate was collected by centrifugation, washed with ethanol and DI water three times, and then dried for 8 h at 60 °C in a drying oven.

2.3. Characterization

The crystal phase and phase purity of the as-synthesized products were obtained by X-ray powder diffraction (XRD) carried out on a Rigaku D/max-RA power diffractometer using Cu Kα radiation (λ = 1.54056 Å) in the 2θ range from 10° to 90°. The composition, structure and morphology of the products were characterized by a field emission scanning electron microscope (FESEM, JSM-7610, JEOL) equipped with an energy-dispersive X-ray spectroscope (EDS). The UV–Vis absorption spectra were performed on a spectrophotometer (Shimadzu UV-2450). For UC emission measurements, a sustained wave diode laser emitting at 980 nm and a HITACHI F-7000 fluorescence spectrophotometer were used. The photoluminescence excitation, emission spectra and luminescence decay curves of powder products were recorded with a HITACHI F-7000 spectrophotometer using a 150 W Xe-lamp as the excitation source. The magnetic properties of the sample were recorded using a vibrating sample magnetometer (VSM) under an applied magnetic field ranging from −20 to +20 kOe. All the measurements were performed at room temperature.