SYNTHESIS AND CHARACTERIZATION OF NANOMATERIALS $TbPO_4.H_2O$ CAPABLE OF EMITTING GREEN LIGHT

TỔNG HỢP VÀ XÁC ĐỊNH ĐẶC TÍNH CỦA VẬT LIỆU NANO $TbPO_4.H_2O$ CÓ KHẢ NĂNG PHÁT XẠ ÁNH SÁNG XANH

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DOI: http://doi.org/10.57001/huih5804.2024.398

ABSTRACT

The article presents the synthesis process of nanomaterial $TbPO_4.H_2O$, which can be used in cancer cell identification. The raw materials include $Tb(NO_3)_3.6H_2O$ and $NH_4H_2PO_4$ with a concentration of 0.00625mol; the pH is adjusted to 6 and 8 with 1mol NaOH solution. The hydrothermal reaction is carried out at 200°C for one day; then, the suspension is washed and centrifuged twice with water, and the product $TbPO_4.H_2O$ is obtained after drying at 80°C for 4 hours. SEM imaging results show that the product is nano-sized and rod-shaped with a diameter of about 20nm. At pH = 6, the length is about 200nm, while at pH = 8, the size is about 187.5nm. By measuring the luminescence spectrum of the product, it was determined that the samples obtained at different pHs all had the most vigorous light emission at a wavelength of 550nm, equivalent to the blue light region. The intensity of the pH = 6 sample was weaker than that of the pH = 8 sample.

Keywords: *Hydrothermal synthesis, nanomaterials, blue light.*

TÓM TẮT

Bài báo trình bày về quá trình tổng hợp vật liệu nano $TbPO_4.H_2O$ có khả năng ứng dụng trong nhận dạng tế bào ung thư. Nguyên liệu bao gồm $Tb(NO_3)_3.6H_2O$ và $NH_4H_2PO_4$ nồng độ 0,00625mol, pH được điều chỉnh về 6 và 8 bằng dung dịch NaOH 1mol. Phản ứng thuỷ nhiệt được thực hiện ở 200°C trong 1 ngày, sau đó, dung dạng huyền phù được rửa sạch và ly tâm 2 lần bằng nước, sản phẩm $TbPO_4.H_2O$ thu được sau quá trình sấy ở 80°C trong 4 giờ. Kết quả chụp ảnh SEM cho thấy sản phẩm có kích thước nano, dạng hình que với đường kính khoảng 20nm. Ở pH = 6 có chiều dài khoảng 200nm; trong khi ở pH = 8, kích thước là khoảng 187,5nm. Bằng cách đo quang phổ phát quang của sản phẩm đã xác định được rằng, các mẫu thu nhận được ở pH khác nhau đều có khả năng phát xạ ánh sáng mạnh nhất ở bước sóng 550 nm tương đương vùng ánh sáng xanh. Cường độ của mẫu pH = 6 yếu hơn so với mẫu pH = 8.

Từ khóa: *Tổng hợp thuỷ nhiệt, vật liệu nano, ánh sáng xanh.*

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Received: 21/8/2024

Revised: 25/9/2024

Accepted: 28/11/2024

1. INTRODUCTION

Cancer is a disease defined by abnormal cell proliferation. Cancer cells occupy the space and nutrition that healthy organs require, causing them to malfunction. Cancer cells proliferate uncontrollably, generating tumours, and can travel to other body regions, resulting in secondary tumours. It is a significant cause of death worldwide.

Currently, tumour detection techniques such as nuclear magnetic resonance imaging, computed tomography, and microfluidic technology exist, but they have disadvantages such as radiation exposure,high costs, and complex operation. Thus, a novel testing platform is required to advance the field of tumour testing. The development of rare earthc- containing luminous nanorods for biomedical applications has recently become a focus for materials science researchers [1-12]. According to prior research, nanorods may have a shorter, more coherent period in interband transitions than nanospheres. As a result, nanorods have a comparatively lengthy decay period, allowing for more consistent luminescence intensity. Furthermore, the nanorods have low radiation damping due to their small volumes [13, 14]. Furthermore, nanorods are of great interest to the scientific community since their form is linked to inherent multifunction in many contact areas [15]. These properties make them ideal potential items for use in high-function gadgets. Wet chemical methods might be used to produce several rare earth- containing luminous nanorods, which would greatly increase luminescent intensity [17-19]. In biomedical applications, high luminous yield with nanosize and biomedical compatibility are still required as essential properties for biolabeling materials. To produce $TbPO_4$ nanorods with a greater luminous intensity for usage in biomedical applications, a stable and high-quality synthesis technique must be developed. Fluorescent nanoparticles are biocompatible, brilliant, and display good subcellular selectivity [6, 9, 14].

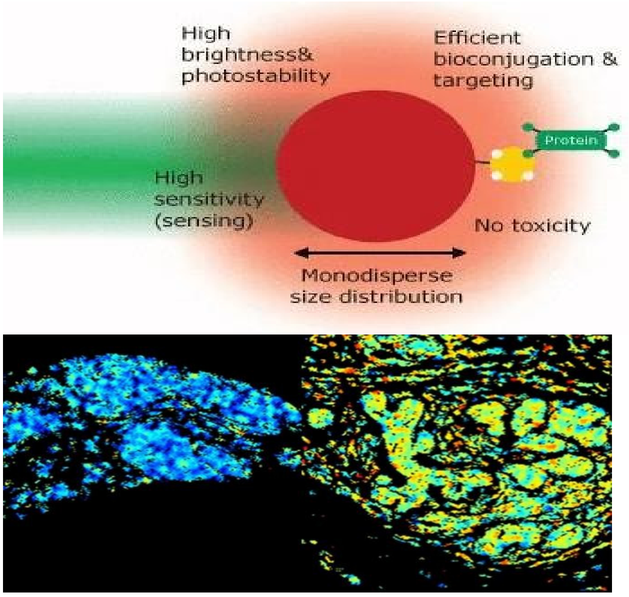

Fig. 1. The characteristics of the optimal fluorescent nanomaterial

Fig. 1 shows how a strongly fluorescent nanoparticle can be absorbed into cells and tissues, such as tumours, causing them to become fluorescent and visible. Currently, there are tumor detection techniques such as nuclear magnetic resonance imaging (MRI), computed tomography, and microfluidic technology but these technologies have limitations like radiation exposure, high costs, and complex operation. Thus, there's a need for a new testing platform to promote the development of the field of tumor testing.

Numerous nanomaterials, such as hydrophilic polymers, quantum dots, and silica nanoparticles, have several problems, including cellular toxicity, limited quantum yield, and vulnerability to the immune system and intracellular enzymes. On the other hand, terbium phosphate $TbPO_4.H_2O$ has numerous advantages, including high stability, intense luminescence, ease of synthesis, and compatibility with the environment and the human body (Fig. 2). As a result, this substance $TbPO_4.H_2O$ was chosen as the project's object.

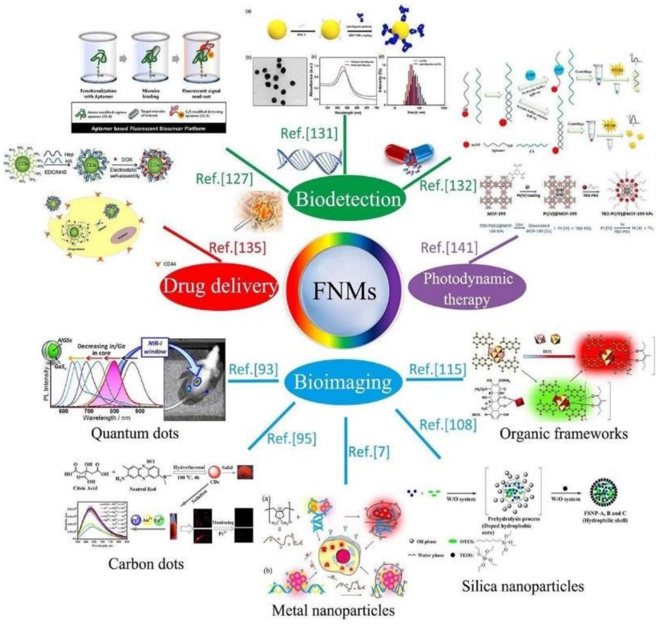

Fig. 2. Different types of fluorescent nanoparticles

The research arms of the article was to use fluorescence imaging technology to outperform traditional tumour detection methods in terms of affordability, speed, sensitivity and specificity.

2. METHOD AND EXPERIMENT

2.1. Materials

- Terbium (III) nitrate pentahydrate ($Tb(NO_3)_3.6H_2O$) (Aldrich, 99.9%).

- Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) (Merck, 99%).

- Sodium hydroxide (NaOH) (Merck, 99%).

2.2. Synthesis of TbPO4.H2O nanorods

Wet chemical methods which include hydrothermal, sol-gel, and coprecipitation synthesis were developed to obtain ultrafine, very homogeneous, and high purity powders. Among these various wet chemical synthesis methods, hydrothermal method was a simple method with cost effectiveness, easy control over material size, and compositions. The nanorods were synthesized as the following procedure: 15ml (0.00625M) terbium (III) nitrate pentahydrate and (0.00625M) ammonium dihydrogen phosphate were mixed in stirred vigorously solution. Afterward, sodium hydroxide was added slowly to the solution and stirred using a magnetic pellet for 6 hours with adjusted pH in the range of 5 ÷ 7. Meanwhile, the reactant $Tb^{3+/-}$ - molar ratio was changed from 1/15 to 1/1 by increasing the amount of terbium nitrate. Next, the mixture solution was put in a Teflon-lined stainless-steel autoclave and heated up at 200°C for 24 hours. The $TbPO_4.H_2O$ was separated by centrifuge at 5800rpm. The achieved product had been washed several times by deionized water and dried at 80°C for 4 hours.

2.3. Determination of nanostructure size of product $TbPO_4.H_2O$

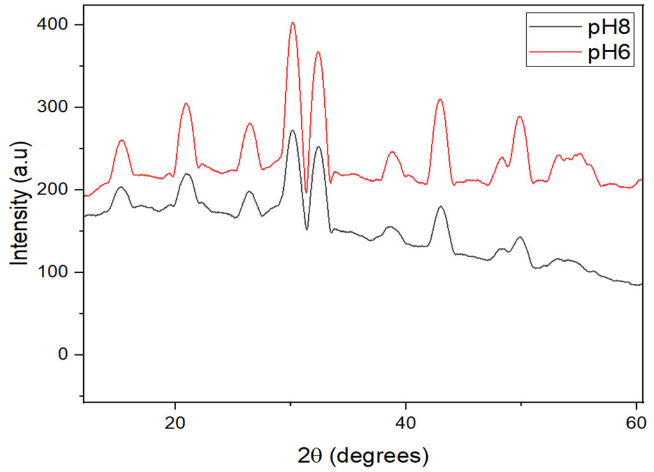

Fig. 3. X-ray diffraction of $TbPO_4.H_2O$ nanorods

Among a variety of techniques, we chose the hydrothermal method. First, we prepare 15 ml of $Tb(NO_3)_3.6H_2O$ (terbium nitrate hexahydrate) and $NH_4H_2PO_4$ (Ammonium dihydrogen phosphate) solutions, both at 0.00625 molar. After slowly dripping them onto each other, we use a magnetic stirrer to stir for 90 minutes while adjusting the pH to 6 and 8 with one molar NaOH (Sodium hydroxide) solution, which results in a mixture solution. Next, it is autoclaved hydrothermally at 200°C for one day. Then, the solution, which is now in suspension, is washed and centrifuged two times with water to filter the material out. Finally, we dry the samples with the heating oven at 80 degrees Celsius for 4 hours and retrieve the $TbPO_4.H_2O$ (terbium phosphate monohydrate) nanomaterial in white powder- some actual photos of the experimental process. After synthesizing the material, we carried out some measurements to check the product as follows: To begin, we use X-ray diffraction analysis (XRD), a technique used in materials science to determine a material's crystallographic structure. Observing the image, we notice 11 peaks with different heights or sizes. Comparing the XRD patterns with the standard crystallographic database, which is the JCPDS card 20-1244, we found that there is a similarity in positions and angles. This indicates the hexagonal structure, and there are almost no secondary peaks of other substances. Therefore, we concluded that terbium phosphate monohydrate crystals have a hexagonal structure. Next, we use the SEM images to determine the shape and size of the materials. The results show that our product is rod-shaped with a diameter of about 20nm. At pH = 6, it has a length of around 200nm; meanwhile, at pH = 8, it is more fragmented and shorter, roughly 188 nm. As a result, we concluded that terbium phosphate monohydrate is a nanorod (Fig. 3).

2.4. Determination of light emission ability of $TbPO_4.H_2O$ product

The requirement of materials used for applications in biomedical fluorescent labelling is that the material must emit strong fluorescence after surface activation. Therefore, to confirm the luminescence properties of the nanomaterial $TbPO_4.H_2O$, we measured the fluorescence spectra of $TbPO_4$. In this work, $TbPO_4.H_2O$ nanorods/nanowires have been prepared by microwave (MW) heating and characterized by scanning electron microscopy (SEM) and x-ray diffraction (XRD). The microwave-assisted synthesis technique is employed because it can provide low-dimensional nanomaterials. It is simple, fast, clean, efficient, economical, non-toxic and eco-friendly. The microwave refluxing apparatus was used with maximum power as high as 30000W. The photoluminescence (PL) spectra under 370nm excitation wavelength of $TbPO_4.H_2O$ nanorods/nanowires were measured in the 450 - 700nm wavelength range.

3. RESULTS AND DISCUSSION

3.1. Synthesis of $TbPO_4.H_2O$ nanomaterials

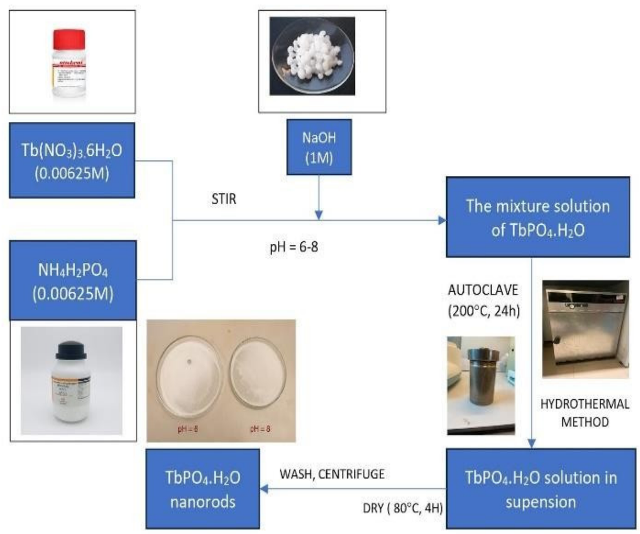

Fig. 4. Synthesis of $TbPO_4.H_2O$ nanorod

According to the reference documents, the steps to perform the hydrothermal synthesis reaction, cleaning and drying of $TbPO_4.H_2O$ nanomaterials is shown in Fig. 4.

The obtained product $TbPO_4.H_2O$ is white and powdery.

3.2. Determine the nanostructure size of product $TbPO_4.H_2O$

The SEM photos were collected to determine the form and size of the product. The results were demonstrated that, the obtained product was a rod-like shape with a diameter of roughly 20nm. At pH = 6, it was around 200nm long; however, at pH = 8, it was more fragmented and shorter, measuring size was approximately 187.5nm. The results showed that the terbium phosphate monohydrate had nano structure and size (Fig. 5 and Fig. 6).

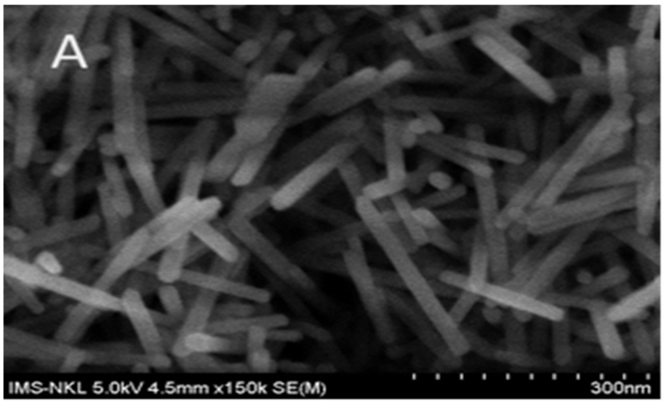

Fig. 5. SEM images of $TbPO_4.H_2O$ nanorods at pH = 6 (A)

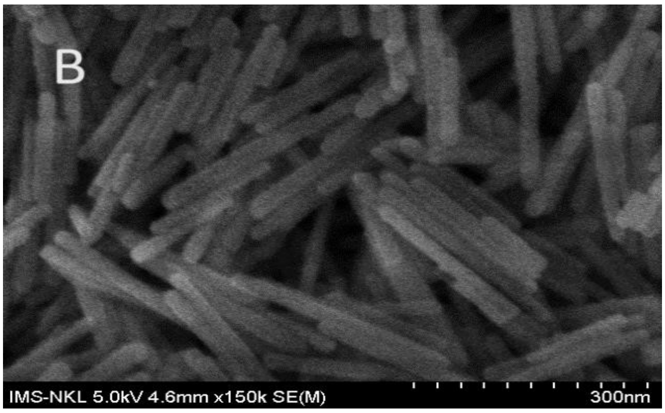

Fig. 6. SEM images of $TbPO_4.H_2O$ nanorods at pH = 8 (B)

3.3. Determination of light emission ability of product $TbPO_4.H_2O$

The measurement result of the light emission ability of product $TbPO_4.H_2O$ is shown in Fig. 7.

The photoluminescence spectroscopy of obtained experimental product was mesured to examine its fluorescent property. For each sample, there were 4 peaks in which the highest was at around 550 nanometres. The intensity of the pH = 6 sample was overall weaker than that of pH = 8. Compared to the visible light spectrum, the terbium phosphate monohydrate mainly was emited the green light.

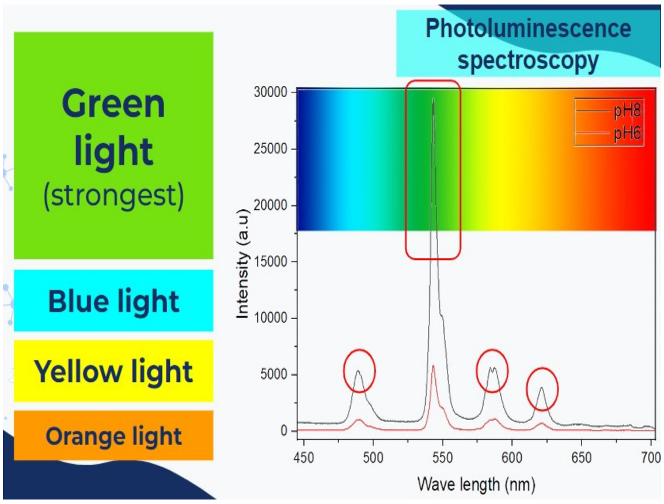

Fig. 7. Photoluminescence spectroscopy of $TbPO_4.H_2O$ nanorods

4. CONCLUSION

The synthesizing $TbPO_4.H_2O$ nanorods was conducted, using the hydrothermal method at the Center for Nano Science and Technology at Hanoi University of Education, Vietnam National University. The products was with properties suitable for optical bioimaging, At the nano level, $TbPO_4.H_2O$ had a rod diameter of 20nm and a length of 187.5nm (pH = 8) or 200nm (pH = 6). The $TbPO_4.H_2O$ was emited green light at a wavelength of 550nm, which was more potent at pH = 8 than at pH = 6.

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