Amines functionalized upconversion nanoparticles synthesis

Chapter 1

Introduction

1. Introduction

To cure deadly disease such as cancer, significant endeavors have been done in synthesizing nanomaterials (Xue et al., 2011). Ideal nanoparticle system will own multimodality for imaging and therapy. It will carry out as an excellent bioprobes to find disease site and as a carriers to target cells. In biomedical field, they have been demonstrated to be useful in immunoassays, gene assays, and photodynamic therapy.

For this application, utilization of upconversion luminescence (UCL) emission is favorable (Zhou et al., 2013). Upconversion luminescence is a process where low energy light is converted to higher energy light through sequential absorption of multiple photons induced by low power continuous wave laser. The utilization of near infrared (NIR) laser to induced the multiple photons energy transfer impart to the minimization of auto-fluorescence, less damage to cells, and larger penetration depth compete with ultraviolet (UV) excitation (Shen et al., 2012).

Inorganic rare earth (RE) (lanthanide) nanomaterials lately have been exposed to be most preferred luminescent biolabels, due to the rigid crystal host lattice maintain the emitting RE dopants from environmental effects. Furthermore, lanthanide ions are acknowledged to show efficient upconversion luminescence.

Inorganic crystals do not exhibit upconversion luminescence at room temperature. The upconversion phenomena particularly takes place in singly or multiply doped host systems. Therefore, researches focus on materials that composed of a crystalline host and RE dopants attached to the host lattice in low concentration.

Behave as multipurpose bioprobes implemented in nanomedicine, upconversion nanoparticles (UCNP) should be come up with uniform size and morphology, water soluble, and appropriate surface functional group for bioconjugation as well as high luminescent efficiency (Sun et al., 2014; Li et al., 2010). To fulfil these requirements, many attempts have been allocated to the controlled synthesis.

2. Previous Study

Kramer et al. (2004) reported the successful preparation of hexagonal sodium yttrium fluoride based green and blue emitting upconversion phosphors. The acquired phosphor materials reveal no deterioration under high-power infrared laser excitation.

Li et al. (2008) prepared hexagonal phase NaYF4: Yb, Er/Tm nanocrystal with a “ user-friendly” method by constructing small solid-state crystal nuclei and further growth and ripening of the nuclei. All the nanocrystals revealed strong upconversion fluorescence.

Li et al. (2008) reported successful preparation of multicolor core/shell-structured upconversion fluorescent nanoparticles. This was the first report in the field using such nanoparticles for bioimaging. In this work, uniform hexagonal-phase $NaYF_4$ nanospheres with strong upconversion fluorescence and core/shell silica/$NaYF_4$ structures are produced, with uniform silica coating on the surface.

Jalil et al. (2008) synthesized uniform silica coated hexagonal phase $NaYF_4$ nanocrystal with strong NIR to visible upconversion fluorescence. The results from this study revealed that the silica coated $NaYF_4$ upconversion nanocrystals displayed good in vitro and in vivo biocompatibility, demonstrating their potential applications in both cellular and animal imaging systems.

Hu et al. (2009) prepared uniform silica-coated $NaYF_4$: 20 mol% Yb, 2 mol% Er nanocomposites with good dispersibility, containing organic dye incorporated in the silica shell and folic acid conjugated on the surface of the shell. The core–shell nanocomposites are 20–22 nm in size, water soluble, and buffer stable, with good photostability and biocompatibility.

Garcia et al. (2012) prepared a novel strategy for the therapeutic delivery of nitric oxide to physiological target. They demonstrated the use of upconverting nanoparticles to facilitate NO uncaging from a well characterized precursor by 980 nm irradiation from a simple NIR diode laser operating in the continuous mode.

Chien et al. (2013) formulated upconversion nanoparticles (UCNPs) as the NIR-triggered targeting and drug delivery vehicles that successfully deliver in vitro and in vivo for near-infrared light photocontrolled targeting, bioimaging, and chemotherapy.

3. Problem Statement

As described previously, UCNPs are considered as useful biomaterials in biomedical application. The unique properties of UCNPs have given interest to many researchers to functionalize the surface for biological usage.

A sort of method to synthesize UCNPs have been evolved. There are three common methods usually used, co-precipitation (Yi et al., 2004), thermal decomposition (Li et al., 2008), and hydro(solvo)thermal (Liu et al., 2007). Thermal decomposition is the best technique to obtain highly monodisperse UCNPs. In this method, rare earth (RE) trifluoroacetates are heated to attain thermal equilibrium in the presence of oleic acid and octadecene. Here, oleic acid function as a stabilizing agent to terminate particle agglomeration, while octadecene behave as a high boiling point solvent (Boyer et al., 2006). The oleic acid forms a coordinate bond to the surface of particles, so causing it hydrophobic. UCNP prepared via thermal decomposition is well dispersed in organic solvents such as cyclohexane but insoluble in aqueous solution.

If employed in biosciences, UCNPs particularly are implemented in aqueous solution. Therefore, they have to be dispersible in water. To make it water dispersible, we need to modify the surface of upconversion nanoparticle. A common method to make it water dispersible is by coating with silica layer (Li et al., 2008).

In order to be applicable in affinity assays and bioassays, the surface of UCNPs has to be functionalized to facilitate covalent immobilization of appropriate biomolecules. Such surface chemistry is expected to be versatile to facilitate immobilization of proteins, receptors, enzymes, or nucleic acid oligomers. Therefore, here we studied about the surface functionalization of upconversion nanoparticles for biological usage.

4. Research Objectives

In this study, amines functionalized upconversion nanoparticles were synthesized using stober process with hydrothermal treatment to enhance the amines stability on the surface. The size and zeta potential of particles are characterized by using dynamic light scattering in various solvent. The morphology of particles are characterized by transmission electron microscopy (TEM). The amines substitution level and amines stability on the surface is characterized by using fluorescamines assay in various solvent.