

Fluorescence lifetime studies of Au@TiO₂ core-shell nanoparticles

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Abstract:

In many studies, this core-shell nanoparticles used as a photosensitizers in PDT. Fluorescence emission of the photosensitizer has been considered as a good candidate to reflect local drug concentration in PDT. In this present work, we synthesised Au@TiO₂ core-shell nanoparticles were synthesised and fluorescence lifetime studies of Au@TiO₂ core-shell nanoparticles were studied in different solvents.

Keywords: Core-shell nanoparticles, Synthesis, Fluorescence lifetime studies.

Introduction

Gold nanoparticles are one of the best optical limiters known so far. However, at high intensities, these are susceptible to damage, leading to photofragmentation, ligand desorption, etc., [1,2]. To make these stable at extreme conditions, it is necessary to protect them with a more stable and chemically inert shell such as oxides. Since then supported gold nanoparticles have drawn the interest of researchers. The factors that affect the catalytic activity of gold are: size of nanoparticles [3], preparation method [4], oxidation state of Au in the catalyst [5], pretreatment of the catalyst [6] and the nature of support among others [7]. However, the key factors that are believed to convert the 'inert gold' into a highly active catalyst are the size of gold nanoparticles and the metal-support interaction [8].

In recent years gold nanoparticles coated with TiO₂ semiconductor nanoparticles are increasing, because TiO₂ has proven to be the most suitable for widespread environment application for its high chemical stability, non-toxicity, low cost and excellent degradation of organic pollutants [9-12]. TiO₂ nanoparticles are easy to attach to the cell membranes and accumulate [13]. The incorporation of gold nanoparticles on TiO₂ can form a Schottky barrier at

the interface, which serves as an electron trap. Hence, the electron-hole recombination rate in the gold-titania (Au/TiO_2) composites can be decreased, leading to an improvement in biological efficiency [14,15]. Additionally, the plasmon effect of gold nanoparticles benefits the light absorption in the visible range [16].

A variety of synthesis approaches, including photo-reduction [17], co-precipitation [18], deposition-precipitation [19], chemical reduction [20], sol-gel routes [21] and flame spray pyrolysis techniques [22-29] have been investigated to prepare Au@TiO_2 composite materials.

In the current study, we prepared the Au@TiO_2 core-shell nanoparticles in one - pot synthesis method, which is simple and time consuming and fluorescence lifetime studies of Au@TiO_2 core-shell nanoparticles were studied in different solvents [30-35].

Experimental section

Materials and methods

Reagents

Titanium (IV) isopropoxide was purchased from Sigma Aldrich. Tetrachloro auric acid was obtained from CDH chemicals. Milli-Q- water was used [36-41].

Synthesis of Au@TiO_2 core-shell nanoparticles

The core-shell type Au@TiO_2 was prepared by slight modification of the method described in the literature [42-45]. 20mM each of Ti (IV) isopropoxide and acetylacetone in 30ml of isopropanol was sonicated for 15 min. 10mM solution of $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ in 5ml of milli-Q water was prepared and 20ml of DMF was added to it and stirred well. To this solution 30ml of the above said sonicated solution was added and stirring continued for another 10 min. The final mixture was refluxed between 60 and 70°C for 1 hr. The solution became pink and the refluxing was continued for another 1 hr. It resulted in the formation of a precipitate which was sonicated for 2 hrs to disperse. On adding toluene the colloidal material was precipitated, which was

washed several times with toluene and redissolved in isopropanol. The solvent was evaporated at room temperature to get a red powder of Au@TiO₂ core-shell nanoparticles.

Time-correlated single-photon counting (TCSPC)

Time-correlated single-photon counting (TCSPC) is a well established and a common technique for fluorescence lifetime measurements, it is also becoming increasingly important for photon migration measurements, optical time domain reflectometry measurements and time of flight measurements.

Generally, one of the inputs to the TCSPC electronics (either START and STOP) will be a pulse generated by a single photon. Single photons can be detected by photodetectors with intrinsically high gain. The majority of those photodetectors is photomultipliers or micro-channel plate photomultipliers, but also single photon avalanche photodiodes. For statistical reasons it is important to ensure no more than one single photon event per light flash is detected. Multi-photon events will affect the histogram statistics and will yield to erroneous measurement results. (This is known in literature as the “pulse pile-up problem”). In order to ensure that only one photon per light flash is detected the photon rate is kept low in comparison to the rate of the exciting lamp; usually 5% or lower.

Result and Discussion

Fluorescence emission spectrum of Au@TiO₂ core-shell nanoparticles

Photoluminescence spectroscopy is one of the most powerful techniques to investigate the exciton structures. The fluorescence spectrum of Au@TiO₂ is illustrated in Fig.1. Fluorescence gives a maximum of 650 nm. Since the absorption maximum of Au@TiO₂ occurs at 570 nm in the UV-Visible spectrum the excitation of Au@TiO₂ nanoparticles was also carried out at 570 nm. The spectrum shows a emission maximum around 650 nm (Fig. 1).

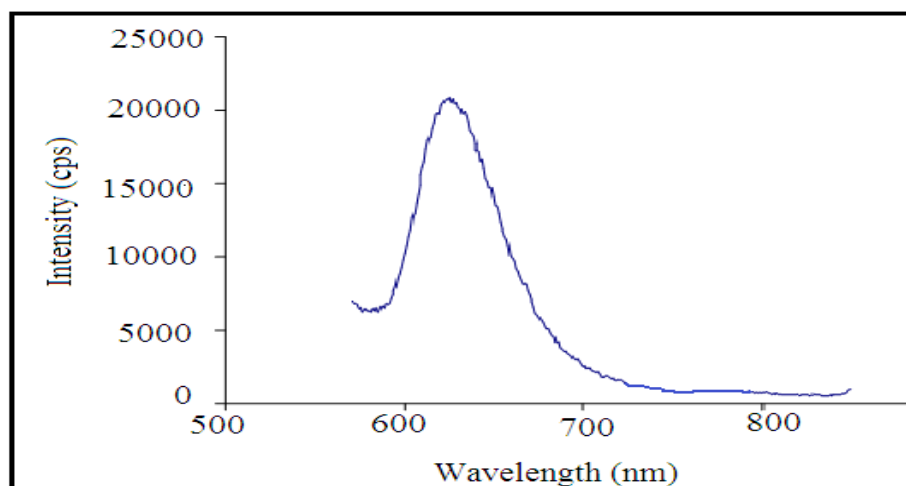


Fig.7.2 Fluorescence emission spectrum of Au@TiO₂ core-shell NPs

Fluorescence lifetime studies of Au@TiO₂ core-shell nanoparticles

All the colloidal suspensions used for this investigation were of uniform concentrations of 100 µg/ml of Au@TiO₂ core-shell nanoparticles in solvents of different polarity. Seven solvents including water and series of alcohols were used. Each observed curve is a combination of biexponential curves for the air dried Au@TiO₂ nanoparticles in different solvent environments. The lifetime and respective amplitudes, and average lifetime are shown in Table1. As in the case of Ag@TiO₂ and Ag@ZrO₂ nanoparticles the lifetime increases from water to ethanol, but it decreased on going to isopropanol. In the case of butanol and octanol the fluorescence lifetime are very short i.e., below nano seconds, which could not be detected by the instrument. Fig.2. (a-e) show the fluorescence decay curves of Au@TiO₂-NPs in the above said solvents.

Table 1 Fluorescence lifetime (ns) of Au@TiO₂ core-shell NPs

Solvent	Viscosity	Dielectric constant	τ_1(ns)	τ_2(ns)	Fluorescence lifetime(ns)
Double distilled water	0.89	78.54	15.61	7.79	11.70
PBS	-	-	14.14	5.02	9.58
Methanol	0.544	32.63	19.76	8.61	14.18
Ethanol	1.094	24.30	18.81	40.07	29.44
iso-Propanol	2.038	18.30	13.08	5.46	9.27
n-Butanol	2.544	17.84	-	-	-
n-Octanol	7.288	10.30	-	-	-

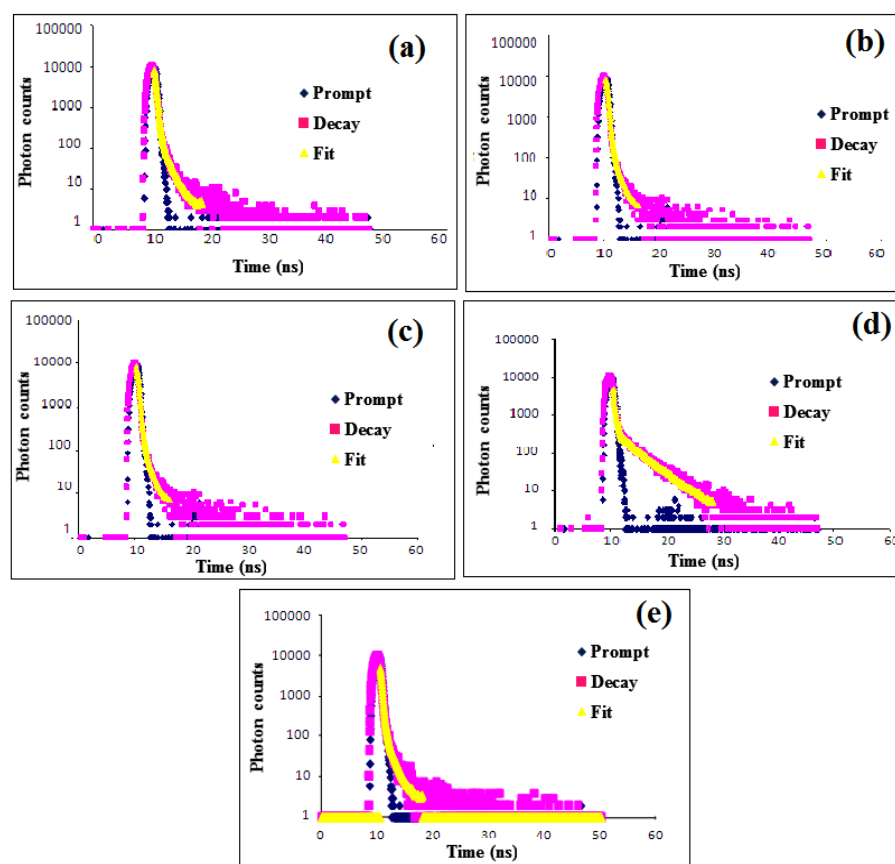


Fig. 7.2. Fluorescence decay curves of Au@TiO₂-NPs in a) water b) PBS
c) methanol d) ethanol e) isopropanol

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