

Fluorescence lifetime studies of Ag@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 are synthesised Ag@TiO₂ core-shell nanoparticles were synthesised and fluorescence lifetime studies of Ag@TiO₂ core-shell nanoparticles were studied in different solvents.

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

Introduction

Metal oxide semiconductor nanoparticles have attracted extensive attention due to its wide potential applications. Among the various semiconductor oxide photocatalysts, titanium dioxide (TiO₂) has gained much interest. However, it lacks its efficiency due to high band gap and low quantum yield. As one of the application of TiO₂ nanoparticle photocatalysts, there is a report that suggested the photokilling property by photoexcited TiO₂, which can be used in the biology application, especially in the field of cancer treatment [1]. When TiO₂ absorbs the light with energy higher than its band-gap energy in the UV region, holes and electrons are generated. The photogenerated holes and electrons have the oxidation and reduction properties respectively, which can cause various photocatalytic reactions [2-6]. The reaction between the oxygen and electrons in the conduction band of TiO₂ can produce reactive oxygen species, which can destroy the structure of cancerous cells. The photokilling property of TiO₂ made it possible to utilize TiO₂ in the photodynamic therapy as a photosensitizer. TiO₂ however, has a disadvantage of being excited only in the UV light region, but UV light cannot penetrate into the biological tissues deeply.

As we know, silver nanoparticles have very nice absorption ability in the visible light region because of the surface plasmon oscillation. Contact of silver and TiO_2 can form the metal-semiconductor Schottky junction [7, 8], which can possibly make the charge separation lifetime long, if electron transfer occurs from silver to TiO_2 . Electron collective motion in silver nanoparticles may enhance the electric field between silver and TiO_2 , which may enlarge the electron density in TiO_2 making the electron transfer efficiency higher. The nice absorption property of silver spherical nanoparticles will make bioapplication of silver- TiO_2 systems possible and interesting utilization of visible light, because the visible light can easily penetrate into biological tissues. As a result, the electrons in the TiO_2 can react with oxygen to generate reactive oxygen species, which may kill cancer cells [9-12].

Based on the above concerns, Ag@TiO_2 core-shell nanoparticles were synthesized by one-pot method and fluorescence lifetime was studied.

Experimental section

Materials and methods

Reagents

Titanium (IV) isopropoxide was purchased from Sigma Aldrich. AgNO_3 was obtained from Merck and all the other chemicals used were of Analar grade. Milli-Q water was used.

Synthesis of Ag@TiO_2 core-shell nanoparticles

The core-shell type Ag@TiO_2 nanoparticles were prepared by slight modification of the method described in the literature [13-19]. In brief 20mM each of Ti (IV) isopropoxide and acetylacetone in 30ml of isopropanol was prepared by sonicating the mixture for 15 min. 10mM solution of AgNO_3 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 sonicated solution was added and stirring continued for 10 more minutes. The final mixture was refluxed between 60 and 70 °C for 1 hr. The solution became greenish black. The refluxing was continued for 1 more hr. The precipitate obtained was sonicated for 2 hrs to disperse. On adding toluene the colloidal material was precipitated and washed several times with toluene and redissolved in isopropanol [20-26]. The

solvent was evaporated at room temperature to get a greenish black powder of Ag@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[27-31], 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[32-39].

Result and Discussion

Fluorescence lifetime studies

Photoluminescence lifetime measurement was carried out using time correlated single photon counting technique and the samples were excited at 430nm. The measurements were made on solutions with a uniform concentration of 100 µg/ml of Ag@TiO₂ core-shell nanoparticles in solvents of different polarity. Totally seven solvents of different polarity ranging from double distilled water to n-octanol were used[40-45]. Each observed decay curve is a combination of two exponential curves for the air dried Ag@TiO₂ nanoparticles in different solvent environments. The lifetime and the respective relative amplitudes and average lifetime are shown in Table.1 The relative amplitude indicates the relative abundance of different sizes of grains. Fig.1. shows the fluorescence spectra of Ag@TiO₂-NPs in different solvents ranging

from water to alcohols. There is a shift in the emission maxima, hence the solvent polarity might play significant role in the emission properties of Ag@TiO₂-NPs. Fig.2(a-g) shows the fluorescence decay curves of Ag@TiO₂-NPs in the above said solvent.

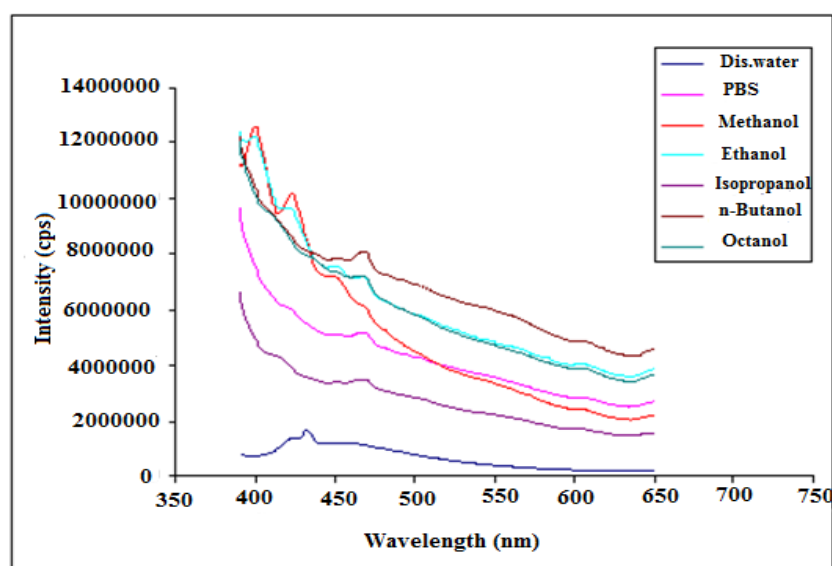


Fig.1. Fluorescence emission spectrum of Ag@TiO₂ core-shell NPs in different solvents

A number of earlier reports have examined the influence of the solvent environment on xanthene dye [14] photophysics but almost no such study was reported using core-shell nanoparticles. Hence, the influence of solvent environment on the fluorescence lifetime of Ag@TiO₂ core-shell nanoparticles was studied. In xanthene dyes shortest lifetime was observed in the water and increased along the series of higher alcohols. Unlike dyes, in the case of nanoparticles whose optical properties are entirely different a variation of fluorescence lifetime was observed with dielectric constant of the solvent. The lifetime increases from water to ethanol, but it decreases in isopropanol and then increases slightly even though the dielectric constant decreases from water to higher alcohols. This discrepancy may be due to the use of colloidal suspension of nanoparticles since they are not completely soluble in alcohols.

Table 1.1 Fluorescence lifetime (ns) of Ag@TiO₂ core-shell NPs

Solvent	Viscosity	Dielectric constant	τ_1(ns)	τ_2(ns)	Fluorescence lifetime(ns)
Double distilled water	0.89	78.54	12.35	1.78	7.06
PBS	-	-	13.35	1.87	7.61
Methanol	0.544	32.63	14.33	7.00	10.66
Ethanol	1.094	24.30	14.99	9.45	12.22
iso-Propanol	2.038	18.30	14.88	5.49	10.18
n-Butanol	2.544	17.84	13.62	15.86	14.74
n-Octanol	7.288	10.30	13.62	9.24	11.43

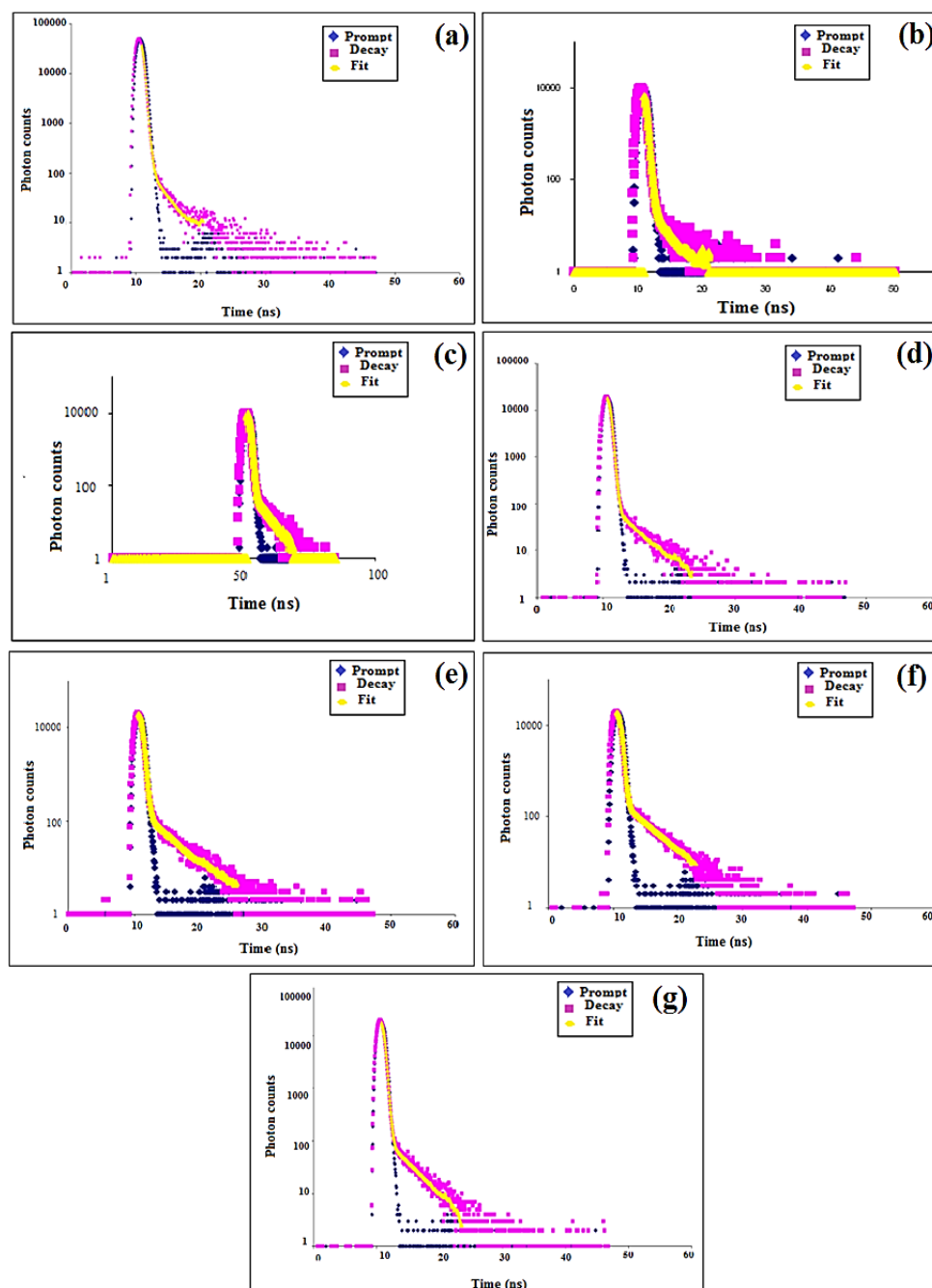


Fig.2.Fluorescence decay curves of Ag@TiO₂ core-shell NPs in a)water b)PBS c)methanol d)ethanol e)isopropanol f) n-butanol g) n-octanol

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