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Monitoring the binding of serotonin to silver nanoparticles: A fluorescence spectroscopic investigation

Bikash Chandra Swain[a], Padmaja Prasad Mishra[b], Hirdyesh Mishra[c], Umakanta Tripathy[a,*]

[a] Department of Applied Physics, Indian Institute of Technology (Indian School of Mines), Dhanbad, 826004, Jharkhand, India
[b] Chemical Sciences Division, Saha Institute of Nuclear Physics, 1/AF Bidhannagar, Kolkata, 700064, West Bengal, India
[c] Department of Physics, MMV, Banaras Hindu University, Varanasi, 221005, India

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ABSTRACT

Serotonin (5-HT) is an important monoamine neurotransmitter that plays a vital role in the regulation of various cognitive and behavioural functions including sleep, mood, pain, depression, anxiety, aggression, learning etc. From the nanotoxicity and neurotoxicity point of view, interaction studies between serotonin and nanoparticles are highly essential to develop an indispensable understanding on the effect of nanoparticles on monoamine neurotransmitters. In the present work, steady-state and time-domain fluorescence measurements were carried out along with binding energy measurements through X-ray photoelectron spectroscopic (XPS) technique to understand the interaction of 5-HT with silver nanoparticles (AgNPs). The emergence of a week red absorption band and quenching of fluorescence intensity along with decrease in full width half maximum, but not the excited state decay time of 5-HT in the addition of AgNPs suggest the formation of a non-fluorescent complex in the ground state that indicates static quenching along with radiative energy transfer among them. This is also confirmed by the low energy shift of Ag transition in $^3d_{3/2}$ and $^3d_{5/2}$ in XPS measurements and a coupling of L_b transition with the surface plasmons of AgNPs in the excitation spectra. The obtained thermodynamic parameters from the fluorescence quenching reveal the nature of interaction between 5-HT and AgNPs is hydrophobic. The increase in binding constant with increasing temperature suggested an enhancement in the strength of this interaction due to rise in the mobility of the molecules and hence increases the sensitivity and association of 5-HT with AgNPs.

1. Introduction

The widely studied metal-nanoparticles represent an admirable biocompatibility and hence, the combination of nanoparticles with biological relevant molecules is a rapidly growing research field at the crossroads of materials science, nanoscience, and molecular biotechnology [1–4]. The unique chemical and physical properties of such hybrid materials lead to the invention of nanoelectronic devices [5,6], and allow promising applications in other fields such as biosensors [7], biomedical including diagnostic & therapeutic treatment of diseases [8,9], detection of pathogenic agents [10,11], drug delivery etc. [12–15]. This is already having an impact in bioanalysis, where nanoparticles of various sizes, shapes, and compositions are being used to replace “traditional” bioanalysis schemes. Additionally, the localization or propagation of the so-called surface plasmon resonance (SPR) of the nanoparticles also strongly depends upon the dimensionality of the nanostructured materials. The collective oscillation of conduction electrons at the metal surface regulates the confinement of light, which is responsible for the peculiar optoelectronic properties of such nanomaterials. Their absorption band can be tuned by changing the size and shape of nanoparticles. Metallic nanoparticles like silver, gold and copper show localized surface plasmon resonance property and also used in fluorescence enhancement [16,17]. As the damping processes of nanoparticle plasmons have contribution of radiative and non-radiative processes, any excited fluorophore during interaction can transfer energy to nearby metal nanoparticles to create surface plasmon modes. If the excited fluorophore is coupled to the dipole mode of the nanoparticle, the plasmons decay like both radiatively and non-radiatively; if it is coupled to the high-order modes, they dissipate energy only non-radiatively. Many theoretical and experimental studies have been reported on the energy transfer rate from a fluorophore to a metal nanoparticle leading to the fluorescence quenching [18,19].

There is equally an increased concern about the impact of nanoparticles (NPs) in the environment due to their inevitable release and

* Corresponding author.
E-mail address: utripathy@iitism.ac.in (U. Tripathy).

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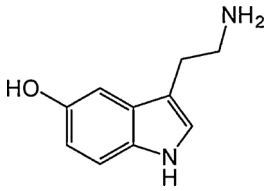

Scheme 1. Chemical structure of Serotonin.

accumulation [20]. As nanosized particles have presented toxicity in a variety of organisms, these nanoparticles may constitute a toxicological risk being generally more toxic than larger particles (bulk) [21]. With the increased application of nanomaterials in the biomedical field, the interaction of nanomaterials with bio-molecules is very important because of their induced cytotoxicity that would alter some specific biological functions in living systems [22].

Serotonin (5-hydroxytryptamine, or 5-HT) is a biogenic mono amine that acts as a neurotransmitter in the central and peripheral nervous systems [23]. The chemical structure of serotonin is shown in Scheme 1. It is present in a variety of organisms, ranging from humans to species having primitive nervous systems [24], and mediates a variety of physiological responses in distinct cell types. It is believed to be involved in the regulation of various cognitive and behavioural functions, including sleep, mood, pain, depression, anxiety, aggression, and learning [25–28]. Disruptions in serotonergic systems have been implicated as a critical factor in mental disorders such as schizophrenia, depression, infantile autism, and obsessive compulsive disorder etc. [29].

With addition to the reports describing interaction of proteins (like BSA and Lysozyme) with nanoparticles and drugs; there arealso reportsregarding interactionsof one of the monoamine neurotransmitter, dopamine with nanoparticles [30–33]. In addition, Özel et al. have studied the effect of cerium oxide nanoparticles on 5-HT both *in-vitro* and *in-vivo* in zebrafish embryos [34]. Their *in-vitro* study suggested a strong binding of 5-HT with cerium oxide nanoparticles whereas a depletion in intestinal 5-HT level leading to neurotoxic effect of cerium oxide nanoparticles in Zebrafish was found through *in-vivo* measurements. However, the interaction of serotonin with one of the transition metal nanoparticles *i.e.*silver nanoparticles (AgNPs) is not yet reported. Therefore, in this study, we have attempted to monitor the interaction and binding parameters between 5-HT and AgNPs. Being an important neurotransmitter, the binding of metallic nanoparticles with serotonin has important implication for safe clinical application of nanoparticles in neurotoxicity point of view. This may find application in drug delivery as well as in the detection of monoamine neurotransmitters [35,36]. We have used different spectroscopic techniques (steady-state & time-resolved fluorescence spectroscopy, and X-ray photoelectron spectroscopy (XPS)) to study the interaction of 5-HT with AgNPs.

2. Materials and methods

2.1. Reagents

Sodium borohydride ($NaBH_4$), Silver nitrate ($AgNO_3$) and Polyvinylpyrrolidone (PVP) was purchased from Sigma Chemical Company, St. Louis, USA. Serotonin hydrochloride ($C_{10}H_{12}N_2O.HCl$) was purchased from TCI chemicals, Tokyo, Japan. All the chemicals were used as received. Mili Q water was used during all experiments.

2.2. Synthesis and sample preparation

Silver nanoparticles were synthesized by chemical reduction method [37,38]. In brief, 10 ml of 1 mM silver nitrate ($AgNO_3$) solution was added to 30 ml of 2 mM sodium borohydride ($NaBH_4$) solution with stirring. The stirring was stopped after all the silver nitrate solution was added. Then 1 ml of 0.3% PVP solution was added to silver nanoparticles solution to prevent aggregation. The synthesized silver nanoparticles were yellow in colour. To observe interaction of 5-HT with AgNPs, different samples were prepared by mixing different concentration of AgNPs to 5-HT solution. The average size of the synthesized AgNPs was found to be 8.7 ± 1.7 nm by analyzing 300 spheres in the transmission electron microscope (TEM) image of AgNPs (Fig. 1(a)). The size distribution of the nanoparticles is shown in Fig. 1(b). The concentration of the as prepared silver nanoparticles was estimated [39] to be ~186 nM. pH of the serotonin solution, silver nanoparticles and serotonin in presence of silver nanoparticles were 7.5, 9, and 8.5, respectively.

2.3. Methods

5-HT and synthesized AgNPs were characterized by steady-state and time-resolved spectroscopic techniques and XPS studies. The absorbance of synthesized silver nanoparticles and 5HT was taken by a dual beamSpectrophotometer (Jasco V-750, Japan) with a 1 cm path length quartz cuvette by ratio recording method. The steady-state fluorescence spectrum was measured by a Spectrofluorometer (QM-400, PTI, Horiba, Canada) by using 1 cm path length quartz cuvette at 288 K, 298 K, & 308 K with excitation at 280 nm. All figures presenting fluorescence and excitation data in this manuscript were corrected for inner filter effect.The time-resolved fluorescence measurements were taken by using time-correlated single photon counting (TCSPC) system (Jobin Yuvon, Horiba) at 295 nm excitation. The transmission electron

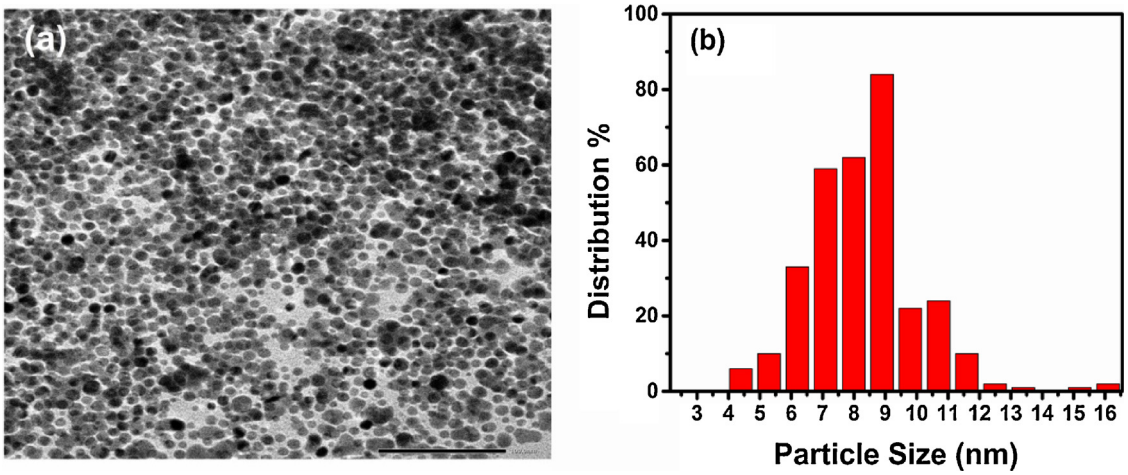

Fig. 1. (a) TEM image of synthesized silver nanoparticles (The scale bar is 100 nm). (b) Size distribution of the nanoparticles.