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Full Length Article

Unsupported platinum nanoparticles as effective sensors of neurotransmitters and possible drug curriers

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ABSTRACT

Herein, surface-enhanced Raman scattering (SERS) activity of positively charged unsupported platinum nanoparticles (PtNPs) with ~12 nm size and narrow size distribution, in an aqueous solution, towards neurotransmitters was monitored at 785 nm excitation wavelength. The pure PtNPs were synthetized by polyol method. Their morphology and structure were checked by scanning electron microscopy (SEM) and X-ray diffraction spectroscopy (XRD) measurements. As a neurotransmitter bombesin (BN), which exhibits autocrine effect on the growth of normal and tumour tissues, and its fragments from the *C*-terminal end: BN^{13-14}, BN^{12-14}, BN^{11-14}, BN^{10-14}, BN^{9-14}, and BN^{8-14} (X-14 fragments of the BN amino acid sequence) were chosen. The collected spectra were interpreted and discussed. This is to determine the adsorption mode of bombesin onto the PtNPs surface and changes in this mode as a result of the bombesin backbone shortening from the *N*-terminal end. This is important from the point of using PtNPs as potential BN carrier into the cancerous tissue and antitumor drug.

1. Introduction

Metal nanoparticles (NPs) are known from antiquity, where they were used to decorate [1]. Nowadays, interest in them continues unabated. Just the opposite, they are the subject of numerous studies due to their pronounced surface sensitivity, low cost, and easy-to-use [2,3]. Thus, nanometer-sized metallic shapes found various applications in catalysis, optics, electronics, and biological and medical sciences as well as for sensing, cosmetics, high density information storage devices, and energy conversion [4–6].

Heterogeneous catalysis is probably the most important area of commercial applications of the metal nanoparticles, where platinum (PtNPs) and platinum-containing nanoparticles, the most stable of all know forms of platinum, are widely used to form commercial catalysts. PtNPs in the blood of humans and animals are also active as catalysts, namely they very effectively support the process of catalytic destruction of cancer cells; e.g. leukemia, without negative symptoms. They show several times higher efficiency than platinum compounds. This is due to the combination of a large active surface with a special form of monocrystalline particles [7]. Surface chemistry of NPs has also opened up prospects for targeting and differentiating tissues by adsorption of specific molecules, enabling the development of radioisotopes for cancer radiotherapy with X-rays [8]. On the other hand, the optical properties in the infrared range have encouraged the development of new technics, such as photodiagnostic and photothermic therapy [9].

Such industrial/biological catalysts should possess the high activity and surface selectivity. Therefore, studies on the adsorption; particularly, in condensed-phase environments wherein bulk solution species assemble at solid/solution interfaces, are important for determining the adsorbed species, their orientation relatively to the surface of metal, and the changes in the strength of the chemical bonds upon adsorption. One of the methods examining the adsorption at solid/liquid interface is surface-enhanced Raman scattering (SERS).

The SERS effect can be seen for molecules in the vicinity of resonators formed from metal nanoparticles. This is because smooth surfaces of metals do not show the effect of SERS as the conversion of energy and momentum between photons and surface plasmons are not fulfilled. The high efficiency of Raman scattering primarily arises from the local amplification of the electric field of the incident electromagnetic wave [10–13], which strongly dependents on surface morphology of metal [14,15]. This local field strengthening results from the excitation of collective oscillations of metal electrons (surface plasmons) by the incident radiation [10–13]. The

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local electric field assumes a large value only when the imaginary part of the dielectric constant of the metal adopts small values at the resonance conditions and when the real part of the dielectric constant of the metal is close to a double negative real part of the dielectric constant of the surrounding environment [11]. For the incident electromagnetic radiation in the visible range, strong SERS effect (enhancement factor up to 10^6 or more) can be obtained on a few metal substrates, like silver, gold and copper, which exhibit high optical reflectivity [10–13].

Initially, transition metals, commonly considered to be non-SERS-active [16,17], like platinum, were used for SERS experiments with an ultraviolet excitation [18,19]. An alternative strategy for obtaining intense SERS spectra on platinum nanostructured substrates is borrowing the enhancement of a closely adjacent nanometer-rough surface of silver or gold. Although one should note that a thin platinum layer may have different electronic properties from those of bulk platinum [20–22]. In this approach, the enhanced field of the rough surface of coinage metal penetrates to the transition metal-aqueous interface, where SERS is excited. Therefore, Weaver and co-workers have used gold substrates coated with a very thin platinum "pinholes free" film (2 atomic layers) [23,24]. Tian et al. have showed the SERS spectra of pyridine immobilized on active core-shell Au-Pt clusters with platinum "pinholes free" shells [25,26] and on platinum surface with gold nanoparticles isolated with very thin shell layer of SiO_2 or Al_2O_3 [25]. Zhao and his colleagues have presented the SERS spectrum of rhodamine B on manipulate Pt-flecks on silver nanoparticles [27]. Jiang et al. have adsorbed water on Pt surface [28], whereas Freunscht and co-workers have measured *trans*-stilbene on platinum modified silver film [29]. Also, Kudelski at al. have demonstrated the SERS effect for mercaptobenzoic acid monolayer on platinum covered with solid and hollow nanoparticles of Au [30]. On the other hand, Creighton has shown SERS results for hydrogen cyanide (HCN) on silver film with platinum over-layers [31].

The application of the excitation in the visible range for measurements of adsorbates on unsupported platinum has been shown for small and/or highly symmetric molecules by a few researchers, only. As we know, until now, Hahn and Melendres have investigated the mechanism of methanol oxidation on platinum electrode [32]. Kim & Kim used platinum nanoaggregates for the adsorption of benzenethiol [33], whereas Bartlett et al. have deposited the same compound on sphere templated Pt films of different thickness [16]. Ikeda et al. have measured self-assembled monolayers of 4-chlorophenyl-isocyanate on single crystalline atomically flat Pt(111) and Pt(100) [34]. Tian et al. have demonstrated SERS utility for pyridine adsorbed on rough platinum electrode [35], whereas Wu et al. have deposited pyridine on platinum microparticles [36]. Li and co-workers have presented the high resolution SERS spectra of water on platinum nanoparticles [37]. Popp and colleagues have reported melamine on PtNPs [18]. Additionally, in the literature it can be found some other SERS reports for acetonitrile (CH_3CN), ethylene ($CH_2 = CH_2$), perchloric acid ($HClO_4$), and carbon monoxide (CO) assembled on platinum [38,39].

To be able to effectively use SERS the compounds under the investigations should readily adsorb on nanostructured metallic surface, prepared in the procedure allowing to obtain reproducible roughened metallic surfaces or sols with uniform particle size, which exhibit a large electromagnetic enhancement [40–42], as well as Raman excitation wavelength should be close to the surface plasmon oscillations. This means that the choice of the excitation line depends on the choice of metal type. The first condition will be satisfied when selecting well scattering molecules consisting of aromatic ring or reach in lone-pairs of electrons. Additionally, there are developed procedures for reproducible SERS substrates and metal such as platinum increases the amount of adsorbate. However, it should be aware that platinum shows catalytic activity, which can lead to products of catalysis as was shown by Feilchenfeld and Weaver for acetylene [43].

Taking into account the properties of platinum and its application in the cancer therapies we decided to use pure unsupported platinum nanoparticles, with a small size (~12 nm) and narrow size distribution, as biosensors of large (224 atoms, including 114 heavy atoms), with complicated secondary structure, neurotransmitter responsible for the growth of cancer cells in the human body. As the large physiologically active molecule, bombesin (BN) (an aminated tetradecapeptide, having the primary structure: pGlu-Gln-Arg-Leu-Gly-Asn-Gln-Trp-Ala-Val-Gly-His-Leu-MetNH_2 (where: pGlu is 5-oxo-proline and all amino acids are in L-conformation)) and its fragments from the *C*-terminal end: BN^{13-14}, BN^{12-14}, BN^{11-14}, BN^{10-14}, BN^{9-14}, and BN^{8-14} (X-14 fragment of BN amino acid sequence) were chosen. The adsorption was examined by means of SERS monitored with 785 nm laser excitation. This is to determine the adsorption mode of bombesin onto the platinum surface and changes in this mode as a result of the bombesin backbone shortening from the *N*-terminal end. Such a system (BN/PtNPs) can be selectively injected into the cancerous tissues. Therefore, can be used as a potential drug or drug carrier.

BN binds with high affinity to the bombesin subtype 3 receptors (BRS-3 or BB_3 receptors), members of the G protein-coupled receptor (GPCR) superfamily [44,45]. These receptors are widely distributed in mammals; especially, in the gastrointestinal tract and in the Central Nervous System (CNS) [46]. Through BN/BRS-3 system they trigger numerous physical and pathological process [47–49]. They have a strong influence on CNS; for instead, influence the heart rate, as well as the digestive, respiratory, urogenital, and immune systems. Importantly, they exhibit autocrine effect on the growth of normal tissues and tumors [50,51]. A number of malignant tumors over-express BRS-3 on their surface (i.e., small cell lung (SCLC) (85–100%), glioblastoma (85%), stomach, pancreatic (75%), prostate (62–100%), breast (62–91%), squamous-cell (100%), or neuroblastoma (72%) [52–54]. Thus, BN/BRS-3 system may play a role in the treatment of cancer [55,56]. Noteworthy is the fact that these receptors can be considered as biomarkers for the small cell and non-small cell lung cancers [57–59].

2. Experimental part

2.1. Compounds

Bombesin and its carboxyl terminal fragments: BN^{13-14}, BN^{12-14}, BN^{11-14}, BN^{10-14}, and BN^{9-14} (X-14 fragments of the BN amino acid sequence) were purchased from Sigma-Aldrich, Japan, whereas BN^{8-14} was purchased from Bachem Co., Switzerland. All the samples were used without further purification.

2.2. Synthesis of platinum nanoparticles

Pure unsupported platinum nanoparticles (PtNPs) were synthetized by reduction of platinum(II) chloride ($PtCl_2$) in ethylene glycol (EG) in boiling for 3 h, according to polyol method by Lewera [58]. EG was used as solvent and reducing agent for platinum nanoparticles formation. PtNPs were separated from the reaction medium by washing and centrifugation with distilled water [59,60]. The pH of the final aqueous solution of PtNPs was 7.

2.3. Ultraviolet–visible (UV–vis) spectroscopy

The UV–vis spectra (see Fig. 1) of an aqueous solution of the Pt nanoparticles and BN/PtNPs system were recorded 180 min after mixing on a Lambda 25 UV–vis spectrometer.