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Recent progress on surface chemistry of plasmonic metal nanoparticles for colorimetric assay of drugs in pharmaceutical and biological samples

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ABSTRACT

Plasmonic metal nanoparticles have been explored as a new class of chemical read-outs for assaying of a variety of chemical and biological species because of their unique physico-chemical and size dependent properties. Metal nanoparticles-based optical technologies are based on either new class of organic molecular assembly or with aggregation-induced optical changes features, which can also improve the sensitivity of drug assays in pharmaceutical analysis. This review describes the advantages of surface chemistry of plasmonic metal nanoparticles (e.g., silver, copper, gold, and platinum) for tuning of their colorimetric sensing applications in various drugs assays in pharmaceutical and biological samples. It provides insights of various plasmonic metal nanoparticles-based sensing strategies for the selective, sensitive and simultaneous colorimetric assay of drugs in pharmaceutical samples. Finally, we listed some research challenges to accelerate the development of plasmonic metal nanoparticles-based colorimetric sensors that are directly applicable for assaying drugs in pharmaceutical samples.

1. Introduction

Metal nanoparticles (metal NPs) hold unique optical and physico-chemical properties that allow to extend their role as specific and selective probes for chemical and biological detection through various signal transduction mechanisms, including electrochemical, optical, and field-effect transistor sensors [1]. Metal NPs (gold - Au, silver - Ag, copper – Cu and platinum - Pt) have hence been employed in colorimetric sensing of various chemical species including pesticides, drugs, biomolecules, metals, and anions at minimal volume of samples [2–4]. As such, metal NPs-based optical sensors have emerged as rising portable analytical devices in multidisciplinary research area including fluorescence resonance energy transfer, localized surface plasmon resonance (LSPR), surface enhanced Raman scattering, quantized charging effect and nonlinear optical properties [5,6]. Among optical properties, plasmonic (surface plasmon resonance (SPR) and LSPR) metal sensors have recently received much attention in colorimetric assaying of various chemical species because of size-dependent visual changes, simplicity, selectivity, and high sensitivity [7]. Generally, metal NPs exhibit two characteristic plasmon absorption bands that are located in the visible region as transverse localized surface plasmon resonance (transverse LSPR) band and in the near-IR region as longitudinal LSPR band [8]. Recently, two reviews have been well explained about the metal SPR properties and their sensing applications in analytical and bioanalytical sciences [9,10]. Furthermore, few reviews have also been extensively discussed about the LSPR mechanisms and the oscillations of electrons of metal NPs with electromagnetic radiation as well as their optical applications [11,12]. Analogous to the definition of metal nanosensor, a plasmonic nanosensor can be defined as a device with dimensions at

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nanometer range that is capable to detect trace level target analytes by measuring their spectral changes with the concentrations of analytes [13,14]. Recently, plasmonic sensors have emerged as a burgeoning subdiscipline of nanosensors that deals the control of light at the nanoscale based on the nature of plasmons [2–4]. To date, none of them has reviewed on the plasmonic metal NPs as probes for colorimetric assays of drugs in real samples. Thus, we intend to provide an authoritative overview on the advancements of plasmonic metal NPs-based colorimetric sensors for assaying of drugs in real samples.

In colorimetric assays, two factors play key role in improving the selectivity and sensitivity of the NPs-based colorimetric sensors. First one is the recognition ability of metal NPs probe towards target analytes *via* specific interactions. Second one is converting and measuring the signaling information from sample into optical response, causing drastic spectral changes with intense colors in the visible range (390–750 nm) [15,16]. Based on these, metal NPs-based colorimetric sensors can be divided into two types: one is the aggregation of plasmonic NPs induced by chemical species while the second one is the single particle morphology method.

Recently, the theory of LSPR, fabrication and sensing applications of metal NPs have been extensively reviewed in the literature [17–19]. Furthermore, analytical applications of plasmonic metal NPs for assaying of biomolecules have already been well illustrated in the literature [20,21]. Apart from these, a few excellent review articles have been published on plasmonic NPs-based colorimetric methods for assay of various target molecules (organic, inorganic, and biomolecules) with improved selectivity and sensitivity [3,7,22]. Therefore, this review will facilitate researchers to understand the role of surface chemistry on plasmonic metal NPs for the sensitive recognition of various drugs in pharmaceutical and biological samples. In this review, optical sensing systems using plasmonic metal NPs (Ag, Au, and Pt NPs) are emphasized based on their surface chemistry interactions with target analytes. Recent advances in the surface chemistry of plasmonic metal NPs for tuning their analytical applications for assaying of various drugs is also described to show their practicality in the pharmaceutical and biological sample analysis. Apart from these, we highlighted the potential applications of plasmonic metal NPs for colorimetric assaying of drugs in pharmaceutical and biological samples.

2. Photonics of metal NPs

Upon closer inspection of the literature, the SPR is due to the coherent oscillations of conduction band electrons in metal NPs when irradiated with electromagnetic radiation, causing polarization of electrons in metal NPs when metal NPs size is smaller than that of incident wavelength [23]. This can lead to create net charge difference on NPs surface, favoring collective oscillation of the surface electrons, which can restore force on metal NPs, known as the LSPR. Generally, noble metal NPs, especially Ag, Au, Al and Cu have exhibited LSPR properties that allows them to use as good candidates in various field of applied sciences. Importantly, nanosize (~20 nm) noble metal NPs (Ag, Au and Cu) have strong ability to absorb energy in UV–visible region because of their intraband transitions, which leads to the collective excitations of free electrons (SPR) [23]. According to the Drude theory, noble metal NPs exhibit interband transitions by jumping up electrons from occupied to empty bulk bands of different index *via* the absorption of enough optical energy. Therefore, the optical spectra of Ag NPs can be observed in between 300 (ultraviolet) to 1200 nm (near-infrared (NIR)). Further, surface plasmon strength (or damping) of noble metal NPs is proportional to the quality factor, which indicates that metal NPs with high quality factor exhibits a strong surface plasmon and with low quality factor shows a weak surface plasmon. It was noticed that Ag NPs exhibit high quality factor than that of other noble metal NPs in the spectral region of 300–1200 nm. Therefore, interband transitions of Ag NPs occur at much higher energies, yielding to appear the SPR band around 390–420 nm, which results to yellow color under visible light excitation. Similarly, these transitions limit their surface plasmon resonance excitation to wavelength >500 nm for Au NPs (cherry red color) and >600 nm for Cu NPs (red color), respectively. Furthermore, the appearance of LSPR band of metal NPs in UV–visible absorption spectra is highly dependent on the diameter of plasmonic metal NPs, since discrete energy gaps may be decreased with increasing the size [24]. In addition, the size of metal NPs can also influence the values of extinction coefficient and scattering intensity of plasmonic metal NPs to higher and stronger, respectively. The appearance of LSPR band in electromagnetic spectrum is strongly dependent on the interparticle distance of NPs through the interparticle plasmon coupling effect. Generally, plasmonic metal NPs have shown pronounced absorbance peak in visible region, and strong electromagnetic fields can polarize the local volume around the NPs, affecting resonance conditions of plasmonic metal NPs *via* various interactions at metal NPs–solution interface, which yields a shift in their LSPR band that can be measured by absorption/extinction or scattering. As a result, the red-shift in the LSPR band is due to the increasing of plasmonic NPs sizes.

Generally, plasmonic NPs exhibit brilliant colors (yellow – Ag NPs, cherry red –Au NPs, red-Cu NPs) on account of their dispersability in water and small size. In brief, two plasmon wavelengths are attributed in Au nanorods (NRs) as a consequence of the free electrons can oscillate at both the long and short axes [25]. Importantly, the longitudinal plasmon band was appeared in NIR region due to the variation in the ratio of the rods, favoring to use them as promising probes in the biological window (700–900 nm) for effective penetration of light through biocomplex samples, thereby enable to detect trace level target biomolecules with high selectivity. Additionally, the other morphologies of gold (nanostars, nanorods and nanoplates) have ability to absorb light with high degree, and exhibited higher scattering cross-section, which make them as NIR sensors [26].

Similarly, edge-length Ag triangles (100 nm) exhibit larger LSPR band than that Ag pentagons with 100 nm size (the distance between opposite corners is known as pentagon length) [27]. As a result, the metal NPs showed quantifiable red-shits or blue-shifts upon the addition of target analytes because of metal NPs-aggregations [28,29]. Due to their size dependent LSPR peak, plasmonic metal NPs-based colorimetric portable sensing approaches have been developed for the analysis of various molecules based on the metal NPs aggregation [7,22]. It was noticed that the dispersed metal NPs exhibits certain wavelength in visible range which is considered as primary LSPR bands and the aggregated metal NPs exhibit the LSPR bands at longer wavelengths, which can be referred as either secondary LSPR bands or red-shift. The significant changes in the LSPR band location represent quantifiable color changes, which allows to establish simple and portable analytical strategies for colorimetric sensing of various molecules. These optical plasmonic properties of metal (Ag, Au, Cu and Pt) NPs are strongly dependent on the interparticle distance of metal NPs, which make them into either dispersion or aggregations. The red-shift and color change of metal NPs are mainly due to the decrease of interparticle distance, causing strong overlapping of plasmon fields of nearby NPs. The recent advances in plasmonic metal NPs have been integrated into analytical chemistry for the design of large numbers of colorimetric sensors for assaying of trace level target analytes from complex samples [30,31]. These plasmonic metal NPs-based approaches have proven to be simple visual readouts for the identification of target analytes because of their