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Full Length Article

Boron nitride/gold nanocomposites for crystal violet and creatinine detection by surface-enhanced Raman spectroscopy

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ABSTRACT

Hexagonal boron nitride/gold nanocomposites (h-BN/Au NCs) were fabricated and developed for ultra-sensitive detection of crystal violet (CV) and creatinine molecules using surface enhanced Raman scattering spectroscopy (SERS). The overgrowth of Au nanoparticles was driven by laser-induced photoexcitation of h-BN, which was monitored by absorption spectra. The h-BN/Au NCs with controllable Au compositions (0–1.85%) were characterized using Transmission Electron Microscopy (TEM), Scan Electron Microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectra (XPS). The microstructural analyses indicated that mono-dispersed Au nanoparticles with size of ~10 nm can be accreted on h-BN via 30 min synthetic reaction. The comparative SERS results reveal that the h-BN/Au NCs with 1.68% Au composition provide enhanced SERS activity in comparison with other nanosubstrates in this paper. The corresponding enhancement mechanism of h-BN/Au NCs has been illustrated in detail, which can be composed of four contributions in our research. Then, the SERS analyses demonstrated that the detection limit of CV molecules was achieved at femtomole level of ~10^{-15} M, leading to ultrasensitive monitoring of dye pollution. More importantly, well-defined linear relationships were established between SERS signal intensities and logarithmical scale of creatinine concentration (10^{-2}–10^{-6} M), providing a precise assessment of creatinine in pathological diagnostics.

1. Introduction

Surface-enhanced Raman scattering spectroscopy (SERS) is a powerful and promising spectroscopic technique, which originated from the intense interaction between laser-induced an electromagnetic wave on rugged plasmonic metallic silver (Ag), gold (Au) or copper (Cu) nanomaterials and probe molecules adsorbed on the plasmonic materials [1–4]. Therefore, the SERS signals derived from the specific vibrational energy of chemical bands during the enhanced inelastic scattering process can be served as a “molecular fingerprint”, which will provide unique molecular information at single molecule level ($< 10^{-9}$ M) [1,2,5–7]. Especially, the ultrasensitive SERS signals carried with vital molecular information are particular favorable for biological and biomedical diagnosis, offering several advantages over standard chemical analysis for clinical applications, such as a rapid evaluation, minimal or no sample preparation, noninvasive process, and wider information content, *etc* [8,9]. For example, a novel optical nanosensor by using borosilicate nanopipettes decorated with Au nanoparticles has been served as excellent SERS substrate for sensitive and nondestructive monitoring of extracellular metabolites near living cells [7,10–12]. Moreover, many interesting work such as ultra-trace detection of methimazole, 2-thiouracil, ketoconazole, naphthalene, phenanthrene, as well as 2-4-6-trichloro- and thribromoanilines have been realized by using SERS technique [3,4,10–14]. It has been widely recognized that the SERS activity highly relies on the plasmonic nanosubstrates with designed structures. In recent years, extensive research efforts have been devoted toward the construction of Ag or Au-based SERS substrates with controllable nano-architectures and tunable compositions [13,14], including the porous, hollow, branched shapes, Ag or Au monometallic and bimetallic nanomaterials, as well as hydroxylamine reduced Ag colloid, *etc*. Because of the intrinsic high cost of noble Au and Ag species, the further development of hybrid functional SERS nanosubstrates based on inexpensive semiconductor decorated with few Ag or Au nanoparticles is highly designable for molecular diagnostics in practical applications.

More recently, two-dimensional (2D) materials decorated with Au

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or Ag nanoparticles as advanced SERS substrates have prompted the renewed interest in ultrasensitive SERS detections, allowing us to take advantage of both plasmonic metal properties and unique 2D structures. Compared with other structures such as zero- or one-dimensional-based nanocomposites, the intriguing prospects of 2D-nanosheets as SERS substrates exhibit several pronounced advantages, such as intrinsic outstanding charge transport properties on flat 2D surface, very high specific surface area, unrivaled mechanical strength, *etc* [6,15–17]. Interestingly, an outstanding work demonstrated that a new kind of SERS-based ultrasensitive sensor developed by graphene oxide (GO) film coupled with Au nanoparticles can not only diagnose gastric cancer but also distinguish early gastric cancer (EGC) and advanced gastric cancer (AGC), giving rise to the primary screening diagnosis and stage determination of stomach cancer [8]. Although many excellent studies have been carried out to illustrate the SERS performances of these novel hybrid substrates, some critical and urgent issues such as metallic particle size, composition or distribution have been far less well exploited to further maximize the SERS activity. Especially, the controllable metallic particle composition in nanocomposites has a promising potential for further enhancing SERS signals, which has been well confirmed in our recent works [18–20]. For example, we have found that the SERS signal peaks of the crystal violet (CV) molecules originated from Au/Ag (Ag: 16.83%) self-assembled monolayers (SAMs) is about 3.6 times higher than that of Au/Ag SAMs with 34.5% Ag [20]. To our knowledge, the convenient construction of 2D materials/metallic nanoparticles with tunable composition will further significantly increase SERS activity, enabling this functional nanocomposite to hold greater promise for the precise diagnostics of various ultratrace molecules. Unfortunately, based on 2D materials coupled with Ag or Au nanoparticles, the structural advantage of the controllable particle size and composites has not been extensively realized in SERS applications up to now.

The aim and motivation of this work was to develop an advanced SERS substrate based on the convenient fabrication of 2D material/Au nanocomposites with an appropriate Au composition for ultrasensitive detection of CV dye molecules and creatinine molecules. Herein, based on hexagonal boron nitride (h-BN), we report on the successful fabrication of a fascinating h-BN/Au NCs with controllable Au composition in range of 0–1.85% by laser-induced photochemical strategy. Different from other 2D materials, the h-BN is highly thermally and chemically stable structure. As for traditional chemical overgrowth of metallic structures, the h-BN nanosheets should be previously and preciously modified by various groups, such as hydroxyl (−OH), alkoxy (−OR), amino ($-NH_2$), amine (−NHR), and other groups (−OCOR, −NHCOR, −COR, *etc.*) [21]. The uniqueness of this work compared with other exciting reports is to employ novel electron donors as unique reducing agent, which is originated from the electron-hole pairs that produced by UV-laser excitation of h-BN semiconductor. In the absence of any functional process of h-BN, the photo-generated electrons is sufficient for the effective reduction of Au ions and then overgrowth of Au nanoparticles on h-BN without the aid of any organic or polymer agents. The composition-dependent SERS analysis of crystal violet (CV) molecules revealed that the h-BN/Au NCs with 1.68% Au content provide maximized SERS activity in comparison with pure h-BN, monometallic Au or h-BN/Au with other Au contents. The distinctive advantage of the obtained h-BN/Au NCs is the enhanced SERS activity. In addition to the conventional SERS enhancement originated from plasmonic Au nanostructures, other important effects have been existed in h-BN/Au NCs. The h-BN/Au NCs with appropriate Au content provide unique long-range electromagnetic effect of Au nanoparticles to significantly enhance the Raman scattering of probe molecules near h-BN semiconductor. Meanwhile, based on Herzberg-Teller mechanism, the vibronic coupling between a charge-transfer state and the lowest-lying $\pi \rightarrow \pi^*$ transition provides a certain contribution of charge-transfer intensity to the overall SERS enhancement of h-BN/Au NCs [22]. The corresponding ultra-low detection limit was located at femtomole level of $\sim 10^{-15}$ M, which is far better than that of many previous works based on hollow Au-Ag nanourchins [23], co-encapsulation of Au nanostars and Fe_3O_4 nanoparticles [24], single Cu_2O superstructure [25], *etc.* and even higher than the recent result with 10^{-14} M by using 2D Ag nanoparticle supercrystals [26]. Furthermore, SERS analysis of creatinine molecules exhibits a well-defined linear response range over a wide concentration (10^{-2}–10^{-6} M), giving rise to the precise assessment of renal impairment in clinical diagnosis. This work is a breakthrough in the controlled overgrowth of metallic nanoparticles with tunable composition on chemical stable 2D materials, which is significant to create other more complex nanocomposites in various applications.

2. Experimental setup

2.1. Chemicals

The pure h-BN nanosheets were purchased from Aladdin Chemistry Co., Ltd (Shanghai, China), ethanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd. Chloroauric acid ($HAuCl_4$) and crystal violet (CV) were purchased from Sigma, and creatinine was purchased from MCE.

2.2. Synthesis of h-BN/Au NCs

The overgrowth of Au nanoparticles on h-BN nanosheets was simply achieved by laser irradiation of h-BN nanosheets in Au ions solution, which is similar to our previous works [19]. In a typical experiment, 0.01 g BN powder was diluted into 20 mL distilled water by 10 min ultrasonic vibration. 40 μL of 0.5 M $HAuCl_4$ and 500 μL ethanol solutions were added into 5 mL h-BN solution. The ethanol molecules with hydroxyl group (−OH) will be served as sacrificial agent in this paper. Under magnetic stirring condition, five groups of these mixed solutions were separately then irradiated by a continuous 405 nm UV laser beam with power of ~500 mW and average diameter of 2 cm.

2.3. Characterization and SERS testing of h-BN/Au NCs

After 10–50 min irradiation, the obtained five groups of product were separately centrifuged at 5000 rpm for 10 min in an ultracentrifuge. The as-prepared precipitates were dropped on the copper mesh and completely dried in an oven for observation using a JEOL JEM-2100F transmission electron microscopy (TEM). Elemental mapping images were acquired by energy dispersive X-ray (EDX) spectroscopy using a JEOL JEM-2100F electron microscope equipped with a scanning transmission electron microscopy (STEM) unit. Morphologies and chemical compositions of the samples were also characterized by field emission scanning electron microscope (SEM, Hitachi S-4800) equipped with energy-dispersive X-ray spectroscopy (EDS). The crystallographic measurements of the products were collected by X-ray diffraction (XRD) patterns (Rigaku, RINT-2500VHF) using Cu Kα radiation ($\lambda = 0.15406$ nm). The detailed surface composition analysis and element valence were performed on a PHI Quantera SXM with an Al Kα = 280.00 eV excitation source by X-ray photoelectron spectra (XPS). The absorption spectra were carried out via UV–Vis-IR spectrometer (UV-1800, Shimadzu). In a typical Raman spectroscopic analysis, 0.1 mg h-BN/Au NCs was separately mixed with 1 mL solutions with different probe molecules concentration. Then, the mixed solution was continuously stirred at a constant speed of 200 rpm for 20 h to ensure the established of adsorption-desorption equilibrium among the nanomaterials and probe molecules. Subsequently, the products were centrifuged at 18,000 rpm for 15 min in an ultracentrifuge. The obtained sediments were carefully dispersed in the cleaned silicon chips by spin-coat method (4000 rpm, KW-4A). The silicon chips were carefully rinsed with $HCl:H_2O_2:H_2O$ (1:1:4 v/v) solution for 20 min, and dried with high purity nitrogen (99.99) condition. The spin-coat method can