



Carbon nanostructure (0-3 dimensional) supported isolated gold nanoparticles as an effective SERS substrate

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ABSTRACT

The present work reports a comparative surface enhanced Raman scattering (SERS) study of nanohybrids of spatially isolated gold nanoparticles (Au NPs) with different carbon nanostructures (CNS). For a meticulous comparative analysis, different CNS covering from zero dimensional to three dimensions were used. SERS activities of developed nanohybrids platforms were evaluated with a Raman marker i.e. Mercaptobenzoic acid (4-MBA, 1 μ M). Synergistic Raman signal enhancement from each Au NP (electromagnetic enhancement) and underlying CNS matrix (chemical enhancement) was observed in nanohybrid enabling detection of very small concentration of 4-MBA i.e. 1 μ M convincingly. Among the different underlying matrix, GQDs-Au NPs based SERS platform have shown highest SERS enhancement by a factor of 10^7 , followed by GO-Au NPs combination ($\sim 3 \times 10^6$) and others. Enhanced SERS activity of GQDs -Au NPs -4-MBA nanohybrid platform is attributed to the D and G bands of GQDs, overpowering the strong fluorescent background of GQDs alone. Reported nanohybrids; specially GQDs-Au NPs offers numerous possibilities to be used as sensitive and reproducible SERS platform for the detection of other biologically/chemically important analytes, showing potential for standardization in near future.

1. Introduction

Beside its numerous usefulness in analytics, traditional Raman spectroscopy (RS) is limited for detecting low concentrations of target analytes with weak vibrational bands due to lower scattering cross-section [1–3]. To overcome such limitation, Resonant Raman spectroscopy (RRS) [1] and Surface-Enhanced Raman Spectroscopy (SERS) [4–10] have been explored in last few decades. However, RRS suffers with a drawback of the simultaneous increase in the fluorescence background as the excitation coincides with the absorption [11]. On the other hand SERS is both surface selective and highly sensitive technique, which offers higher magnitude of increased intensity (10^8 - 10^{14}), suppresses the fluorescence signal while selectively enhancing the Raman signal, producing chemical fingerprint with sensitivity enough to enable single-molecule detection [12,13]. Electromagnetic enhancement (EE) and chemical enhancement (CE) are two well accepted mechanisms that explain the SERS activity. Surface plasmon resonance

effect of plasmonic nanostructures are the chief contributor to the EE [4,14] while CE is based on the charge transfer between a nanomaterial and adsorbed analytes [15]. And the combination of both EE and CE resulted to $\sim 10^{14}$ times enhancement in SERS signal.

In last few years, nanostructures of certain metals like gold (Au) and silver (Ag) with their roughened surfaces have shown interesting SERS activities attributed to the enhanced surface plasmons resonance on excitation [16,17]. In most of the SERS studies, gold nanoparticles (Au NPs) have been used as a popular SERS substrate and it is due to their certain beautiful properties like long term stability, better control over size and shape and biocompatibility [18,19]. However, the SERS potentials of Au NPs have not been fully exploited in previous studies due to less control on particles orientation and aggregations while fabricating their SERS substrates. Some well-known techniques like electrochemical routes, vacuum evaporation and nano-lithography were employed to overcome above mentioned challenges for fabrication of Au NPs based SERS platform. But these techniques are costly and

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tedious in operation. Therefore, some alternate strategies for making efficient Au NPs based SERS substrates are highly required. In recent years, carbon nanomaterials have been used as a unique support matrix for manipulation of plasmonic properties of metallic nanoparticles, which have been used in several applications ranging from light-emitting devices [20], to data storage [21] and in bio-sensing [22,23]. Adding to this, monolayer single-crystalline graphene grown by CVD method was reported as a flexible and transparent substrate for SERS [24]. Apart from the suitability as a supportive matrix [25], the combination of unique properties of carbon nanomaterials with metallic nanoparticles, not only provide a synergy of CE and EE, but also offers several exciting future applications, which is not possible individually. An relevant example is the application of Ag-SiO₂-CNT based nanoporous freestanding SERS substrate for detection of trinitrotoluene [26]. Several recent studies have demonstrated the SERS potential of different carbon nanostructures with metal nanoparticles [27–32]. Most importantly, carbon nanomaterials have shown their unique ability to provide the ultimate dielectric spacer which is very crucial for high optical field-enhancements in plasmonics, arises due to sub-nanometer gaps among metallic nanostructures [33,34]. With this background information, the SERS study of these metallic nanoparticles becomes more important in their spatially isolated state. And it is believed that carbon nanostructures will not only work as an efficient support matrix for spatial isolation of Au NPs, but also contribute significantly in SERS signal enhancement via CE. With this motivation, the current study is aimed to explore the SERS activities of spatially isolated Au NPs on different carbon nanostructures i. e. covering zero dimensional (0D) graphene quantum dots (GQDs), 1D carbon nanotube (CNTs), 2D graphene oxide (GO) and reduced graphene oxide (RGO), and 3D graphene hydrogels (GHs). Thus to compare the dimensionality effect of on spatial distribution, hence SERS activities of Au NPs, different carbon nanostructures have been used for the study.

2. Material and methods

2.1. Materials

Graphite flakes (NGS Naturgraphit GmbH, Germany), tetrachloroauric acid (HAuCl₄), polyvinylpyrrolidone (PVP), 4-MBA, 5,5'-Dithiobis (2-nitrobenzoic acid) (DTNB), H₂SO₄, H₃PO₄, KMnO₄, H₂O₂, hydrazine hydrate, ferrocene, xylene, ammonia solution, ethanol, etc. used were of technical grade and were procured from Sigma-Aldrich.

2.2. Synthesis of different carbon nanostructures and PVP stabilized gold nanoparticles

The synthesis procedures for all the CNS base materials and the PVP stabilized gold nanoparticles were elaborated in detail in the supporting information (SI).

2.3. Preparation of CNS-Au NPs composites

All CNS materials used except GQDs were taken at a concentration of 2 mg/mL in DW in separate vials. 2 mL of GQDs solution taken in another vial. All these six dispersions were sonicated for 30 min to make a homogeneous dispersion. From the well dispersed CNS solution, 700 μ L taken out in a 2 mL eppendorf and added 300 μ L of diluted spherical Au NPs of \sim 50 nm size. This was further sonicated for 10 min and kept in a vibrating stand until the thin film for SERS is made on silicon.

2.4. Fabrication of CNS-Au NPs nanohybrid SERS platform and immobilization of Raman marker

Pre-cleaned silicon (Si) of 5 \times 5 mm dimension were used for fabrication of SERS platform. A 10 μ L of hybrid solution was spin coated at

1000 rpm to get a uniform nanohybrid films over entire substrate. These substrates were dried at 70 $^{\circ}$ C for 30 min. Several optimization experiments were carried out before developing a uniform SERS platform. 5 μ L of 4-MBA (1 μ M Raman marker) was added on to the developed platform and incubated for overnight at RT and further used for the SERS study. Here, Si substrate is used to spin coat the material rather than SiO₂/Si substrate in order to reduce the interference-enhanced Raman scattering (IERS) effect which usually arises from Si substrate with metal oxide layer of specific thickness.

2.5. Characterization of the materials

The structural characterization of CNTs, GO, RGO and GHs were carried out by X-ray diffraction (XRD) technique (Rigaku miniflex-II diffractometer at 30 kV, 15 mA). The wavelength of Cu-K α 1 radiation of $\lambda = 1.5405 \text{ \AA}$ was used for obtaining the XRD pattern. TEM characterization of CNS and CNS-Au NPs nanohybrid were carried out by using a Zeiss EM 902 instrument. The Raman and SERS measurements were conducted with a confocal Raman microscope (WITec Alpha 300R, 30 cm focal length and 600 grooves per mm grating spectrometer) equipped with an EM-CCD. A 632.8 nm line from a He-Ne laser was focused onto the sample using a 40x objective (Olympus) with a numerical aperture of 0.6 (5 mW laser power at the sample; laser spot diameter \sim 1.286 μ m). For the Raman mapping, an area of 100 \times 100 μ m is scanned with an interval of 2 μ m with an integration time of 1 s. Raman mapping data were processed by the WITecProject software and the graphs were plotted by Origin software. The intensity scale bar in the Raman mapping images are in the unit of CCD cts.

3. Results and discussion

3.1. XRD studies of the CNS base materials

The XRD pattern of the as-synthesized CNS base materials except GQDs, namely CNTs, GO, RGO and GHs are presented in Fig. S1 (Supporting Information). The XRD peak observed at \sim 25.9 $^{\circ}$ (Fig. S1a) corresponds to the characteristic peak of CNTs (002). GO shows a strong diffraction peak at \sim 11 $^{\circ}$ (Fig. S1b), which corresponds to the (002) reflection plane with an interlayer spacing of \sim 8.0 Å [35]. Further the weak and broad band around 42 $^{\circ}$ in GO corresponding to the (100) reflection and is due to the turbo static band of disordered carbon material. The most prominent diffraction peak of RGO is observed at \sim 24. 5 $^{\circ}$ (002) attesting the characteristic band of RGO (Fig. S1c) with an interlayer spacing of \sim 3.4 Å . This value matches with the well-known XRD peak of RGO [36]. Fig. S1 (d) shows the diffraction pattern of GHs with a peak centered at \sim 25.7 $^{\circ}$ (002). The XRD profile of GHs matches with that of the earlier report [37].

3.2. Transmission electron microscopy (TEM) studies

The Fig. 1 is a representative TEM micrograph of Au NPs, GQDs, CNTs and their nanohybrid which were used for the SERS study. In Fig. 1(a), a uniform distribution of PVP stabilized Au NPs is seen. The size of the particles was measured to be \sim 50 nm. In Fig. 1(b), an isolated Au NP is shown which were achieved through the dilution of Au NPs stock solution. Fig. 1(c) showed the TEM images of homogeneously packed and well separated GQDs with lateral size \sim 10 nm (height profile ranging from \sim 1–5 nm: from AFM topography in Fig. S3 of Supporting Information). The nanohybrid of GQDs-Au NPs as shown in Fig. 1(d) is an indication of very unique phenomenon took place during the synthesis of this nanohybrid. In close observation, it was noticed that each Au NP is surrounded by several GQDs because the size of GQDs are much smaller than the Au NPs. Fig. 1(e) showed the well separated CNTs. Here the individual CNTs are of approximately 30 nm in diameter and in micrometers in length. Further, these CNTs are of quite good in its homogeneity and are almost free from impurities. In

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