

STUDY OF PREPARATION, GROWTH MECHANISM AND SERS PERFORMANCE OF SILVER-CARBON AND GOLD-CARBON NANOCOMPOSITE MATERIALS

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Surface-enhanced Raman scattering (SERS) technique is an important and powerful analytical tool, which has attracted much attention for environmental monitoring, chemical analysis and biomedical research. In this paper, we develop a facile method to fabricate the silver-carbon nanocomposites (Ag/CSs) and gold-carbon nanocomposites (Au/CSs). The composites were prepared by one-step hydrothermal reduction method using trioctylamine (TOA) as the soft template and extractant. According to the different amount of TOA added, we prepared a different morphology of the composite material. When the amount of TOA is 1.0 mL, the core-shell composite was obtained. The shape of the silver core shows the hexagon shape and we consider that TOA and glucose selectively adsorb the Ag (111) crystal face resulting in this growth pattern of the silver core. The hydrothermal carbon shell not only effectively avoids the agglomeration of nanoparticles core, but also serves as a protective layer of the SERS active nanostructure during the whole course of the experiment. The detection limit of Ag/CSs for CV molecules up to 10^{-9} M. The results show that the as-obtained Ag/CSs hold tremendous potential for SERS applications for its long-term stability and superior SERS performance.

I. INTRODUCTION

Carbon materials have been widely used for many applications, ranging from the energy storage [1], electrochemistry [2], to catalysis [3] and adsorption [4], due to the good stability, high conductivity and thermal conductivity. Hydrothermal carbon has recently attracted attentions from the scientific community [5-7], among the wide family of carbon-based materials. It is well known that hydrothermal carbon spheres are rich in hydroxyl, carboxyl, carbonyl and other oxygen-containing functional groups [8], which is beneficial to its further processing such as loading, modification and other operations. It is a cheap, easy and green route to product carbon spheres by the hydrothermal carbonization of biomass.

As we all know, silver and gold NPs exhibit the phenomenon known as Surface-enhanced Raman Scattering (SERS) and silver is the most efficient metal for SERS application [9]. AgNPs have been widely recognized for its application in a wide range of fields due to the high conductivity, catalytic antibacterial, and unique surface plasmon features. Therefore, the synthesis of AgNPs with a controllable morphology and particle size is essential and critical for their applications. AgNPs exhibit enhanced SERS properties and have emerged as a powerful analytical technique for monitoring trace amounts of chemical because of its high sensitivity and rapid response. SERS is a good tool for molecular detection. However, it has still not gained wide acceptance as a general spectroscopic tool owing to the poor SERS substrate stability until now, which, to a great extent, limits the exploration of SERS-based devices [10]. In other words, it is crucial to prevent noble nanoparticles from oxidizing. In order to solve the problem, a significant amount of efforts have gone into preparing core-shell structure materials [11-13]. The

carbon shell can prevent the noble metal from oxidation and extend the SERS-active shelf life [14].

Herein, we introduce a cheap, convenient and green route to prepare Ag/CSs and Au/CSs by one-step hydrothermal method. Through the whole process of reaction, glucose, silver nitrate and TOA have a synergistic effect between each other. The Ag/CSs presents a regular spherical structure with a hexagon silver core. As the immersing time prolonged, the thickness of the loose hydrothermal carbon shell is significantly reduced, which indicates that the thickness of the shell can be controlled after the preparation stage. In order to analyze the SERS activity of as-obtained Ag/CSs, two kinds of SERS substrates were prepared. The intensities of SERS signals from substrates are strongly dependent on the contact time between probe molecules and composites.

II. EXPERIMENT

II.1. Regants

Chloroauric acid (HAuCl_4 , AR) was ordered from Energy Chemical. Silver nitrate (AgNO_3 , AR), glucose (AR), and ethanol (AR) were purchased from Sinopharm Chemical Reagent Co. Ltd. Crystal violet (CV) and trioctylamine (TOA, 90%) were obtained from Sigma-Aldrich. Rhodamine 6G was bought from Aladdin. All the chemicals were used as received without further purification. Deionized water was used throughout all the experiments.

II.2. Synthesis of Au/CSs

The hydrothermal synthesis of Au/CSs was carried out in a stainless steel reactor with an inner volume of 100ml. In a typical procedure, 1.290 g of glucose were dissolved in 60 ml deionized water to form a clear solution. Then 70 μL of 0.1M HAuCl_4 aqueous solution was added slowly to 60mL of glucose solution under vigorous stirring. The obtained mixture was clear with light yellow. After being stirred for 10 min 1.5 ml of TOA was added into the mixture. Then the mixture was ultrasonic-treated for 10 min to form the emulsion. Transferred and sealed the emulsion to 100 ml Teflon-lined autoclave quickly. The autoclave was kept at 180°C for 12 h before being cooled to room temperature in air naturally. The thick suspensions as formed were usually deeply brown in color. The suspension was purified by repeated redispersion/centrifugation/redispersion procedures in deionized water and anhydrous ethanol until supernatant became a clear solution. Then the precipitate was collected after centrifugation. Finally, the resultant precipitate was vacuum-dried at 60°C for 12 h.

II.3. Synthesis of Ag/CSs

In a typical procedure, 30 mL of AgNO_3 aqueous solution (0.014 M) and 30 mL of glucose aqueous solution (0.016 M) were mixed under magnetic stirring at room temperature. Then 0.8–1.5 mL TOA was added into the obtained mixture. Next, the mixture was ultrasonic-treated for 10–15 min to form the emulsion. Transferred and sealed the emulsion to 100 mL Teflon-lined autoclave quickly. The autoclave was kept at 180°C for 6–12 h before being cooled to room temperature naturally. The suspension was purified by repeated dispersion/centrifugation/dispersion procedures in deionized water and anhydrous ethanol until supernatant became a clear solution. Finally, the precipitate was collected and dried at 60°C in oven. The synthesized precipitate also can be resuspended in ethanol for further use. The final product was labeled as Ag/CSs.

II.4. Characterization

The morphology studies of samples structure were carried out on a scanning electron microscope (SEM, HITACHI S-4800) and a transmission electron microscope (TEM, FEI F-30). FT-IR spectra of samples were obtained using Thermo Scientific Nicolet IS-10 spectrometer. The structure characterization was carried out on X-ray (German Bruker AXSD8 advance). The Raman spectra were recorded on a Renishaw Invia system, equipped with a Leica microscope. Samples were excited with a 514 nm laser line. Power at the sample was kept at 2 mW. A long working distance 50×objective was used to collect the Raman scattering signal. The SERS spectra were recorded on five different spots and the average intensity spectrum was selected for analysis.

II.5. Fabrication of substrate

Two kinds of SERS substrates were prepared as follows. (1) Drop and dry the aqueous solutions of Ag/CSs and probe molecules on a clean silicon wafer followed by analysis through Raman spectra. Briefly, the cut 0.5×0.5 cm silicon was placed in acetone, ethanol, deionized water ultrasonic cleaning for 10 min, respectively. Then, 10 µL of the Ag/CSs suspension was dropped on the treated wafer and placed in a drying oven for 5 min, and different concentrations of probe molecules solution (10^{-6} , 10^{-7} , 10^{-8} , 10^{-9} and 10^{-10} M) prepared. Then, 10 µL of the solution was withdrawn using a micropipette and dropped cast onto silicon wafer loaded with Ag/CSs. The wafer was dried at 60°C before tested, which was called the Substrate1 (S2). (2) Immersed the treated wafer in different concentrations of probe molecular solution for few hours and then dried at 60°C before tested (S1).

When adsorbed onto the substrates, molecules exhibit an enhanced Raman signal usually several orders of magnitude higher compared to free molecules. To estimate the SERS properties of the as-prepared Ag/CSs, we compared the intensity of the peaks of 10^{-6} M R6G with the spectra of pure CV powders and calculated the enhance factor (EF) according to the equation [15]:

$$EF = \frac{I_{SERS} / N_{SERS}}{I_{bulk} / N_{bulk}}, \quad (1)$$

where I_{SERS} denotes the SERS intensity of the CV adsorbed on the as-prepared substrate. I_{bulk} denotes the normal Raman scattering intensity of the same peak of pure CV powder. N_{SERS} and N_{bulk} mean the number of CV molecules probed on the substrate surface and in the bulk sample effectively excited by the laser, respectively.

III. RESULTS AND DISCUSSION

III.1. Morphology study of composites

Figure 1 shows the scanning electron microscope (SEM) and transmission electron microscope (TEM) images of the as-prepared Au/CSs. When the temperature maintained at 160°C for 12 h, the solution changed to brown but there is no precipitation generation in the resultant solutions. Moreover, if the reaction time decreased to 180°C, the cores size were around 60nm while the shell thickness of the nanoparticles were around 20 nm (Fig. 1b), suggesting the formation of Au/C core-shell structure. In order to obtain more detailed information about the surface topography of the samples and the particle sizes, we examine the sample with a scanning electron microscope (SEM). The SEM image for the Au/C Core/Shell Structure is shown in Fig. 1a. Overall, the nanoparticles in Fig. 1a

are similar in circle shape and have smooth surface. As can be seen in Fig. 1c, when TOA is not used as surfactant that core-shell structure disappeared and nanoparticles begun to agglomerate. The surface of the resulting carbon sphere is not very smooth and there are some small gaps. The diameter of the carbon spheres is about 200 nm, and the distribution is narrow. However, some carbon spheres agglomerate and stick together, resulting in poor dispersion.

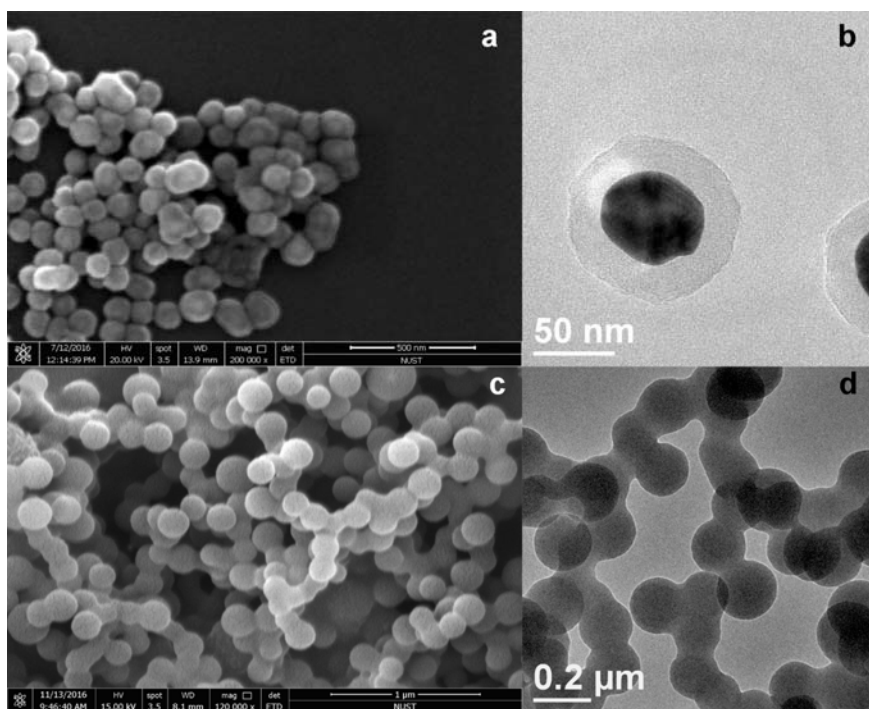


Fig. 1. SEM and TEM images of as-prepared Au/CSs with TOA (a) and without TOA (b).

As shown in Fig. 2a, many large chunks could be observed and no core-shell composites formed. However, when the amount of TOA ranged from 0.8 to 1.5 mL, all the composites produced a core-shell structure but the particles size and morphology were not the same (Fig. 2b-d). The illustrations show TEM images of the corresponding Ag/CSs nanocomposites. As shown in Fig. 2b, the core-shell structure began to appear after adding 0.8 mL TOA. The TEM image in Fig. 2b further confirmed the structure is not traditional spherical core-shell, but similar to the shape of the fried egg. The formation of this shape may due to the growth of hydrothermal carbon been inhibited in some direction. There is a selective adsorption of the surfactant in the solution during the process of silver nanoparticle growth. When the amount of TOA is not enough, the silver nanoparticles preferred to adsorb on the (111) crystal plane [16], leading to the adsorption and growth lag behind other planes. Fig. 2c shows the SEM image of Ag/CSs (1.0-180-9). The well-defined core-shell structure can be clearly identified from the strong black/white contrast in TEM image. The Ag/CSs exhibit a common spherical shape with a narrow size distribution (around 180 nm), and the carbon layer thickness was ~20 nm. It is worth mentioning that the silver core shows the hexagon shape, while the carbon layer exhibits a uniform spherical shape. This is mainly because the glucose polycondensation

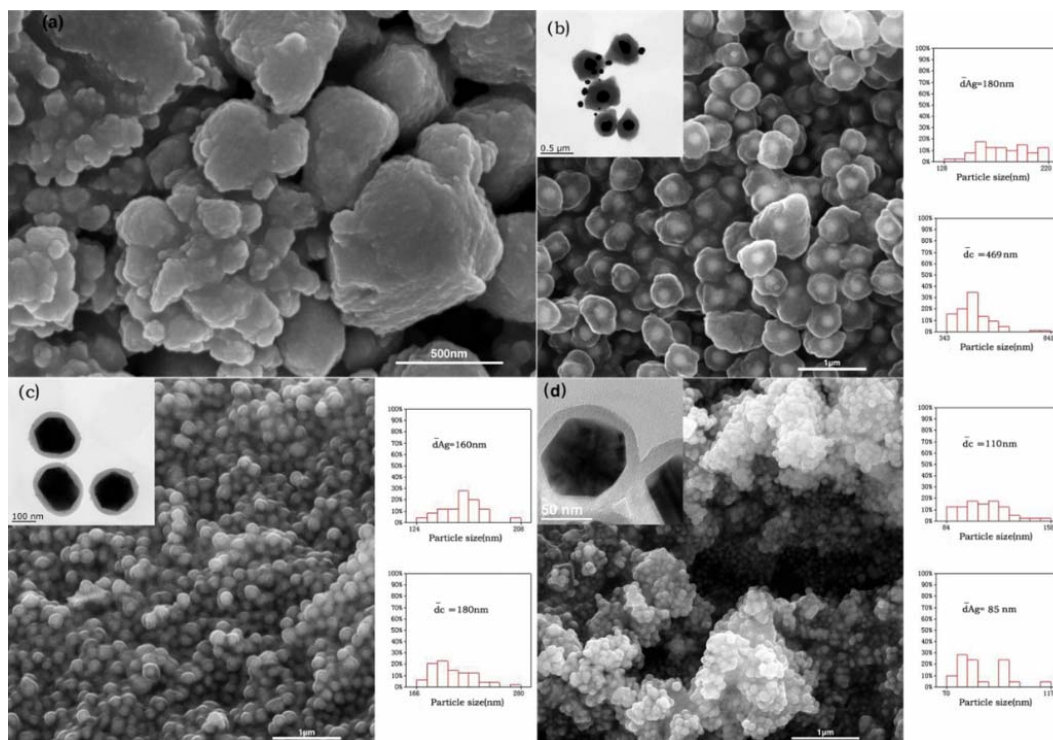


Fig. 2. SEM and TEM images of Ag/CSs with different content of TOA: 0 mL (a), 0.8 mL (b), 1.0 mL (c) and 1.5 mL (d).

products chose the lowest potential energy way to wrapped silver core. The SERS enhancement of probe molecules absorbed on metal substrates depends on the metal shape, aggregation extent and so on. The regular silver core prepared in our experiment may exhibit a higher enhanced SERS characteristic than circular silver core due to the enhanced local field effect near its sharp corners and edges. When the amount of TOA reached 1.5 mL, the as-prepared Ag/CSs (1.5-180-9) were spherical shape with average diameter decreased to 110 nm (Fig. 2d). The dispersion of particles decreased and carbon shell became aggregated. TEM image shows that the size of silver core reduced to nanometer (approximately 85 nm). In addition, the shape of the core is still hexagonal, and the thickness of carbon layer decreased to 15 nm.

III.2. Characterization of composites

The hydrothermal carbon contains large amounts of oxygen-containing functional groups on its surface and can easily combined with other molecules, ions or functional groups to form new functional materials [17]. In Fig. 3a, the FTIR spectra of sample shows lots of characteristic peaks, including -OH stretching vibrations, C-OH stretching and -OH bending vibrations at 3350 and 1050 cm^{-1} , which indicate the existence of hydroxyl groups. The vibration band at 1692 cm^{-1} is attributed to C=O vibrations. Additional, the band at 880 cm^{-1} is corresponding to the vibration of aromatic C-H groups. What's more, the characteristic vibration peaks of benzene framework positioned at 1600, 1558, 1507, 1453 cm^{-1} unambiguously indicates the existence of benzene ring structure in the carbonaceous shell. The biggest difference between the two samples is

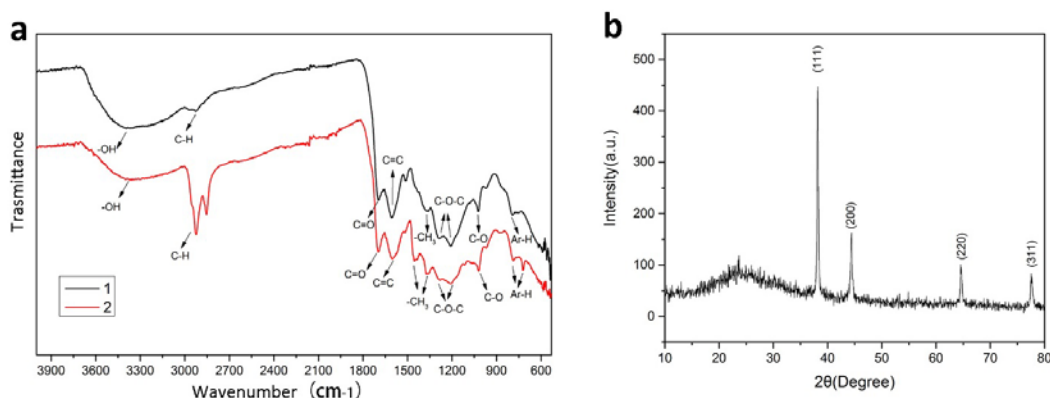


Fig. 3. (a) FT-IR spectra of Au/CSs without TOA (1) and with TOA(2); (b) XRD pattern of the as-prepared Au/CSs

that there is a distinct absorption peak at 700 and 794 cm⁻¹, which corresponds to the stretching vibration of -CH₂ [18]. This structure cannot be obtained by hydrothermal carbonization of glucose, and we speculated that the structure of the surfactant TOA was ultimately retained in the product.

Figure 3b shows the XRD patterns of as-prepared Au/CSs. Four distinct diffraction peaks were clearly observed at 2θ value of 38.14°, 44.32°, 64.48° and 77.45° corresponding to the (111), (200), (220) and (311) crystalline planes of Au, respectively, which is in good agreement with the reported data (JCPDS #04-0784). This is not only the evidence to support the presence of the gold and carbon elements in the final samples, but also implies that the HAuCl₄ has already been reduced to Au by glucose. In addition, there is an obvious broad peak at around 24°, which indicates an amorphous phase and is corresponded to the carbonaceous composition of the carbon shell. In contrast, the peak shifts to the right slightly in the Au/C and the intensity of the peak that belongs to the carbon decreases. It means that the disorder of carbonaceous composition increased.

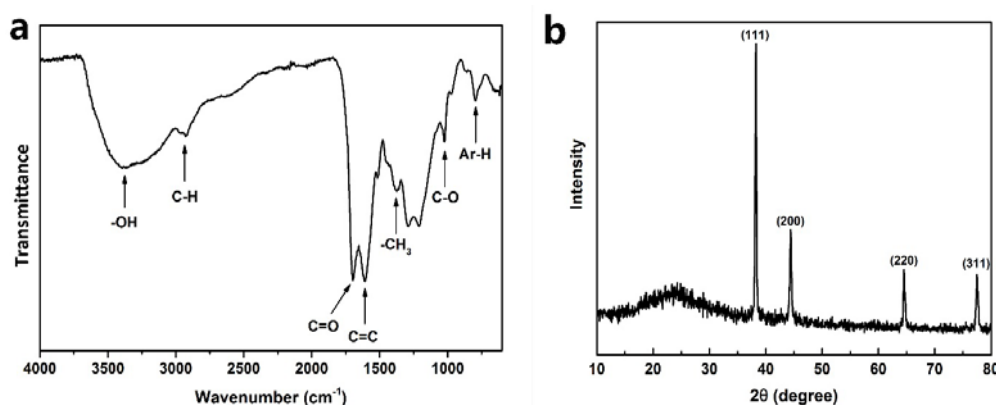


Fig. 4. FT-IR (a) and XRD (b) pattern of the as-prepared Ag/CSs.

The functional groups present on the as-prepared Ag/CSs (1.0-180-9) were investigated by FT-IR (Fig. 4a). The broad absorption peak between waves of 3000 cm⁻¹

and 3500 cm^{-1} is the stretching vibration peak of -OH . The vibration band at 1692 cm^{-1} is attributed to C=O vibrations probably from a carboxyl group or a carbonyl group formed through dehydration. Besides, the peak at 1020 cm^{-1} means that the C-O bond was generated under the hydrothermal condition. The presence of these peaks demonstrated that the hydrothermal carbon shell contains a large amount of oxygen-containing functional groups. Additionally, the band at 1620 cm^{-1} is corresponding to the vibration of C=C double bond stretching vibration. What's more, the characteristic vibration peaks of benzene framework positioned at 790 cm^{-1} and 690 cm^{-1} unambiguously indicate the existence of benzene ring structure in the carbonaceous shell [21].

Figure 4b shows the XRD pattern of as-prepared Ag/CSs (1.0-180-9). Four distinct diffraction peaks clearly been observed at 2θ value of 38.14° , 44.32° , 64.48° and 77.45° corresponding to the reflections of (111), (200), (220) and (311) crystalline planes of cubic Ag, which is in good agreement with the reported data (Silver-3C, JCPDS #04-0783). It is worth pointing out that the diffraction peak at 38.14° is much stronger than that of others, which implies that more of the (111) plane of Ag was exposed. In addition, there is an obvious broad peak at around 24° , indicating an amorphous phase and corresponding to the carbonaceous composition of the carbon shell. Those observations confirm the successful preparation of Ag/CSs hybrid.

III.3. Study of SERS performance

The Raman spectra of Au/CSs was shown in Fig. 5a. The spectra been divided into two peaks (G-peak and D-peak) by Gaussian fitting. The D-band is originated from the breathing modes of sp^3 atoms in rings induced by disordered-activated aromatic modes of A_1 symmetry, and the G-band is originated from the bond stretching of all pairs of sp^2 atoms in both rings and chains [19]. The area ratio of D-band to G-band (I_D/I_G) was calculated and recorded in the upper right corner of each picture. I_D/I_G is often used to measure the crystallinity of carbon materials, the smaller the value, the higher the degree of crystallinity.

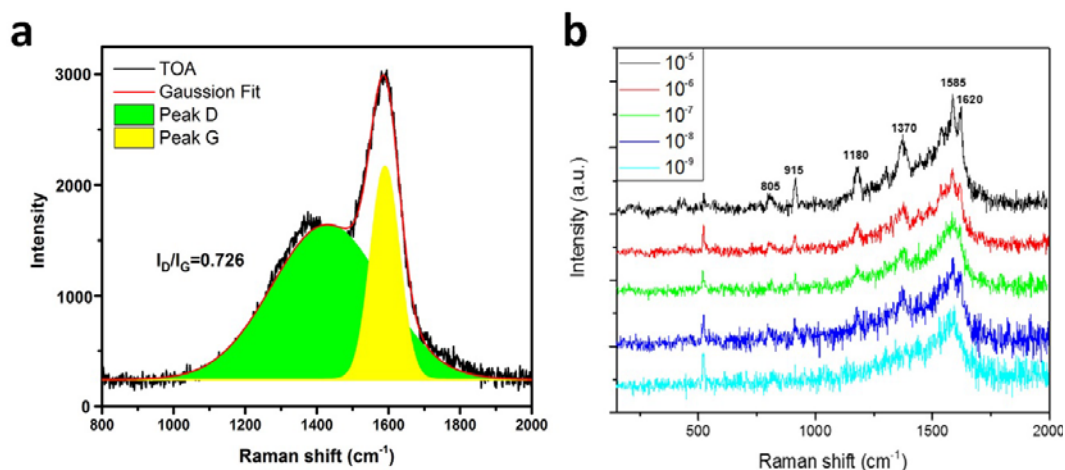


Fig. 5. Raman spectra of Au/CSs (a) and different concentration of R6G adsorbed on Au/CSs substrate (b).

In order to verify the SERS enhancement effect of nanocomposites, crystal violet (CV) was chosen as probe molecular. All fluorescence backgrounds which generate in

Raman spectroscopy of CV molecules excited at 514.5 nm were subtracted. Figure 6a shows the SERS spectra of different concentrations of CV adsorbed on the Au/CSs, which were 10^{-5} M, 10^{-6} M, 10^{-7} M, 10^{-8} M and 10^{-9} M, respectively. The intensity of the Raman modes is found to be different for these concentrations, which implying different Raman enhance factor(EF). As can be seen, the main Raman bands at 807, 913, 1178, 1378, 1582 and 1620 cm^{-1} are typical peaks of CV molecules confirmed according to the reported work [20]. Obviously showed that the intensity of Raman signals could be amplified in the presence of as-prepared substrate.

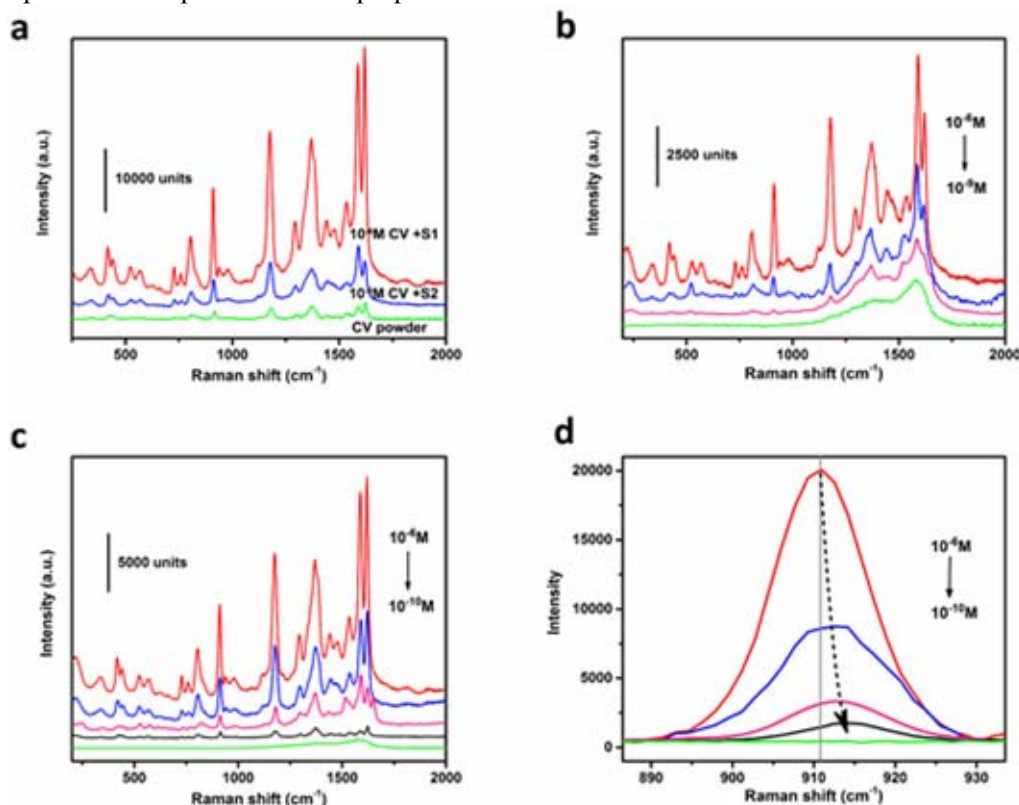


Fig. 6. Comparison of 10^{-6} M R6G adsorbed on S1 and S2 (a) different concentration of CV adsorbed on S2 (b); different concentration of CV adsorbed on S1 (c); Enlarged view of Raman peaks for different concentration of CV adsorbed on S1 (d).

Figure 6a compared the SERS signal intensities of CV obtained from two types of Ag/CSs substrates (S1 and S2). It is clearly observed that in Fig. 6a the SERS signal from S1 is stronger than that of S2, indicating the S1 substrate is superior to the S2 for the enhancement effect. It should be emphasized that we delimited the detection limit of the probe molecule to be the concentration which any one of characteristic peaks disappears. When the characteristic peaks are not complete, we considered the concentration to be the detection limit. Fig. 6c shows Raman spectra of CV adsorbed on the S1 with different concentration of 10^{-6} , 10^{-7} , 10^{-8} , 10^{-9} and 10^{-10} M, respectively. As the probe molecules concentration decrease, the intensity of characteristic peaks is gradually weakened but no significant changes were observed in overall features. As shown in Fig. 6c, some characteristic peaks disappeared, when the concentration of CV reduced to 10^{-10} M. The

enhancement effect was significantly improved by three orders of magnitude after the substrate was immersed in probe solution for a period of time. This indicates that the interaction of the probe molecules with the substrate requires a process. Fig. 6d shows the enlarged view of Raman peaks for different concentration of CV adsorbed on S1.

IV. CONCLUSION

In summary, we have introduced a cheap, convenient and facilely route to prepare silver-carbon and gold-carbon nanocomposite materials as the SERS substrate. The Ag/CSs presents a regular spherical structure with hexagon silver core. Moreover, the stability of the substrate is improved, benefiting from that carbon shell which acts as the protective layer to inhibit the oxidation of the Ag NPs. The utility of our substrates is clearly demonstrated in the analysis using a fluorescent probe molecular, CV. By comparing the Raman signals of probe molecules on S1 and S2, we observed the intensities of signals from the substrate are strongly dependent on the time in which the probe molecules in contact with the Ag/CSs. The Ag/CSs presents a regular spherical structure with hexagon silver core. Moreover, the stability of the substrate is improved, benefiting from that carbon shell which acts as the protective layer to inhibit the oxidation of the Ag NPs. The utility of our substrates is clearly demonstrated in the analysis using a fluorescent probe molecular, CV. The detection limit of Au/CSs for CV molecules is up to 10^{-8} M. The detection limit of Ag/CSs for CV molecules is up to 10^{-9} M. By comparing the Raman signals of probe molecules on S1 and S2, we observed the intensities of signals from the substrate are strongly dependent on the time in which the probe molecules in contact with the Ag/CSs.

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