Controllable optical activity of non-spherical Ag and Co SERS substrate with different magnetic field*

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We experimentally fabricate a non-spherical Ag and Co surface-enhanced Raman scattering (SERS) substrate, which not only retains the metallic plasmon resonant effect, but also possesses the magnetic field controllable characteristics. Raman detections are carried out with the test crystal violet (CV) and rhodamine 6G (R6G) molecules with the initiation of different magnitudes of external magnetic field. Experimental results indicate that our prepared substrate shows a higher SERS activity and magnetic controllability, where non-spherical Ag nanoparticles are driven to aggregate effectively by the magnetized Co and plenty of hot-spots are built around the metallic Ag nanoparticles, thereby leading to the enhancement of local electromagnetic field. Moreover, when the external magnetic field is increased, our prepared substrate demonstrates excellent SERS enhancement. With the 2500 Gs and 3500 Gs (1 Gs = 10^{-4} T) magnetic fields, SERS signal can also be obtained with the detection limit lowering down to 10^{-9} M. These results indicate that our proposed magnetic field controlled substrate enables us to freely achieve the enhanced and controllable SERS effect, which can be widely used in the optical sensing, single molecule detection and bio-medical applications.

Keywords: magneto-optical materials, tunable, surface-enhanced Raman scattering

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1. Introduction

Surface-enhanced Raman scattering (SERS) is a powerful detection technique, which has the ability to fingerprint the molecule vibrational mode. It is widely used in the ultra-sensitive chemical or biomedical analysis.[1,2] Based on the SERS phenomenon, a high-vacuum tip-enhanced Raman spectroscopy system with high spatial and spectral resolution, which allows in situ sample preparation and measurement, has been built which is beneficial for basic surface studies. Such a system shows simultaneously activated infrared and Raman vibrational modes, Fermi resonance, and some other non-linear effects.[3] The SERS happens with the aid of the metallic nanoparticles, arrays or their aggregations, where increased Raman signal arising from the enhanced surface plasmon resonance is obtained.[4–6] Two kinds of enhancement mechanisms are involved for the SERS.[7] One is the chemical enhancement caused by the charge transfer. The other is the local electromagnetic enhancement that originates from the excitation of the collective oscillations of free electrons in noble or transition metals. The extent of enhancement strongly depends on the surface morphology of SERS substrate like the size, shape and aggregation form of nanoparticles.[8–10] Much work has been carried out on the non-spherical nanoparticles, like the hierarchical nanoparticles with nanogaps and nanotips built on the nanoparticle surface,[11–13] rough surface substrate of nanoarchitectures with hedgehog-shaped, cauliflower-shaped, or bunch-of-grapes-shaped surface features,[14] various branched metallic architectures,[15–17] large-scale monocrystalline metallic nanooctahedra,[18] multifarious metallic nanoparticles architectures, etc.[19] Their SERS activities are considerably higher than those of normal spherical mono-metallic nanoparticles.[20]

One critical requirement for the surface-enhanced Raman scattering application is to design a stable and reproducible surface-enhanced Raman scattering substrate. To meet the above challenge, much effort has been made to fabricate the surface-enhanced Raman scattering substrates with the help of external field like the electric field,[21] temperature, or magnetic field.[22,23] Among them, magnetic materials with noble metals (Au or Ag) are commonly used to form composite structures. It can not only reduce the cost of noble metals but also make it easy to be separated and concentrated.[24] Several types of magneto–plasmonic hybrid nanoparticles have been reported including Co/Au core/shell nanoparticles with one-step seeding-growth,[25] and Co@Cu nanoparticles via pulsed laser dewetting method,[26] Ag/FeCo/Ag core/shell/shell nanoparticles by the hot injection method in combination with the polyol method and Au–Fe_3O_4 heterostructured nanoparticles.[27] Our group has synthesized

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the Ag–Fe_3O_4 nanocomposites by the redox reaction between Ag_2O and $Fe(OH)_2$ in the absence of additional reductant at a temperature of 90 °C and under atmospheric condition.[28]

Here in this study we present the synthesis and applications of novel magneto-optical surface-enhanced Raman scattering substrate comprised of non-spherical silver and cobalt nanoparticles. These materials present unique optical properties and magnetic field controllability. The surface-enhanced Raman scattering enhancement behavior is checked with different applied external magnetic fields and molecule detection concentrations. As expected, our prepared substrate provides excellent surface-enhanced Raman scattering signal, which is caused by the closed packed metallic nanoparticles induced by the magnetic field. The detailed influence of magnetic field on our prepared surface-enhanced Raman scattering substrate is clearly described in the following sections.

2. Experiment

Cobalt nanoparticles are prepared by a very facile reduction method at ambient temperature.[29] The 0.2 g of $CoCl_2{\cdot}6H_2O$ and 0.1 g of $NaBH_4$ are added to 10 mL of deionized water at the same time. The reaction undergoes as the following equation:

$$2CoCl_2 + NaBH_4 + 2H_2O = 2Co + 2H_2 + 4HCl + NaBO_2.$$

A minor revision of the polyol synthesis method is carried out to synthesize the non-spherical silver nanoparticles, where reduction of Ag^+ ions by ethanol glycol (EG) leads to the formation of nuclei.[30] The 25-mL EG is pre-heated to 140 °C, then 5-mL HCl (25 mM) is added. Ten minutes later, 15-mL $AgNO_3$ (93 μM) and PVP (147 μM) is added dropwise simultaneously. Then the reaction continues 8 h. Finally, the solution is centrifuged and cleaned with ethanol and clean deionized water three times respectively.

The morphology of nanoparticles is characterized with JSM-6700F field emission scanning electron microscopy (FE-SEM). JEM-100CX transmission electron micrograph (TEM) is used to characterize its morphology. Absorption spectra are taken by a UV 3150 UV-VIS-NIR spectrophotometer. Raman spectra are collected at room temperature by Renishaw-2000 Raman spectrometer (Britain) with 532-nm laser excitation. The laser is focused onto the samples from the top by an objective lens (50x, NA, 0.55). To prepare the SERS substrate, the magnetic field is initiated during the sample preparation. We firstly deposit cobalt colloid on the pre-cleaned glass slide, where different sizes of the magnetites are placed underneath the glass slid. Then mixed solution of silver colloid and test molecule is deposited. Finally, let the substrate dry under ambient conditions. All samples are used after preparation for SERS measurements. Ten Raman spectra are measured at random positions on each substrate and then averaged.

3. Results and discussion

SEM images of our prepared non-spherical Ag nanoparticles with rough surface are shown in Figs. 1(a)–1(c). The red region indicates that three Ag nanoparticles are uniform in morphology. The right one is the enlarged view of the nanoparticles with size around 180 nm. The surface of each nanoparticle is rough, which can greatly increase the local electromagnetic field due to many hot spot built around the non-spherical Ag nanoparticles. Figures 1(d) and 1(e) show the TEM image of the Ag nanoparticles which give further the details in structure analysis. The TEM images show an incompact structure with non-spherical surface, which is caused by the shape selective oxidative etching of Ag nanostructures of Cl^{-1}.[31] The morphology of the non-spherical silver nanoparticles indicates that uniform and narrow size distribution of the nanoparticles can be obtained. The absorption peak of the non-spherical silver nanoparticles is shown in Fig. 1(f). The adsorption peak of the non-spherical silver nanoparticles is located at about 442 nm. The shoulder at 382 nm appears due to a quadrupole contribution, indicating the formation of non-spherical silver nanoparticles with rough protuberance.[32]

The morphology and size of the as-synthesized Co nanoparticles are characterized by TEM as indicated in Figs. 2(a) and 2(b). The size of our prepared spherical Co nanoparticles is around 200 nm. In order to evaluate optical properties of colloidal Co nanoparticles, the UV-VIS analysis is performed, which is shown in Fig. 2(c). No obvious resonant peak can be found in the spectrum. According to Mie's theory, Creighton and Eadon[33] have reported the calculated optical spectrum of Co nanoparticles in water, indicateing that Co nanoparticles have very weak absorption in the visible range. Thus, our experimental result is consistent with those in Refs. [33] and [34].

With 10^{-6}-M CV serving as the test molecule, SERS activity of the non-spherical Ag and Co SERS substrate is investigated in Fig. 3. Most SERS signals come from the probed molecule adsorbed around the surface of the non-spherical Ag nanoparticles. It is demonstrated that the enhanced SERS enhancement is related to local electromagnetic field around the silver nanoparticles as compared with the Raman spectra of solid CV power. 0H represents the case of no applied external magnetic field, where the Ag and the cobalt nanoparticles are randomly distributed on the glass slip. Tunable plasmonic resonance arising from the metallic Ag nanoparticles is responsible for the enhanced SERS effect. The assignment of each peak can be found to be in good agreement with that in Ref. [15]. The signal of CV molecule located at 339 cm^{-1} band is attributed to the in-plane vibration of ph-C^+-ph bending. The peak at 422 cm^{-1} is ascribed to the out-of-plane vibration of ph-C^+-ph bend. The peaks at 525 cm^{-1} and

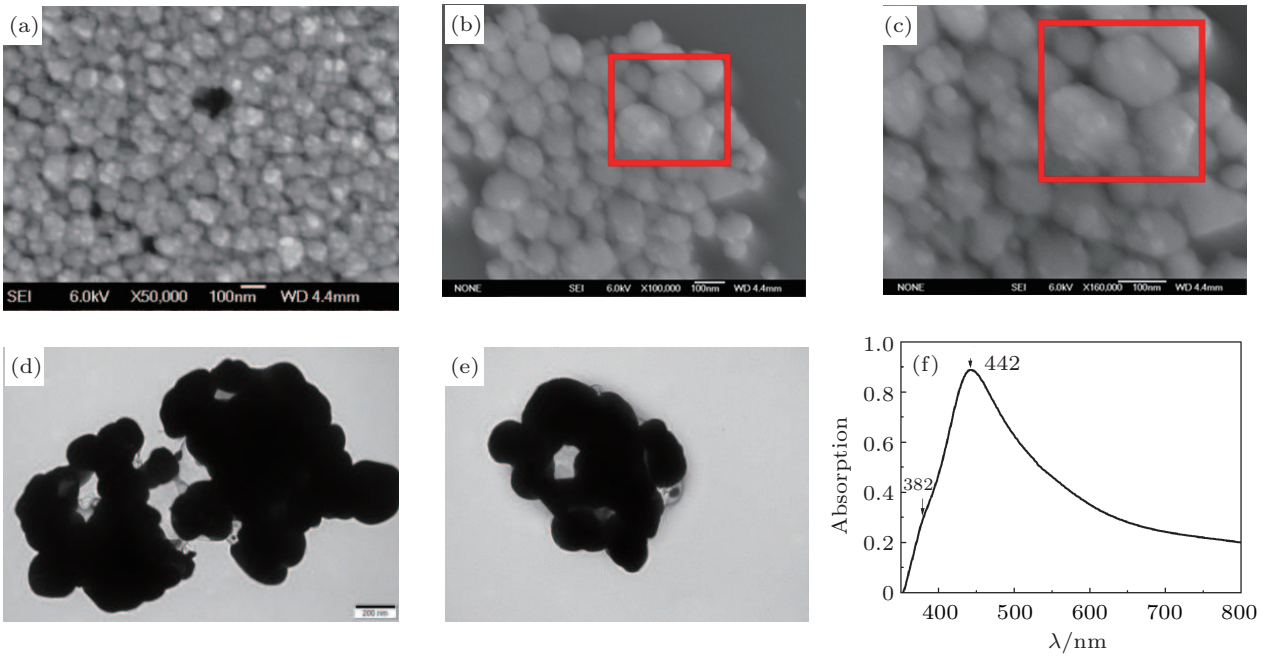


Fig. 1. (color online) (a)–(c) SEM images of the prepared non-spherical silver nanoparticles with different magnifications; (d) and (e) TEM images of the non-spherical silver nanoparticles; (f) absorption spectrum of the non-spherical Ag colloid.

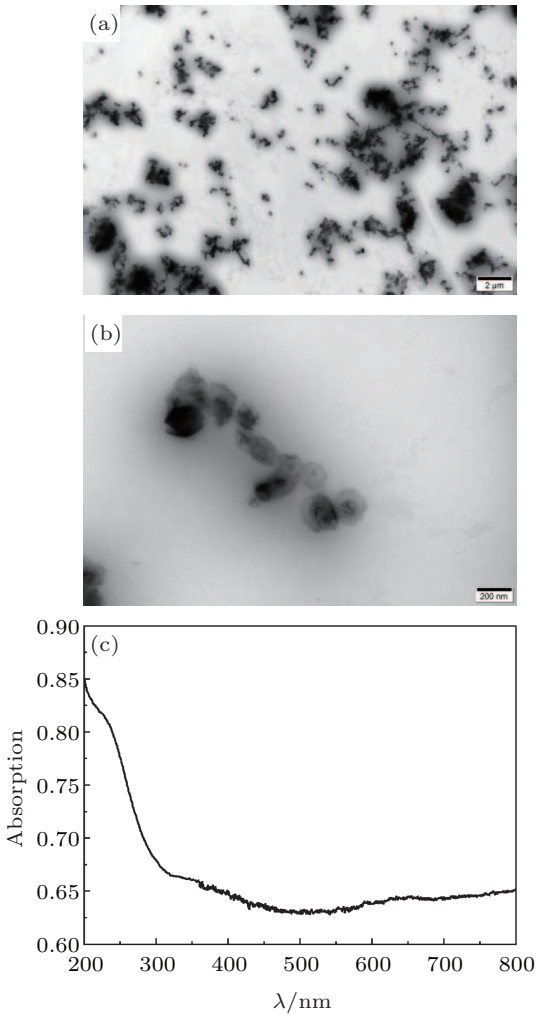


Fig. 2. (color online) (a) and (b) TEM images of the prepared Co nanoparticles with different magnifications; (c) absorption spectrum of the non-spherical Ag colloid.

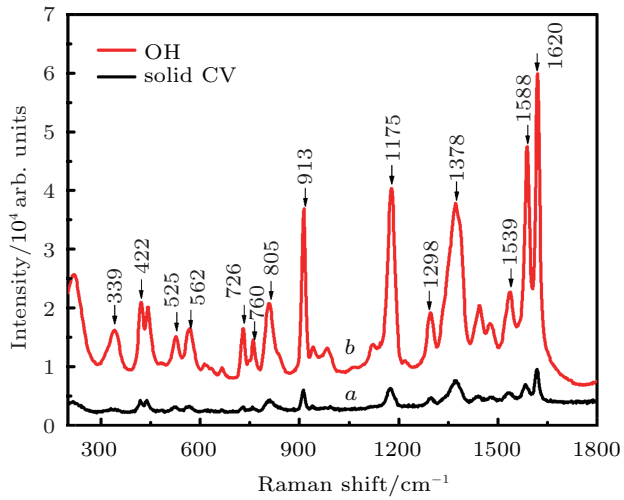


Fig. 3. (color online) (curve *a*) Raman spectra of solid powder CV, and (curve *b*) 10^{-6}-M CV absorbed on SERS substrates without external magnetic field.

562 cm^{-1} are assigned to the ring skeletal vibration of radial orientation and the peaks at 726, 760, 805 cm^{-1} originate from the out-of-plane vibration of ring C–H bend. The peak at 913 cm^{-1} is caused by the ring skeletal vibration of radical orientation. The peaks at 1175 cm^{-1} and 1298 cm^{-1} are from the in-plane vibration of ring C–H bend, 1539 cm^{-1} is from the phenyl ring C–C stretching + N^+ = phenyl stretching, 1588 cm^{-1} is from the phenyl ring C–C stretching and bend, and 1620 cm^{-1} is from Phenyl ring C–C stretching + N-phenyl stretching.

To fully explore the magnetic field controllable SERS activity, we investigate the substrate with four different magnitudes of external magnetic field. Here 1H, 2H, 3H, and 4H represent the external magnetic fields of 1500 Gs, 2000 Gs,

2500 Gs, and 3500 Gs, respectively. Ferromagnetic Co nanoparticles have uniform vector magnetization due to the superparamagnetic properties. The direction of its magnetization is determined by the applied magnetic field. When the difference between the maximum and minimum values of free energy per unit volume is very large in comparison with the thermal energy, we may ignore thermal agitation and calculate the static magnetization at each magnetic field. Any aggregation in the nanoparticle solution before the initiation of the magnetic field due to the magnetic dipole interactions can be neglected.[27] With the different magnitudes of the magnetic field, the Co nanoparticle will be redistributed, thus providing the platform with different arrangements. Probed molecules can locate themselves at highly SERS-active sites during the rearrangement of the metal nanoparticles. As is well known, the excitation of surface plasmons at smooth surface is usually not possible because of mismatch of the momentum of the photon with that of the surface plasmon.[35,36] Thus, rough surface is necessary for the SERS measurement. Due to the superparamagnetic response of the Co nanoparticles, our prepared non-spherical Ag and Co SERS substrate simultaneously possesses both strong magnetic responsiveness and tunable plasmonic properties. Excellent SERS activity can be found in Fig. 4 with increasing magnetic field, where the neighboring non-spherical Ag nanoparticles cause the polarization of the plasmon to strengthen, thereby generating large enhancement SERS signal from molecules. Thus, the closely packed cobalt nanoparticles caused by the external magnetic field induces the density of well-defined hot spots around the silver nanoparticles to exhibit enormous near-field enhancements for large SERS enhancements.

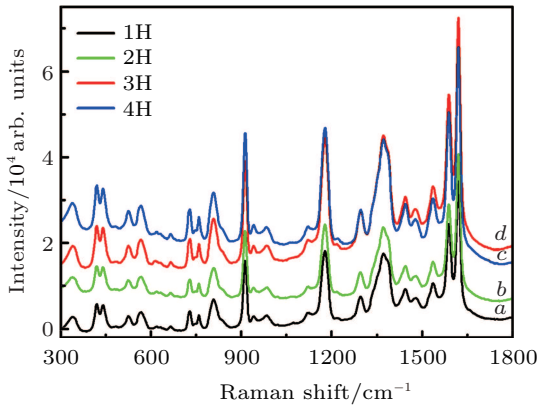


Fig. 4. (color online) Raman spectra of 10^{-6}-M CV molecule absorbed on the SERS substrates with increased magnetic field: (curve *a*) 1H (1500 Gs), (curve *b*) 2H (2000 Gs), (curve *c*) 3H (2500 Gs), (curve *d*) 4H (3500 Gs).

To explore the sensitivity of our prepared cobalt and silver SERS substrate, different concentrations of the investigated CV molecules are investigated, and the results are shown in Figs. 5(a) (2H) and 5(b) (4H). The experimental results show that the enhanced SERS can be obtained even with 10^{-9} M for CV molecule. It demonstrates the determination capability of our prepared SERS substrate. Moreover, the Raman activity of the 4H is even more obvious. It originates from the enhanced local electromagnetic field caused by the closed packed non-spherical Ag nanoparticles. Based on previous studies, it appears that two major factors are necessary in order to achieve high SERS enhancements using nanoparticles, namely, increased hot spots located around the non-spherical silver nanoparticles and an optimized spatial arrangement. The superparamagnetic cobalt nanoparticles will aggregate under the influence of the external magnetic field, which is a platform for the metallic nanoparticles to redistribute.

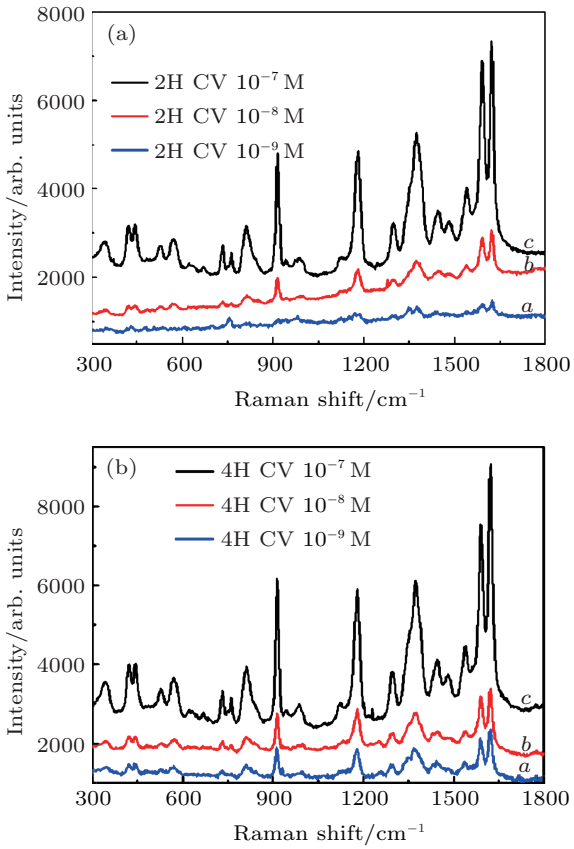


Fig. 5. (color online) Raman spectra of CV molecule absorbed on the SERS substrate under 2H (2000 Gs) and 4H (3500 Gs) magnetic field with different concentration: (curve *a*) 10^{-7} M, (curve *b*) 10^{-8} M, and (curve *c*) 10^{-9} M.

Employing 10^{-6}-M R6G as the test molecules, we also investigate the SERS activity with and without magnetic field, and the results are shown in Fig. 6. It demonstrates the enhanced Raman effects with the initiation of magnetic field. The cases of different magnitudes of the applied magnetic field, i.e., 0H, 1H, 2H, 3H, and 4H, are also investigated as shown in Fig. 6. The increased Raman scatting effect can be obtained with using a larger applied magnetic field, which is caused by field enhancement around the surface of the non-spherical Ag nanoparticles. The variation of magnetic field effect on R6G molecule can provide valuable information to clarify the uniform Raman signal. And the resultis consistent

with that of the CV molecule. It demonstrates the determinations capability of our prepared SERS substrate. And these findings offer an insight into magnetic field controlled SERS substrate that can be realized by changing the externally applied magnetic field.

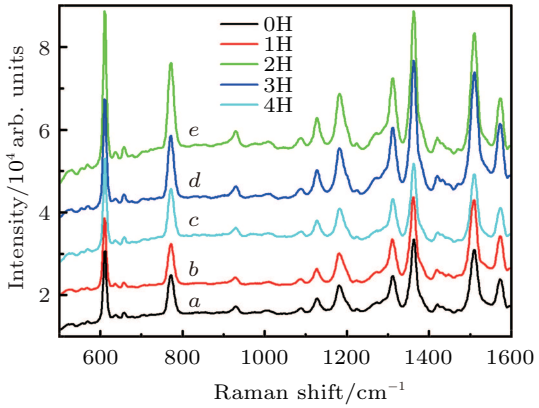


Fig. 6. (color online) Raman spectra of 10^{-6}-M R6G molecule absorbed on the SERS substrate with different applied magnetic fields: (curve *a*) 0H, (curve *b*) 1H (1500 Gs), (curve *c*) 2H (2000 Gs), (curve *d*) 3H (2500 Gs), and (curve *e*) 4H (3500 Gs).

In addition, we also carry out the SERS experiment with R6G probed molecule at 4H magnetic field to verify that our detection limit can be downloaded to 10^{-9} M. The results are shown in Fig. 7. Probed R6G molecule could be detected and distinguished from each other at 10^{-6}-M level without any pretreatment.

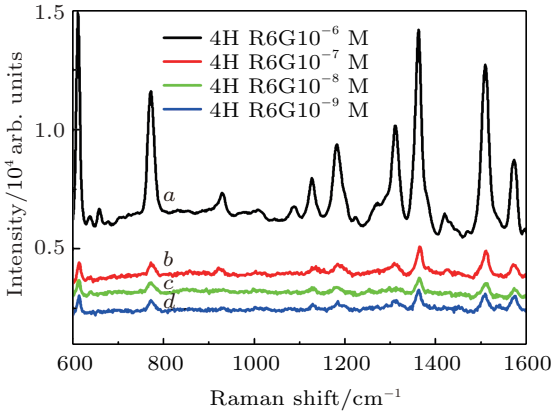


Fig. 7. (color online) Raman spectra of R6G molecule absorbed on the SERS under 4H (3500 Gs) magnetic field with different concentrations: (curve *a*) 10^{-6} M, (curve *b*) 10^{-7} M, (curve *c*) 10^{-8} M, and (curve *d*) 10^{-9} M.

The experimental results in Figs. 5 and 7 show that enhanced SERS can be obtained even with 10^{-9} M for CV and R6G molecule. It demonstrates the determination capability of our prepared SERS substrate. The integration of cobalt nanoparticles and noble metal nanoparticles can result in simultaneous magnetic activity and optical response. Moreover, the optical property of the whole system could be modulated by controlling the magnitude of an external magnetic field. Under the influence of the external magnetic field, the superparamagnetic cobalt nanoparticles in the host liquid form a disordered array. The stronger the external magnitude magnetic field, the more densely the nanoparticles are packed together. In this way, the electromagnetic hot spots located between the neighboring Ag nanoparticles can be tuned by the external magnetic field. It provides the platform with different arrangements. Probed molecules can locate themselves onto highly SERS-active sites during rearrangement of the metal nanoparticles. The bigger density of the hot-spots and amplitude of the electric field in the hot-spot are responsible for the enhanced SERS effect. In a word, we have proposed a facile approach to fabricating the low-cost and highly tunable SERS substrate by using non-spherical silver and cobalt nanoparticle SERS substrates.

4. Conclusions

As a consequence of the surface plasmon resonance where the metallic nanoparticles provide the necessary enhancing properties and magnetic field responsive cobalt nanoparticles, the enhanced Raman effects can be obtained in the presence of the external magnetic field, with using our prepared non-spherical silver and cobalt SERS substrates. Here we pay special attention to the role of tunable magnetic field effect on the SERS activity, and the results show that the enhanced SERS effect can be obtained with a larger magnetic field. It happens due to the closely packed metallic nanoparticles under the influence of the external magnetic field. The local enhancement effects of test molecules (CV and R6G) are matched with each other. Thus, our experimental results illustrate that integration of cobalt and noble metal nanoparticles results in simultaneous magnetic activity and optical response. Employing such magneto–optical systems, it is a great desire to achieve dynamic control of localized surface plasmon resonance wavelength through external magnetic field, which would be a breakthrough in biology-related nanotechnology.

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