

Synthesis of silver/silver chloride/graphene oxide composite and its surface-enhanced Raman scattering activity and self-cleaning property

Nan Zhao^{a, b}, Xiao Fei^a, Xiaonong Cheng^b, Juan Yang^{b, c}

^a Jingjiang College of Jiangsu University, Zhenjiang, 212013, P.R. China

^b School of Materials Science and Engineering, Jiangsu University, Zhenjiang, 212013, P.R. China

^c Key Laboratory of Soft Chemistry and Functional Materials, Nanjing University of Science and Technology, Ministry of Education, Nanjing, 210094, P.R. China

Corresponding author e-mail address: yangjuan6347@mail.ujs.edu.cn

Abstract. Recently, silver nanoparticles decorated with graphene and graphene oxide (GO) sheets can be employed as surface-enhanced Raman scattering (SERS) substrates. However, their SERS activity on macromolecular compound detection is all one-time process. In order to solve this issue and decrease the cost of routine SERS detection, silver/silver chloride (Ag/AgCl) with photocatalytic activity under visible light was introduced. In this study, a novel, simple and clean approach is carried out for synthesis of the Ag/AgCl/GO composite. The Ag/AgCl colloidal solution is obtained by hydrothermal method and then mixed with GO solution to obtain the Ag/AgCl/GO composite using a facile electrostatic self-assembly method. Results showed that the Ag/AgCl/GO composite has the optimized SERS activity to Rhodamine 6G molecules with the maximum enhancement factor value of 3.8×10^7 . Furthermore, the Ag/AgCl particles with high efficient and stable photocatalytic activity under visible light lead to an outstanding self-cleaning property of the Ag/AgCl/GO composite.

1. Introduction

In recent years, graphene (GE) and its derivatives are the hot and novel carbonaceous material study for a significant research endeavor since their excellent and uniquely mechanical, electrical as well as chemical properties [1-3]. The important theme in GE-based study is to survey their surface-enhanced Raman scattering (SERS) properties, particular in the noble metal-GE or graphene oxide (GO) composite (such as silver, gold) [4]. The SERS technique allows for highly sensitive detection and structural analysis with ultra-low concentrations, and has exhibited potential applications in different areas, such as chemistry, biomedicine, energy saving, and environment science [5]. Zhao et al. have prepared uniform silver nanoparticles (Ag NPs) with small sizes on GE nanosheets for active SERS substrate by an etching copper template strategy [3]. Cheng et al. reported that a SERS substrate of Ag NPs/GO can be fabricated by covalent assembly of Ag NPs and GO [5]. Our previous work [4, 6] has successfully synthesized Ag NPs-GE and gold nanoparticle/graphene oxide composite films by electrostatic self-assembly method. Due to the good SERS effect, the Raman signals of Rhodamine 6G (R6G) adsorbed on Ag NPs-GE substrate have been enhanced obviously and the mechanism was also discussed.



However, to the best of our knowledge, almost all of the SERS detection process of the GE or GO-based nanocomposite materials on molecules are not recyclable. It is believed that the Raman detections are always on macromolecular compounds, if the macromolecules can be degraded after detection, which means apart from SERS sensitivity, the composite material also has a good photocatalytic activity, and then the substrate material used in Raman detection can be reused. To address this challenge, silver chloride (AgCl) was introduced into the composite materials in this work. The AgCl particles are well-known as a photosensitive material and a semiconducting material with direct/indirect band gap of 5.6 eV and 3.25 eV, respectively [7]. A semiconductor photocatalyst has good optical performance that can transfer the light energy into chemically available charge carriers. And then, the redox reactions will be driving on the surface of photocatalyst when the absorbed incident photons energy is higher than the band gap of the photocatalyst [8]. Lately, many reports [7, 9] have illustrated that the Ag/AgX (X=Cl, Br) compounds possess outstanding photocatalytic performance and high stability owing to the surface plasmon resonance (SPR) effect of the noble metal nanoparticles at diverse light irradiations, especially the Ag/AgCl has lured arresting attention as a rising photocatalyst work for pollutant degradation under visible light irradiation. So the optimized SERS activity and excellent self-cleaning property could be integrated into the designed Ag/AgCl/GO composite substrate.

Herein, self-assembly process is utilized to prepare Ag/AgCl/GO composite. Ag/AgCl particles are firstly obtained by hydrothermal method followed by mixing with GO solution by electrostatic self-assembly method to obtain Ag/AgCl/GO composite. The R6G molecules, as the probing molecules, were served for testing the SERS sensitivity of the obtained composite and the self-cleaning property was characterized by UV-vis and Raman experiments. This kind of composite is promising for the routine SERS detection.

2. Methods

2.1. Preparation of GO solution and Ag/AgCl

GO was prepared according to the reported Hummers method [10]. 10 mg of GO powders were firstly dispersed in 100 mL deionized (DI) water with stirring for 1 h and sonication for 2 h. Then, the prepared GO solution was preserved and used for the following experiment.

The Ag/AgCl was prepared by a hydrothermal method. As a typical synthesis recipe, the milky AgCl colloidal solution was prepared by mixing AgNO₃ (20 mL, 0.02 M), polyelectrolyte-poly (diallyldimethylammonium chloride) (PDDA) (20 mL, 0.2 M) and NaCl solution (20 mL, 0.02 M), followed by adding and mixing glucose (60 mL 0.84 mM) with vigorous stirring for 2 h. The molar ratio of [AgNO₃]/[NaCl] was fixed at 1:1 in our experiment. Then the colloidal solution was transferred into a pressure-resistant vessel, and was heated to 180 °C in vacuum for 24 h. After the reaction, the resulting dispersion was washed and centrifuged three times. Then the final pellet was dissolved in 20 mL of deionized water and preserved in a vial.

2.2. Preparation of Ag/AgCl/GO composite substrate

The glass substrates were firstly cleaned by immersing in ethanol with sonication for 12 h. The 10 mL of freshly prepared GO solution was mixed with 10 mL of Ag/AgCl suspension slowly with stirring for 12 h. Afterwards, the pretreated glass substrates were immersed in the Ag/AgCl/GO solution for 30 min and then rinsed with DI water followed by drying in flowing nitrogen. The samples were disposed by identical process for four times to prepare Ag/AgCl/GO composite substrate at room temperature.

2.3. Preparation of sample for SERS measurements

The prepared SERS substrates were firstly immersed in 20 mL, 10⁻⁵ M R6G ethanol solution for 6 h. The R6G molecules can be adsorbed on the surface of substrates. After that, the unabsorbed molecules were removed by DI water rinsing for three times. Finally, the above-mentioned substrates were dried

under room temperature for SERS measurements. The whole preparation process was carried out in a dark room.

2.4. Characterization

The crystal structure of the composite was conducted on a Philips 1730 powder X-ray diffractometer (XRD) with Cu K α radiation ($\lambda=1.5406$ Å). The morphologies of the samples were observed by the JEOL-6460 scanning electron microscope (SEM) equipped with an Oxford INCA Energy SEM 350 EDS system. A thermos ESCALAB 250 spectrophotometer of the X-ray photoelectron spectroscopy (XPS) measurements with Al-K α radiation were used to analyze the constitution of the substrates. The absorption spectra were performed on a Shimadzu UV-2550 spectrophotometer. The Raman spectra were recorded by a MXR Raman system operating at 532 nm with irradiation power of 1 mW and the laser spot size is ca. 2.1 μm^2 . The acquisition time of each measurement is 10 s. The relative standard deviation (RSD) is within 5% based on the strongest band intensity of R6G on the Raman spectrum.

3. Results and discussion

Fig. 1(a, b) show the SEM images of the Ag/AgCl samples synthesized using chemical transformation of AgNO₃ by hydrothermal method. In Fig.1 (a), it can be seen that the products were consist of many homogeneous particles with special polyhedral morphology. Under the microscope, most of the particles show cube-like morphology with the particle size of about 100 nm. Fig. 1(b) is the high-resolution SEM picture of the Ag/AgCl products and the structure presented distinct facets and slippy exterior surfaces. Fig. 1(c) is the SEM image of the surface of Ag/AgCl/GO composite substrate. SEM precisely presented the microcosmic morphology and detailed structure of the Ag/AgCl/GO products. It is well-known that the oxygen-containing groups of GO carry negative charges. The Ag/AgCl colloidal solution was positively charged for the participation of PDDA [9]. The Ag/AgCl particles combined with the GO faultlessly by electrostatic self-assembly method as shown in Fig. 1(c). Fig. 1(d) shows the XRD pattern of the Ag/AgCl products. The distinct diffraction peaks at 2θ of 38.1° (111), 44.3° (200), 64.4° (220), 77.4° (311), corresponding to the representative cubic phase of Ag (JCPDS card No. 65-2357), could be unambiguously detected, which reveals the triumphant phase transformation from AgCl to cubic Ag. Furthermore, the accessional peaks at 27.8° (111), 32.2° (200), 46.2° (220), 54.8° (311), 57.4° (222), 67.5° (400) and 74.5° (331) in Fig.1 (d) could match with the classically cubic phase of AgCl (JCPDS card No. 35-0270). The relatively low and weak intensity of the peaks of AgCl indicates the low content or poor crystallinity of AgCl in the sample. The XRD results prove that the coexistence of metallic Ag and AgCl is in the Ag/AgCl.

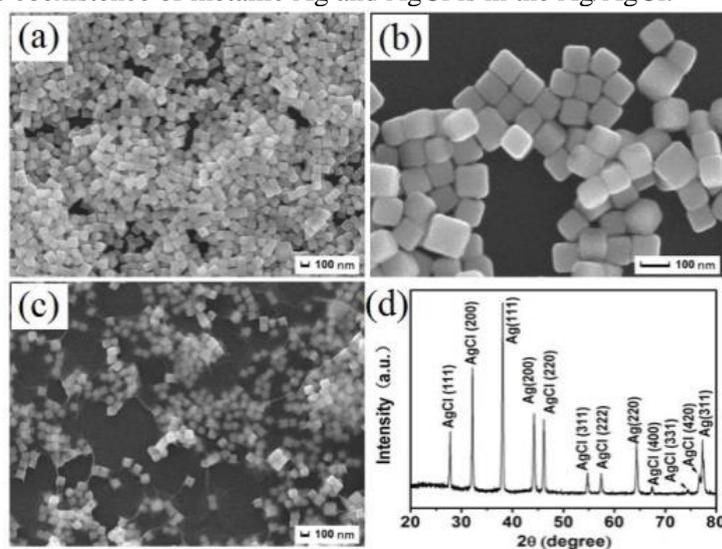


Fig 1 (a, b) SEM images of Ag/AgCl and (c) Ag/AgCl/GO composite substrate (d) XRD pattern of Ag/AgCl.

XPS is also employed to characterize the surface chemical states of the sample. In Fig. 2 (a), the characteristic peaks in the Cl 2p spectrum are at approximately 197.6 eV and 199.2 eV, corresponding well with Cl 2p 3/2 and Cl 2p 1/2, which indicates the presence of chlorine as Cl⁻. Fig. 2 (b) displays the typical Ag 3d spectrum of the prepared Ag/AgCl/GO composite. The characteristic peaks for the Ag 3d at around 367.34 eV and 373.0 eV are attributed to Ag (+) 3d 5/2 and Ag (+) 3d 3/2, respectively. The peaks at 368.73 eV and 374.2 eV are assigned to the binding energies of Ag (0) 3d 5/2 and Ag (0) 3d 3/2, respectively. The XPS analysis indicates that the Ag presented as Ag⁺ in AgCl and as Ag⁰ in metallic Ag [11]. The C 1s XPS spectrum of Ag/AgCl/GO composite in Fig. 2(c) can be deconvoluted into four peaks arising from C=C/C-C (284.8eV) in the aromatic rings, C-O (286.3eV) of epoxy and alkoxy, C=O (287.7eV) and O-C=O (288.8eV) groups, respectively [6]. The result illustrates that the Ag/AgCl nanoparticles have been decorated on the surface of GO, which is accordant with the results of SEM and XRD.

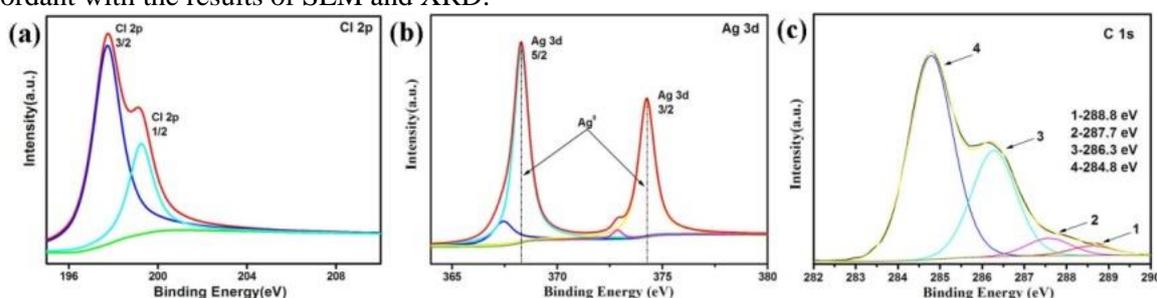


Fig 2 XPS spectra of (a) Cl 2p (b) Ag 3d and (c) C 1s of the Ag/AgCl/GO composite.

The SERS property of the obtained Ag/AgCl/GO substrate was studied in detail by using R6G as probing molecule. First of all, Ag/AgCl/GO substrate was immersed in 20 mL R6G ethanol solution (10^{-5} M) for 6 h. The tested SERS spectrum for the above substrate is shown in Fig. 3(A)-(a). The Raman spectra of 0.02 M R6G solution measured at 532 nm is also shown in Fig. 3(A)-(c). In the normal Raman spectrum of R6G, the absorbed bands are all relatively weak, but the R6G molecules adsorbed on Ag/AgCl/GO substrate exhibits the stiffening of characteristic bands for explicit excitation energy, and the five strong bands are observed at 611, 773, 1184, 1363 and 1649 cm^{-1} (Fig. 3(A)-(a)). The band at 611 cm^{-1} is ascribed to the C-C-C ring in-plane vibration mode, and the band at 773 cm^{-1} is assigned to the C-H out-of-plane bend mode. The two bands at 1129 and 1184 cm^{-1} are both attributed to the C-H in-plane bend modes. The bands at 1311 as well as 1574 cm^{-1} are assigned to the N-H in-plane bend modes, while the bands at 1363, 1509 and 1649 cm^{-1} are ascribed to the C-C stretching modes. These results illuminate that the Raman signals of R6G molecules adsorbed on Ag/AgCl/GO substrate are enhanced remarkably. Experiment was designed to explore the effect of GO on the SERS activity of the composite substrate. In the comparison of Fig. 3(A)-(a) and Fig. 3(A)-(b), it can be seen that Ag/AgCl/GO has the more powerful enhancement effect on R6G molecules than that of Ag/AgCl, which indicates that the GO sheet indeed amplified the SERS signal of the R6G probe molecules. Fig. 3(B) shows the SERS spectra of R6G with diverse concentrations on Ag/AgCl/GO substrate. As the concentration of R6G decreases, the characteristic bands of R6G such as 611, 1363 and 1649 cm^{-1} are quite sensitive to the concentration, so these vibration modes were used as sign for detecting the presence of R6G. The obtained detection limit of R6G in our experiment is as low as 1×10^{-7} M.

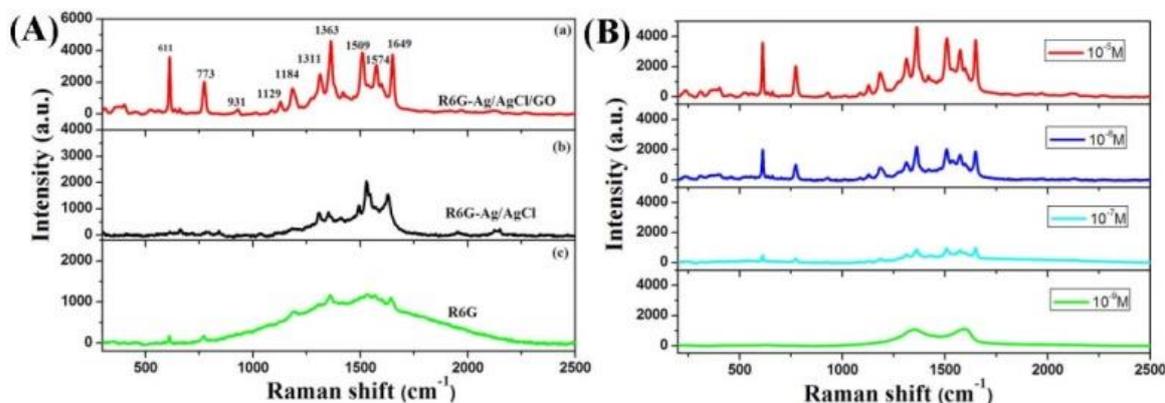


Fig 3 (A) SERS spectra of (a) R6G (10^{-5} M) adsorbed on Ag/AgCl/GO substrate (b) R6G (10^{-5} M) adsorbed on Ag/AgCl substrate and (c) 0.2 M R6G solution measured at 532 nm. (B) SERS spectra of R6G adsorbed on Ag/AgCl/GO substrate with different concentrations.

The self-cleaning property of the Ag/AgCl/GO composite film was firstly investigated by visible-light degradation. Ag/AgCl/GO film after SERS detection was illuminated under visible-light and tested by UV-vis spectrometer and the results are shown in Fig. 4(A). After SERS detection, there is an obvious absorption band around 532 nm, indicating the existence of R6G on the composite substrate [4]. The obvious decrease of absorption peak with irradiation time indicates that the R6G absorbed on the composite substrate could be degraded under visible light and R6G could be almost completely decomposed after irradiation for 12 h. For comparison, the Ag/AgCl/GO composite substrate after absorption of R6G was put in dark and it was found that the intensity of UV-vis spectra maintained even after 30 h. Ag/GO composite without AgCl was also prepared for comparison, which could not lead to the photocatalytic decomposition of R6G shown in the inset of Fig. 4(A). The results suggest that the degradation of R6G was caused by the photocatalytic reactions of AgCl on Ag/AgCl/GO sample under visible-light.

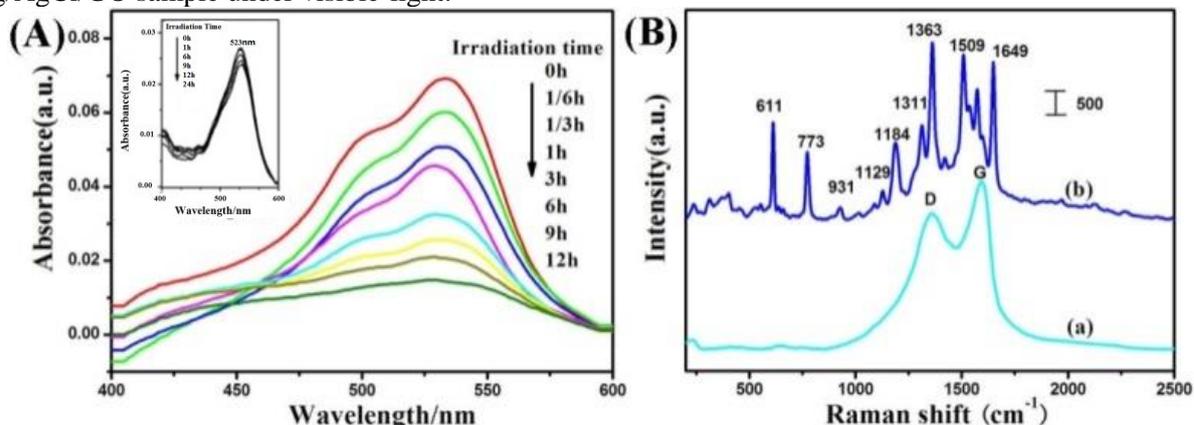


Fig 4 (A) Changes in UV-vis absorption spectra of R6G adsorbed on Ag/AgCl/GO substrate, the inset is changes in UV-vis absorption spectra of R6G adsorbed on Ag/GO substrate as a function of irradiation time. (B) The SERS spectra of samples (a) the Ag/AgCl/GO substrate after SERS detection and then irradiated under visible light for 12 h (b) the photo-degraded Ag/AgCl/GO substrate adsorbed R6G again.

Raman experiments were also carried out to detect the self-cleaning property. As shown in Fig. 3(A)-(a), the Raman signals of R6G adsorbed on Ag/AgCl/GO composite substrate are enhanced prominently. After the Raman detection, the film was irradiated under visible-light for 12 h and characterized by Raman again. It is clearly seen in Fig. 4(B)-(a) that the signals of R6G disappeared, only characteristic peaks of GO can be found, the D band (1355 cm^{-1}) and the G band (1600 cm^{-1}),

which represent the amount of sp³ carbons in the surroundings and the E_{2g} phonon of sp² C atoms, respectively [6]. Results indicated that the R6G can really be decomposed under the photocatalytic degradation. After the photocatalytic degradation, the Ag/AgCl/GO substrate was immersed into 20 mL 10⁻⁵ M R6G ethanol solution again and the Raman spectrum was recorded in Fig. 4(B)-(b), which states clearly the SERS effect. This is the first cycle and we repeated the procedure for five cycles and the results are shown in Fig. 5, the enhancement factor (*EF*) values are also given. The *EF* value can be estimated as follows: $EF = (I_{SERS}/I_{bulk}) / (N_{ads}/N_{bulk})$ [4]. Where *I*_{SERS} is the intensity of a vibrational mode in the SERS spectrum and *I*_{bulk} is the intensity of the same mode in the Raman (non-SERS) spectrum. The *I*_{SERS}/*I*_{bulk} can be obtained from the SERS spectra directly [6]. The *N*_{bulk} and *N*_{ads} are estimated by approximate calculation using monolayer-absorbed mode [4].

In Fig. 5(a), it can be seen that the SERS intensity decrease gradually with the growth of cycling numbers and the intensity decrease obviously after 5 times. In Fig. 5(b), the tendency can be seen clearly by the *EF* values. The *EF* values from 0 to 5 times are 3.8×10⁷, 3.5×10⁷, 2.9×10⁷, 2.1×10⁷, 7.4×10⁶ and 7.2×10⁶, 6.7×10⁶, 3.6×10⁶, 3.4×10⁶, 1.5×10⁶ for C-C-C ring in-plane vibration (ca. 611 cm⁻¹) and C-C stretching (ca.1363 cm⁻¹) respectively. The decay of the SERS property during the recycle might be caused by the oxidation of Ag⁰ on the surface. The mechanism study and property improvement are carrying out in our Lab.

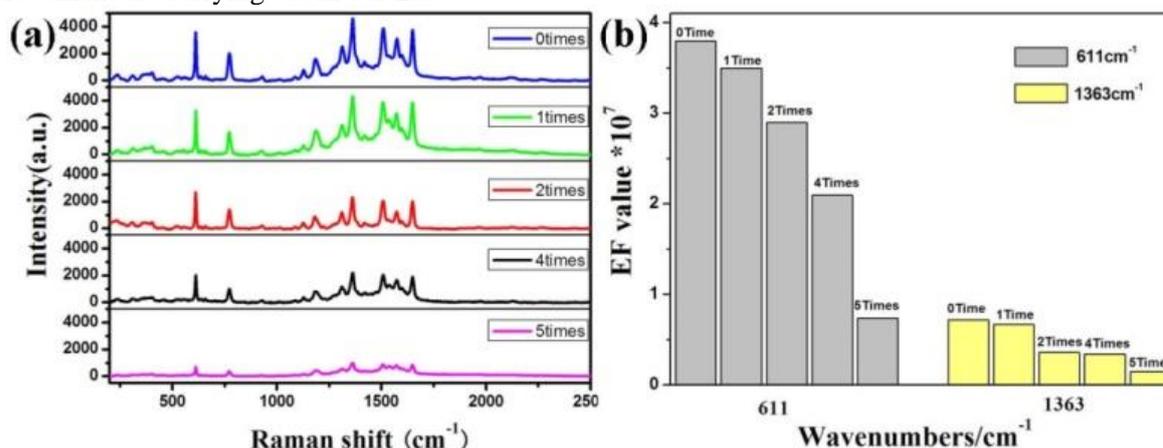


Fig 5 (a) The SERS spectra of R6G adsorbed on Ag/AgCl/GO substrate for different self-cleaning cycles; (b) Raman *EF* values at 611 cm⁻¹ and 1363 cm⁻¹ with different self-cleaning cycles.

4. Conclusion

The Ag/AgCl/GO composite with superior SERS activity and self-cleaning property has been prepared through the hydrothermal method followed by electrostatic self-assembly process. All the preparation processes are fast, green and simple. The prepared materials exhibit enhanced SERS activity for R6G and high visible-light photocatalytic performance for the degradation of R6G. The composite is recyclable, readily prepared and disposable, which possesses a huge convenience for the conventional SERS detection.

Acknowledgements

This work was supported by National Science Foundation of China (51572114), Key University Science Research Project of Jiangsu Province (16KJB430009), Fundamental Research Funds for the Central University (No.30920140122003), Undergraduate Students of Jiangsu Province (201513986003Y) and Senior Talent Foundation of Jiangsu University (15JDG078).

References

- [1] K.S. Novoselov, A.K. Geim, S.V. Morozov, D. Jiang, M.I. Katsnelson, I.V. Grigorieva, S.V. Dubonos, A.A. Firsov, Two-dimensional gas of massless dirac fermions in graphene, *Nature*. 438 (2005) 197-200.

- [2] Y. Li, J. Yang, S.H. Zheng, W.W. Zeng, N. Zhao, M. Shen, One-pot synthesis of 3D TiO₂-reduced graphene oxide aerogels with superior adsorption capacity and enhanced visible-light photocatalytic performance, *Ceram. Int.* 42 (2016) 19091-19096.
- [3] H. Zhao, H.G. Fu, T.S. Zhao, L. Wang, T.X. Tan, Fabrication of small-sized silver NPs/graphene sheets for high-quality surface-enhanced Raman scattering, *J. Colloid. Interface. Sci.* 375 (2012) 30-34.
- [4] Y. Li, J. Yang, Y.Z. Zhou, N. Zhao, W.W. Zeng, W.W. Wang, Fabrication of gold nanoparticles/graphene oxide films with surface-enhanced Raman scattering activity by a simple electrostatic self-assembly method, *Colloid. Surface A* 512 (2017) 93-100.
- [5] Z.J. Qian, Y.C. Cheng, X.F. Zhou, J.H. Wu, G.J. Xu, Fabrication of graphene oxide/Ag hybrids and their surface-enhanced Raman scattering characteristics, *J. Colloid. Interface. Sci.* 397 (2013) 103-107.
- [6] Y.Z. Zhou, X.N. Cheng, D. Du, J. Yang, N. Zhao, S.B. Ma, T. Zhong, Y.H. Lin, Graphene-silver nanohybrids for ultrasensitive surface enhanced Raman spectroscopy: size dependence of silver nanoparticles, *J. Mater. Chem. C* 2 (2014) 6850-6858.
- [7] P. Wang, B. Huang, X. Qin, X. Zhang, Y. Dai, J. Wei, M.H. Whangbo, Ag/AgCl: a highly efficient and stable photocatalyst active under visible light, *Angew. Chem. Int. Ed.* 47 (2008) 7931-7933.
- [8] S.M. Liu, J.L. Zhu, Q. Yang, P.P. Xu, J.H. Ge, X.T. Guo, Facile fabrication and enhanced photocatalytic performance of Ag/AgCl-activated sepiolite heterostructure photocatalyst, *J. Mater. Sci.* 51 (2016) 2565-2572.
- [9] Y.Z. Zhou, R. Chen, T.T. He, K. Xu, D. Du, N. Zhao, X.N. Cheng, J. Yang, H.F. Shi, Y.H. Lin, Biomedical potential of ultrafine Ag/AgCl nanoparticles coated on graphene with special reference to antimicrobial performances and burn wound healing, *ACS. Appl. Mater. Interfaces.* 8 (2016) 15067-15075.
- [10] W.S. Hummers, R.E. Offeman, Preparation of graphene oxide, *J. Am. Chem. Soc.* 80 (1958) 1339-1339.
- [11] Y.Z. Zhou, J. Yang, T.T. He, H.F. Shi, X.N. Cheng, Y.X. Lu, Highly stable and dispersive silver nanoparticle-graphene composites by a simple and low-energy-consuming approach and their antimicrobial activity, *Small* 9 (2013) 3445-3454.