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## COMMUNICATION

## High performance surface-enhanced Raman scattering from dummy molecular imprinting onto silver microspheres

Shaona Chen,<sup>a</sup> Xin Li,<sup>\*ba</sup> Yuanyuan Zhao,<sup>c</sup> Limin Chang<sup>\*c</sup> and Jingyao Qi<sup>d</sup>

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A new strategy for high performance SERS was proposed by using dummy molecular imprinting technique. The obtained core-shell composite can effectively improve the signal-to-noise ratio and the veracity of trace analysis in SERS detection.

Surface enhanced Raman spectroscopy (SERS) is a powerful analytical tool for obtaining structure information of analytes with potential single-molecule sensitivity.<sup>1,2</sup> During the past decades, intensive works have been carried out to provide high-quality SERS. Among them, a hybrid concept was introduced as a novel detection strategy for SERS, in which the recognition ability of molecularly imprinted polymers (MIPs) and SERS active surfaces was integrated. The advantages of this integrated approach are its high selectivity and sensitivity toward analytes, and environmental stability. Recently, Bompert et al. have reported SERS detection of (*S*)-propranolol by using core-shell composite MIP particles as nanosensors.<sup>3</sup> Liu et al. have prepared molecular imprinting-based SERS sensor.<sup>4</sup> Xue et al. have fabricated surface-imprinted core-shell Au nanoparticles as a specific functional SERS substrate for the highly selective detection of bisphenol A.<sup>5</sup> Very recently, we have demonstrated that core-shell Ag@MIP hybrid nanostructures can be a promising SERS platform for ultrasensitive sensing and biological applications.<sup>6</sup> However, a barrier for the practical applications of this method is template leakage and remain. In preparation processes of MIPs, a relative excess of template molecules is normally used to generate molecularly imprinted binding sites. Unfortunately, it is very difficult to remove all of template from the resulting polymer matrix after polymerization. As pointed out by Cormack and Mosbach,<sup>7</sup> 5% or so percent of template remains in the polymer network. This fact would influence the accurate quantification of analytical results in SERS detection. Obviously, it is necessary to eliminate residual template interference in SERS signals.

On the other hand, to date, the majority of MIPs have been prepared through non-covalent approach where template-functional monomer complexes are formed relying on non-covalent interactions. In general, a target analyte is itself as the template in analytical processes.<sup>8</sup> For SERS detection, however, some target analytes might limit especially for preparation of MIPs, owing to their expensive price, instability under the polymerization conditions, low solubility, or low affinity.

In this work, we introduce a new strategy based on dummy molecularly imprinted polymers (DMIPs) to prepare Ag@DMIPs SERS substrates with reasonable signal-to-noise ratios. Our results show that this novel system exhibits high performance SERS due to the background suppression. In addition, we believe that the obtained Ag@DMIPs hybrid material is promising for more practical SERS applications.

The fabrication and SERS application of Ag@DMIPs are schematically shown in Fig.1. First, Ag particles were first synthesized via a liquid-phase reduction method, and were then modified with 3-methacryloxypropyltrimethoxysilane (MPS). The resulting MPS-grafted Ag microspheres (Ag-MPS) were coated with MIP layer by using abietic acid as dummy template. Finally, the SERS behavior of the obtained Ag@DMIPs was investigated by using crystal violet (CV) as probe (ESI<sup>†</sup>). Herein, abietic acid, whose structural skeleton is similar to that of CV (Fig. S1<sup>†</sup>), was chosen to produce DMIPs.

Fig.2 shows scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of Ag particles and Ag@DMIPs hybrid. Fig.2a and 2b show that the bare Ag particles are nearly spherical shape with an average diameter around 1.0  $\mu\text{m}$ . As revealed by Fig.2c and 2d, the as-prepared Ag@DMIPs hybrid materials are almost spherical with the rough surface structures. Compared with the surface of Ag microsphere (Inset in Fig.2b), Ag@DMIPs microsphere shows obvious core-shell structure (Inset in Fig.2d). The thickness of the polymer shell was estimated to be about 4.7 nm. The polymer layer displays a uniform, and provides great stability to SERS probes due to the some protection of SERS-active surface.<sup>9</sup>

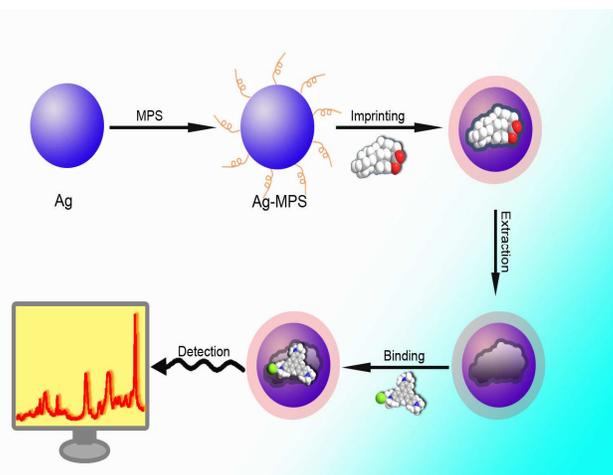
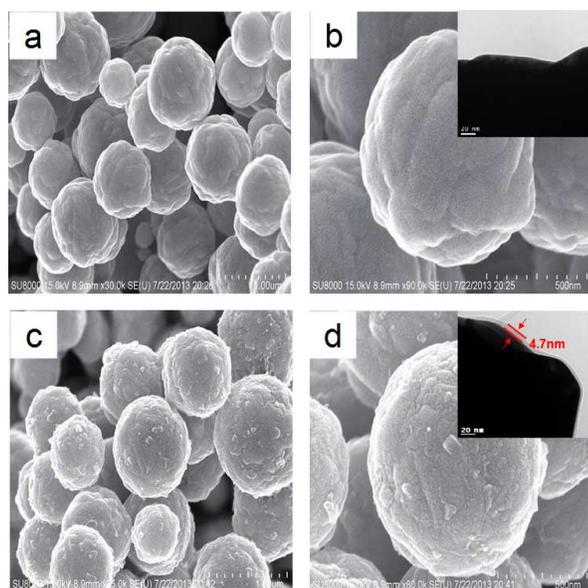


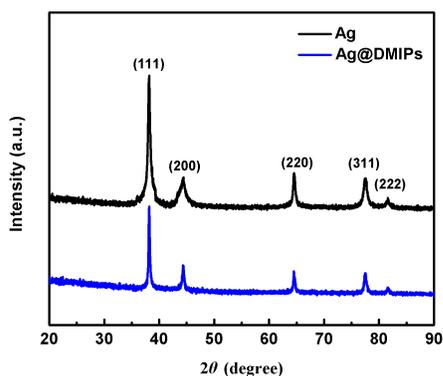
Fig.1 Schematic illustration of the prepare process of Ag@DMIPs.



**Fig.2** Low magnification SEM images of Ag particles (a) and Ag@DMIPs (c). High magnification SEM and TEM images of Ag particles (b) and Ag@DMIPs (d).

The structures of Ag particles and Ag@DMIPs hybrid were further characterized by X-ray diffraction (XRD) analysis, as shown in Fig.3. In the case of Ag particles, the five diffraction peaks located at  $2\theta=38.18^\circ$ ,  $44.4^\circ$ ,  $64.57^\circ$ ,  $77.52^\circ$ , and  $81.60^\circ$  match well face-centered cubic (fcc) Ag (111), (200), (220), (311), and (222) crystal planes according to JCPDS card (No. 04-0783). After encapsulation of Ag microsphere with DMIPs shell, the intensity of all diffraction peaks became weak, suggesting the forming of Ag@DMIPs. Furthermore, Fourier transform infrared (FTIR) spectra of the samples (Fig. S2<sup>†</sup>) and the area mapping analysis of Ag@DMIPs (Fig. S3<sup>†</sup>) also indicated that Ag particles were encapsulated by DMIPs.

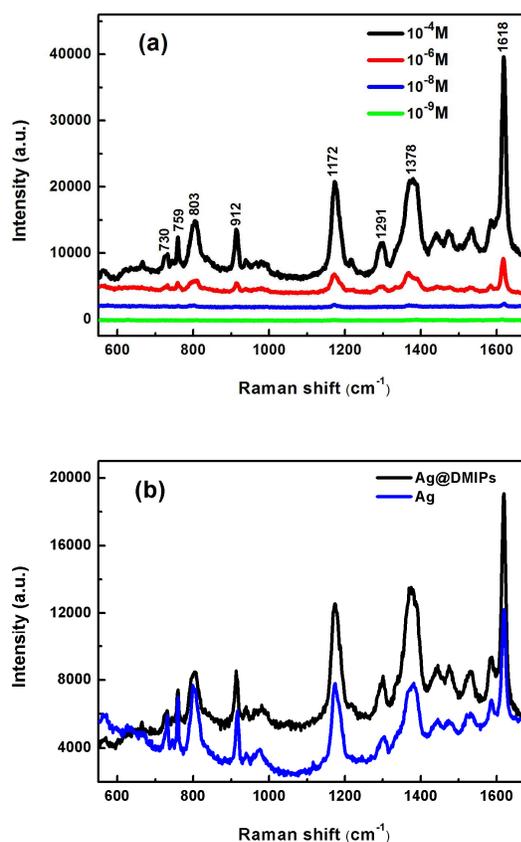
To quantify the performance of Ag@DMIPs, the Raman spectra of CV under different concentration were recorded using 633 nm laser excitation. As shown in Fig.4a, the characteristic bands of CV at 730, 759, 803, and  $1172\text{ cm}^{-1}$  are assigned to the ring (C-H) bending mode, whilst a prominent band at  $912\text{ cm}^{-1}$  is responsible for the ring skeletal vibration and a strong band at  $1378\text{ cm}^{-1}$  is ascribed to the N-phenyl stretching vibration. In



**Fig.3** XRD patterns of Ag particles and Ag@DMIPs.

addition, the other two bands at  $1297$  and  $1618\text{ cm}^{-1}$  are attributed to the ring C-C stretching vibration.<sup>10</sup> These Raman bands are consistent with the previously reported works.<sup>11</sup> Although the SERS intensity decreased with the decrease in CV concentration, Raman signal of CV can be clearly observed at a concentration of  $10^{-9}\text{ M}$  (Fig. S4<sup>†</sup>). Employing the CV peak at  $1618\text{ cm}^{-1}$ , the enhancement factor was estimated to be  $6.55 \times 10^6$  (ESI<sup>†</sup>). Fig. 4b compares the Raman spectra of a  $10^{-5}\text{ M}$  solution of CV adsorbed on Ag@DMIPs and pure Ag, respectively. As expected, Raman signal from the Ag@DMIPs is stronger than that from the pure Ag. Importantly, no any Raman signals can be observed in the extracted Ag@DMIPs (Fig.4). In addition, the selectivity of the Ag@DMIPs also was investigated (Fig. S5<sup>†</sup>).

Good SERS performance of Ag@DMIPs can be attributed to both the core-shell structure and the DMIPs. For the molecular specific recognition of Ag@DMIPs, specific shape and functional character are two major synergistic effects.<sup>12</sup> In our case, besides the swelling effect of solvent,<sup>13</sup> CV could enter the imprinted cavity left by abietic acid due to the structural similarity between the CV and abietic acid. On the other hand, it is possible that the ionic interaction was the main re-binding force. The positively charged nitrogen atom of CV can bind with negatively charged carboxylic group residues of the abietic acid in the imprinted cavity to form ionic binding for higher selectivity on DMIPs. In MIP-based SERS, the background may be attributed primarily to



**Fig.4** (a) Concentration-dependent SERS spectra of CV obtained from the Ag@DMIPs. (b) Raman spectra of Ag@DMIPs and Ag particles in a  $10^{-5}\text{ M}$  solution of CV.

the template leakage and remain, which results in low signal-to-noise ratio (Fig. S6<sup>†</sup>, Fig. S7<sup>†</sup>). On Ag@DMIPs, however, the dummy template can effectively eliminate the background noise from the Raman spectrum, improving the signal-to-noise ratio and reproducibility (Fig. S8<sup>†</sup>). Furthermore, it should be noted that the template is the key factor affecting the quality and performance of DMIPs.<sup>14</sup> The selection of appropriate dummy template is required for DMIPs with high selectivity and sensitivity.<sup>15</sup> Therefore, further studies are highly desirable.

As has been discussed previously in our study,<sup>6</sup> there are two main contributions for the high SERS in this case. First, CV molecule may reach the surface of Ag-core through template-specific imprinted channels in DMIPs due to the “gate effect”.<sup>16</sup> The effective charge transfer between CV molecules and Ag particles forms the chemical enhancement mechanism of SERS. Second, the majority of SERS enhancement is caused by the electromagnetic (EM) mechanisms. The EM enhancement results from localized surface plasmon resonance (SPR) and is a long-range effect.<sup>17</sup> For our Ag@DMIPs, an ultrathin DMIPs shell was coated on the surface of a dielectric Ag core, which leads to a high-intensity plasmon-resonant local field for enhanced Raman signal.<sup>18</sup> The combination of chemical and CM effects results in the significant SERS enhancement.

## Conclusions

Our approach presents an opportunity for molecular imprinting technique for high performance SERS since the background noise can be suppressed by using dummy template. We anticipate that our strategy may open avenues for reliable quantitative SERS detection.

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## Notes and references

<sup>a</sup> Department of Chemistry, Harbin Institute of Technology, Harbin 150001, PR China.

<sup>b</sup> State Key Lab of Urban Water Resource and Environment, Harbin Institute of Technology, Harbin 150090, PR China. Email: lixin@hit.edu.cn

<sup>c</sup> Key Laboratory of Preparation and Applications of Environmental Friendly Materials, Ministry of Education, College of Chemistry, Jilin Normal University, Siping, 136000, PR China. Email: aaaa2139@163.com

<sup>d</sup> School of Municipal and Environmental Engineering, Harbin Institute of Technology, Harbin 150090, PR China.

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