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Rapid In-situ Analysis for Methyl Ethyl Ketone Dissolved in Transformer Oil Using Surface Enhanced Raman Scattering

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Abstract. Methyl ethyl ketone dissolved in transformer oil is a new chemical mark of thermal insulation degradation. As an effective detection method, Surface-enhanced Raman scattering (SERS) could directly perform rapid detection for methyl ethyl ketone in transformer oil without complex preprocessing steps, which can provide in-situ capability to overcome the shortcomings of traditional method. First, sliver nano-bulks were synthesized on the copper foil surface by the galvanic displacement. silver nanobulks were used as the SERS substrate to detect standard transformer oil samples with different methyl ethyl ketone concentrations. The SERS peak at 763 cm^{-1} was selected as the characteristic SERS peak for qualitative and quantitative analyses. In addition, the quantitative analysis model was built between the Raman intensity at 763 cm^{-1} and methyl ethyl ketone concentrations by applying the least square method. Experimental results showed that SERS method could be used to analyze methyl ethyl ketone dissolved in transformer oil quantitatively and effectively. With further improvements of the detection limit, the SERS method will provide a useful approach to achieving rapid in-situ analysis for methyl ethyl ketone dissolved in transformer oil.

1. Introduction
The reliability of transformers is of great significance to ensure the stability and security of power systems [1]. In the aging process of transformers, insulating oil and paper decompose and produce materials which can reflect the degradation of the oil-paper insulation. Recently, methyl ethyl ketone has been given considerable attention as a new chemical indicator of degradation in transformer internal insulation, because of its high amounts and good chemical stability. Methyl ethyl ketone dissolved in transformer oil is mainly derived from the oxidation of insulating oil [2-3]. At present, the main method for detecting the concentration of methyl ethyl ketone dissolved in transformer oil is gas chromatography–mass spectrometry (GC-MS) [4]. Its detection sensitivity and reliability have been confirmed; however, this method is complicated to operate and requires complex preprocessing steps.

Surface enhanced Raman spectroscopy (SERS) is deemed a powerful, non-destructive and ultrasensitive analytical technique for biological and chemical analyses [5]. Generally, SERS can enhance the Raman signals of detected molecule up to six orders of magnitude or more. Substantial efforts have been focused on how to obtain the SERS substrate with higher average enhancement factor and better spatial uniformity. In recent years, galvanic displacement has been widely used to directly deposit silver or gold nanoparticles on solid substrates [6]. In comparison with other methods, the galvanic displacement is easier to repeat and scale up. However, there are only dendritic and flakiness nanostructures produced by galvanic displacement, which may limit its SERS applications in oil or other solvents.

In this paper, we demonstrate a simple and effective method to fabricate stable silver nanobulks on copper foil by modified galvanic displacement. The sliver nanobulks were used as the SERS substrates for the analysis of methyl ethyl ketone dissolved in transformer oil. Furthermore, A quantitative analysis model between Raman intensity I_{763} and methyl ethyl ketone concentrations was built. Experimental results showed that the SERS method could achieve non-contact and non-destructive rapid in-situ detection for methyl ethyl ketone dissolved in transformer oil without complex preprocessing steps.

2. Preparation of SERS Substrate

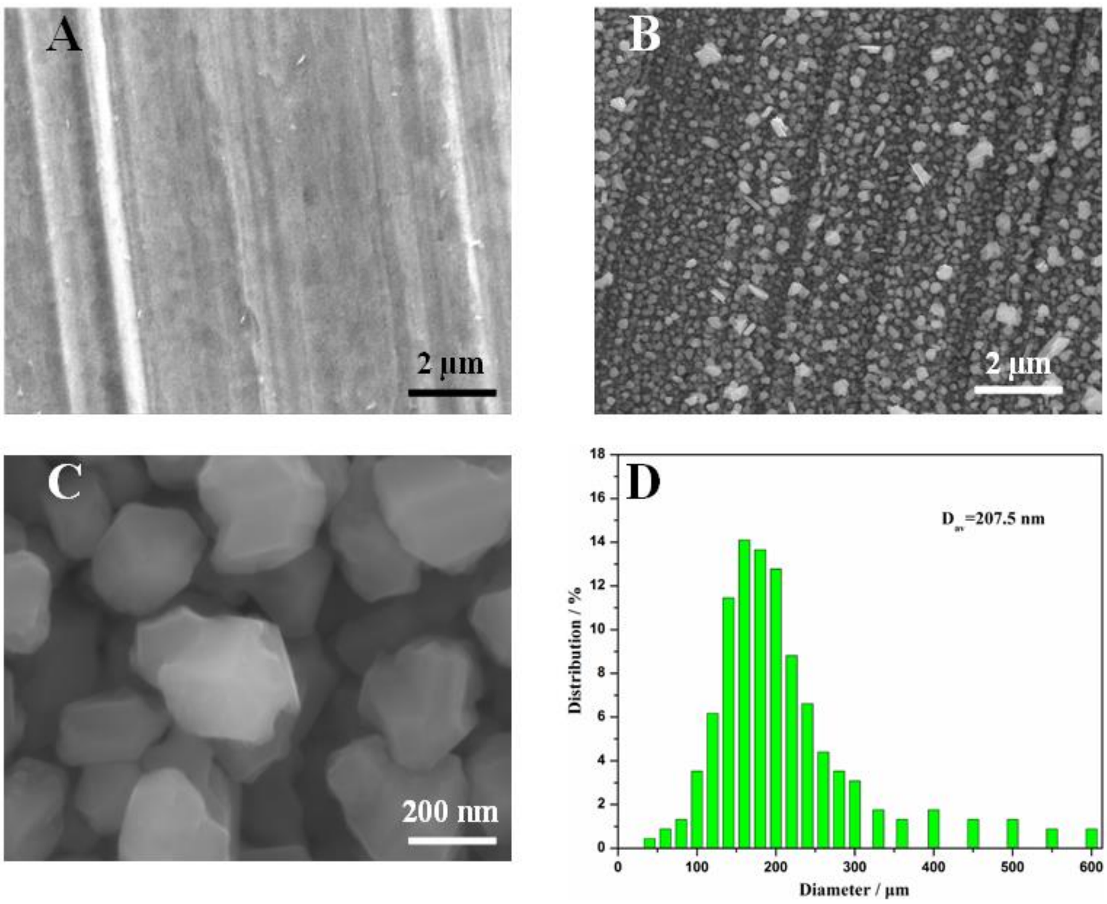

Figure 1. Low magnification SEM images of copper foil (A) and nanobulks (B), high magnification SEM images of nanobulks (C), the diameter distribution of nanobulks (D).

Silver nanobulks were synthesized by modified galvanic displacement. The commercial copper foil was cut into several 0.5 cm × 0.5 cm square pieces, and they were cleaned by anhydrous ethanol and deionized water and dried in a vacuum-drying oven. Subsequently, five pieces of copper were dipped into the solution containing 0.2 mmol of silver nitrate, 0.3 mmol of 2-nitrobenzoic acid, and 200 mL of deionized water. After three minutes, the copper pieces changed from purple red to dark gray, and they were then washed three times with deionized water and anhydrous ethanol, respectively. Finally, these cleaned square pieces were dried in a vacuum-drying oven and stored in a nitrogen box at room temperature.

Figure 1A presents that there are many gully-like machining marks on the surface of commercial copper foil. After galvanic displacement reaction, the surface of copper foil is covered by dense nanobulks, as shown in Figure 1B and 1C. Figure 1D shows the diameter distribution of these nanobulks and indicates that their diameters mainly range from 100 to 300 nm with the average value of 207.5 nm.

3. Experimental

The Raman spectroscopy liquid detection test plat form has been set up in the laboratory [7]. For the qualitative and quantitative analyses, standard oil samples were prepared with different methyl ethyl ketone concentrations of 1×10^{-2} M, 5×10^{-3} M, 1×10^{-3} M, 5×10^{-4} M, 1×10^{-4} M, and 5×10^{-5} M, respectively.

Based on the Raman spectroscopy liquid detection test plat form, the SERS detection can be accomplished by the following procedures:

1) Place the SERS substrate into the quartz cuvette made of fused silica. Then, fill the cuvette full with measured oil sample and seal with the container. In order to make the SERS substrate be completely exposed to measured oil sample, shake the cuvette and place it sit over 5 minutes.

2) Place the cuvette onto the microscope stage, whose height should be adjusted to focus the laser on the surface of the SERS substrate, as exhibited in Fig. 2.

3) Set the slit width at 50 μm, output power of the laser at 20 mW, integration time at 0.5 s, and integral number at 300 times.

4) Collect the Raman spectrum by spectrometer. After that, pretreat the Raman spectra by smooth filtering, fluorescence background elimination, and intensity normalization.

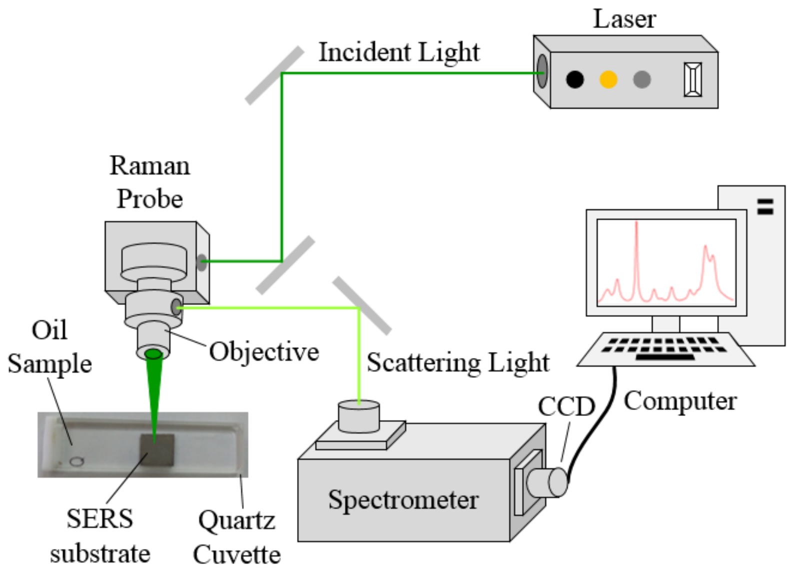

Figure 2. Schematic of the SERS detection.

4. Results and Discussions

4.1 The selection for characteristic SERS peak of methyl ethyl ketone dissolved in transformer oil

In order to make it easy for qualitative and quantitative analyses, the characteristic SERS peak of methyl ethyl ketone dissolved in transformer oil should be determined. The pure methyl ethyl ketone, and pure transformer oil were detected by laser Raman spectroscopy directly. Moreover, the transformer oil sample containing 1×10^{-2} M methyl ethyl ketone was detected by SERS with silver nanobulks, as shown in Figure3.

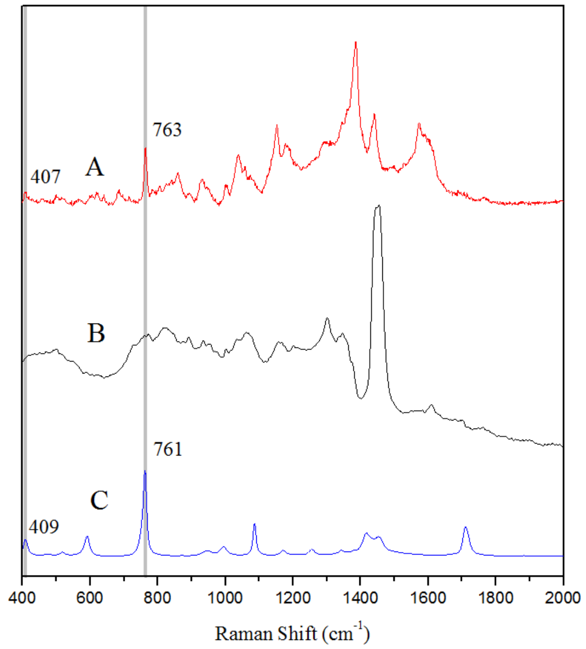

Figure 3. Measured Raman spectra of (A) oil sample with methyl ethyl ketone enhanced by SERS substrate, (B) pure transformer oil , and (C) pure methyl ethyl ketone.

In Figure 3, there were many Raman peaks enhanced by the SERS substrate. By comparing (A) with (B) and (C), it can be preliminarily determined that Raman peaks at 407 and 763 cm^{-1} are derived from methyl ethyl ketone dissolved in transformer oil. Interestingly, it can be found that these two Raman peaks was at 409 and 761 cm^{-1} in the Raman spectrum of the pure methyl ethyl ketone. The shift is mainly due to the impacts of the transformer oil, such as the non-coincidence effect (NCE) [8]. By GaussView 5.0 and Gaussian 09W software, the vibration modes of methyl ethyl ketone can be determined [9-10]. Thus, it can be inferred that the methyl ethyl ketone molecule is likely to be adsorbed on the silver surface by aldehyde group in transformer oil.

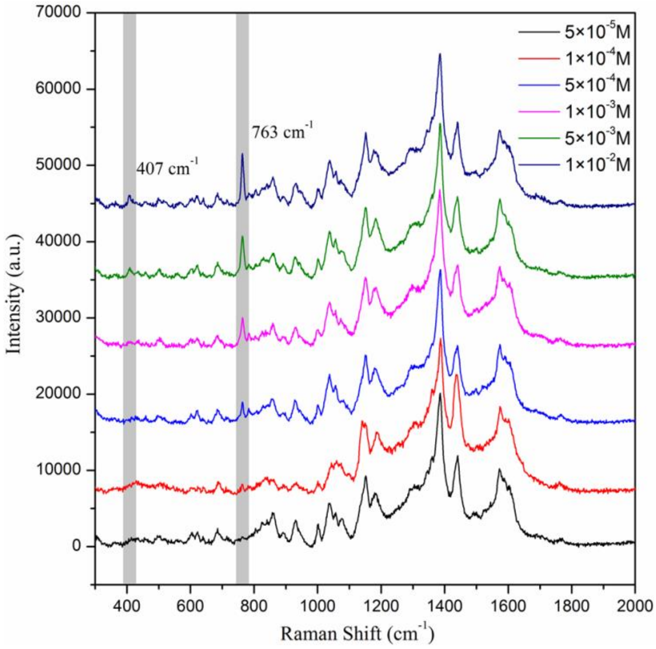

Figure 4. SERS spectra of transformer oil samples with different methyl ethyl ketone concentrations.

As a standard characteristic SERS peak, it should own higher intensity and relatively independence. From Figure 3, we can see that the enhanced Raman peak of methyl ethyl ketone at 763 cm^{-1} displayed the highest intensity and the least affected by other Raman peaks. Therefore, the SERS peak at 763 cm^{-1} is more suitable as characteristic SERS peak of methyl ethyl ketone dissolved in transformer oil. To further confirm that the Raman peak at 763 cm^{-1} is derived from methyl ethyl ketone molecule, six transformer oil samples with different methyl ethyl ketone concentrations were detected by the SERS method. As illustrated in Figure 4, the intensity of the Raman peak at 763 cm^{-1} gradually decreased as the methyl ethyl ketone concentration decreased from 1×10^{-2}M to 5×10^{-5}M. As a result, the Raman peak at 763 cm^{-1} can be selected as the characteristic SERS peak of methyl ethyl ketone dissolved in transformer oil.

4.2 *Quantitative analysis for methyl ethyl ketone dissolved in transformer oil*
The Raman intensity I_{763} of different transformer oil samples with methyl ethyl ketone were calculated. As shown in Figure 5, there was a good linear relationship between the intensity of SERS peak at 763 cm^{-1} and methyl ethyl ketone concentrations in transformer oil from 1×10^{-2} M to 5×10^{-5} M. Based on the least squares method, the intensity of SERS peak at 763 cm^{-1} and methyl ethyl ketone concentration were set as y and x, respectively [11]. The unary linear regression was calculated, and its equation was as follows:

$$y = 25256 lgx + 109927 . \qquad (1)$$

The goodness of fit was R^2=0.9584. And the methyl ethyl ketone concentration in transformer oil could be obtained using the equation.

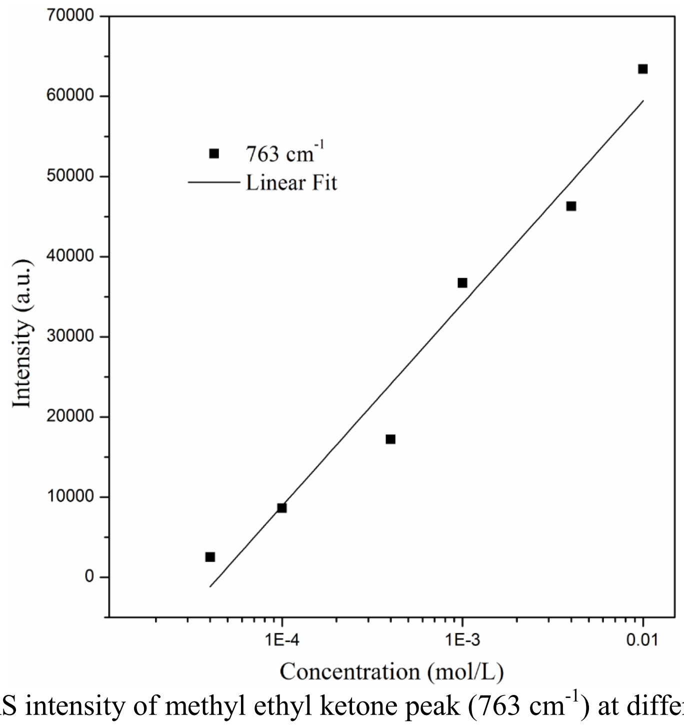

Figure 5. The SERS intensity of methyl ethyl ketone peak (763 cm^{-1}) at different concentrations.

5. Conclusions
In this paper, we demonstrated the SERS method for directly detecting the concentration of methyl ethyl ketone dissolved in transformer oil without complex preprocessing steps.

1) Silver nano-bulks were synthesized by the galvanic displacement method and used as the SERS substrate to analyze methyl ethyl ketone dissolved in transformer oil.

2) The Raman peak at 763 cm^{-1} was selected as the characteristic SERS peak of methyl ethyl ketone, which could be used for quantitative analysis.

3) The quantitative model was constructed between the Raman intensity I_{763} and methyl ethyl ketone concentration in transformer oil.

SERS detection is more suitable for in-situ detection and on-line analyses, but further improvements in the detection sensitivity will be needed for the application in methyl ethyl ketone quantitative analysis. Generally, the enhancement of SERS signal could be promoted by ameliorating the morphology of the SERS substrate, employing more sensitive optical element, and so on. In addition, we are attempting to combine the microfluidics technology and SERS detection method to achieve the rapid online detection of methyl ethyl ketone concentration in transformer oil.

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