Preparation of Ag/Ag₂W₂O₇ nanoribbons and their SERS detection for dye molecules

1 | INTRODUCTION

1D nanomaterials including nanorods, nanowires, nanoribbons, etc. have attracted research interests [1], and quickly became research frontier in the nanoscience and nanotechnology due to their optical, electrical, and magnetic properties. Therefore many methods have been developed to fabricate 1D nanomaterials, such as chemical vapour deposition [2], template [3], and hydrothermal and solvothermal [4] methods etc. However, up to now, there is no literature to report synthesis of ultrathin 1D Ag₂W₂O₇ NRs except Ag₂W₂O₇ powder [5] and nanowires [6]. Non-metallic [7] and triclinic structure phases Ag₂W₂O₇ belongs to the direct bandgap semiconductor material [8] with a band gap width 3.18 eV [9]. It is difficult to prepare Ag₂W₂O₇ thin NRs because it is not stable.

In this work, we prepared Ag₂W₂O₇ NRs by hydrothermal method via strictly controlling pH value and temperature and then reduced them to Ag/Ag₂W₂O₇ NRs by NaBH₄. Band Rh B were used as target molecules for evaluating SERS performance. It revealed that the Ag/Ag₂W₂O₇ NRs possess high enhancement factor (EF) \(2.78 \times 10^7, 4.34 \times 10^6\) and low LOD \(8.91 \times 10^{-13} \text{ M}, 8.71 \times 10^{-12} \text{ M}\) for MB and Rh B. Compared with other substrates [10], our Ag/Ag₂W₂O₇ NRs have supersensitivity to inorganic dyes. Furthermore, according to the literature investigation, there is no report on SERS performance of 1D Ag₂W₂O₇ NRs. Therefore, it can be extend to detect food addittives and carcinogens.

2 | EXPERIMENTAL DETAILS

2.1 | Materials

Sodium tungstate dehydrate (Na₂WO₄·2H₂O ≥ 99.5%), sodium borohydride (NaBH₄, ≥98%) and HNO₃ was purchased from Macklin Chemical Co., Ltd. Silver nitrate (AgNO₃, ≥ 99.8%), ethanol absolute was received from Tianjin Sailboat Chemical Reagent Technology Co., Ltd. Methylene blue (MB) and Rhodamine B (Rh B) were bought from Tianjin scientific chemical reagent Co., Ltd. Monocrystalline silicon chip were purchased from Kailhua Lijing Silicon Material Co., Ltd. Deionized water (> 8.2 MΩ) was used as solvent in all experiments.

2.2 | Synthesis of Ag₂W₂O₇ NRs

The synthesis of Ag₂W₂O₇ NRs can be divided into several steps: 200.8 mg dehydrated tungstate sodium (Na₂WO₄·2H₂O) and 101 mg silver nitrate (AgNO₃) were dissolved in 30 mL deionized water respectively, and then stirred by magnetic stirrers for 10 min. The completed AgNO₃ solution was dropwise added to the Na₂WO₄·2H₂O solution. Then, HNO₃ solution was dropped in the mixture to adjust its pH value to 2.8, and stir the suspension again for 2 h. Transfer the prepared reagent to a stainless steel autoclave lined with Teflon (100 mL) and keep it at 200 °C for 24 h. Take out and cool naturally to room temperature. After centrifugation, wash with alcohol and ionized water several times. Finally, Ag₂W₂O₇ NRs were obtained by vacuum drying at 60 °C for 5 h.

2.3 | Fabrication of Ag/Ag₂W₂O₇ NRs powder

Ag/Ag₂W₂O₇ NRs were prepared by a simple chemical reduction. 1 mg Ag₂W₂O₇ NRs were dispersed into 10 mL deionized water under sonic oscillation to make them homogeneous. Then, 50 mg NaBH₄ was dissolved in 10 mL of deionized water. Then, 20 μL of the obtained NaBH₄ solution were dissolved in the Ag₂W₂O₇ solution under magnetic stirring for 30 min to get uniform Ag/Ag₂W₂O₇ NRs. In the end, the obtained black precipitate was centrifuged and washed several times with deionized water, and dried in vacuum at 60 °C for 5 h.

2.4 | Characterization

The morphology of the samples were observed by a scanning electron microscope (SEM), which was operated at an accelerating voltage of 20 kV. The microstructures of the samples were further characterized by transmission electron microscopy (TEM) and high-resolution electron transmission microscopy (HRTEM). The phase composition of the sample was examined by x-ray diffraction (XRD). UV–visible absorption spectroscopy (UV–vis) was recorded on a UV–vis spectrophotometer (U-4100, Hitachi, Japan) in the range of 200–800 nm. Raman
spectra were performed for measuring SERS signals by Raman spectrometer (Andor, England).

2.5 SERS examination

The SERS performance of the Ag$_2$W$_2$O$_7$ and Ag/Ag$_2$W$_2$O$_7$ NRs were investigated by selecting MB and Rh B as probe molecules. Before the SERS activity measurement, some single crystal silicon wafers (0.7 cm × 0.7 cm) were rinsed several times by acetone and alcohol, drying it at atmosphere. 20 μL of Ag$_2$W$_2$O$_7$ NRs (180 mg/L) solution were dropped onto the treated silicon wafer and dried naturally. Then, 10 μL of probe molecule solution were dropped on the prepared substrate. The SERS measurement was performed under a confocal Raman spectrometer (Andor, England).

3 RESULT AND DISCUSSION

3.1 XRD of the samples

In order to reveal the crystal structures of Ag$_2$W$_2$O$_7$ NRs and Ag/Ag$_2$W$_2$O$_7$ NRs, XRD patterns of the samples were denoted in Figure 1(a,b). The diffraction angles 2θ located at 13.59°, 34.05°, 27.29°, 29.02°, 29.99°, 30.74°, 31.71°, 32.46°, 35.69°, 36.46°, 37.28°, 41.35°, 45.13°, 46.95°, 49.09°, 51.25° and 53.20° correspond to the (010), (002), (-121), (-102), (112), (200), (-122), (1-12), (-220), (-1-12), (122), (030), (-230), (004), (004), (3-21) and (1-32) crystal planes of anorthic Ag$_2$W$_2$O$_7$ (JCPDS No:75-1506), respectively. The peak in Figure 1(b) demonstrates the cubic phase structure of Ag at 2θ = 38.12° and 2θ = 44.26° (JCPDS No: 04-0783), which matched with the (111) and (200) crystal planes (marked by red indices).

SEM image of Ag$_2$W$_2$O$_7$ NRs is presented in Figure 2(a). It is seen that the product consists of high dense ribbon-like structures with lengths of 30–40 μm and widths of 200–400 nm. HRTEM and SAED images of the Ag$_2$W$_2$O$_7$-NPs are shown in Figure 2(b). The lattice spacing between adjacent planes are 0.219 nm, which correspond to the (030) crystal planes of Ag$_2$W$_2$O$_7$. The SAED pattern confirms the single-crystal quality and can be indexed to a triclinic structure with lattice parameters $a = 6.033$, $b = 7.051$ and $c = 7.735$ Å. The SEM image of Ag/Ag$_2$W$_2$O$_7$ NRs were demonstrated in Figure 2(c). The silver nanoparticles (NPs) were homogeneously distributed in the surface of Ag$_2$W$_2$O$_7$ NRs.

TEM image of the Ag/Ag$_2$W$_2$O$_7$ NRs are depicted in Figure 2(d). It shows that the Ag/Ag$_2$W$_2$O$_7$ NPs are covered with many Ag NPs. The average diameter of the Ag NPs is about 20–30 nm. In addition, the upper inset of Figure 2(d) is HRTEM image of Ag/Ag$_2$W$_2$O$_7$ NRs, the lower inset is HRTEM image of the silver NPs. The interplanar distance was 0.239 nm, corresponding to the (111) crystal plane of Ag NPs. Meanwhile, the interplanar distance was 0.219 nm, corresponding to the (030) crystal plane of Ag$_2$W$_2$O$_7$ NRs. It is further revealed that the Ag/Ag$_2$W$_2$O$_7$ NR is composed of Ag$_2$W$_2$O$_7$ NPs and Ag NPs.

The UV–vis spectrum was used to characterize the absorption property of Ag$_2$W$_2$O$_7$ NRs, as shown in Figure 3(a). It is observed that the wide absorption peaks of Ag$_2$W$_2$O$_7$ NRs and Ag/Ag$_2$W$_2$O$_7$ NRs were in the range of from 250 to 650 nm. The optical band gap of the Ag$_2$W$_2$O$_7$ and Ag/Ag$_2$W$_2$O$_7$ can be calculated according to the Kubelka and Munk method [11], which can be expressed by the following equation [12]:

$$\alpha h\nu = C (\nu - E_{gap})^{1/n}$$

where $n = 2$, $b$ is Planck’s constant, $\nu$ stands for the energy of photons, $\alpha$ is the absorbance, and $C$ is a constant. The energy bandgaps can be determined from the intercept of the tangent by plotting ($\alpha h\nu$) 2 to $\nu$. The energy bandgaps of the Ag$_2$W$_2$O$_7$ NRs and Ag/Ag$_2$W$_2$O$_7$ NPs were estimated as 3.11 and 2.94 eV respectively, as described in Figure 3(b). Ag$_2$W$_2$O$_7$ NRs has a smaller band gap than Ag$_2$W$_2$O$_7$, which conclude that the silver NPs cause the bandgap to shrink [13].

3.2 SERS measurements

To further explore the applications of Ag$_2$W$_2$O$_7$ and Ag/Ag$_2$W$_2$O$_7$ NRs in the sensing field, the as-prepared SERS substrates were used to detect MB molecule in ethanol solution. MB is a cationic dye, which is very sensitive to change in the polarity of its surrounding environment [14]. Cationic MB and anionic WO$_4^{2-}$ interact with each other, and the high conductivity between MB-Ag can amplify the signal [15]. In addition, MB can reach a reversible balance between oxidation and...
reduction, so it is widely used as an electron transfer medium [16]. Therefore, in most similar sensors, MB has been studied in most of the similar sensors. Figure 4(a) is the Raman spectra of Ag$_2$W$_2$O$_7$ NRs and Ag/Ag$_2$W$_2$O$_7$ NRs substrates without analytes. Both of them exhibit similar vibrational modes in the range of 200–1400 cm$^{-1}$, they also have little effect on the SERS spectrum of the probe molecule. The normal Raman spectra of MB with different concentrations on the Ag$_2$W$_2$O$_7$ and Ag/Ag$_2$W$_2$O$_7$ NRs are presented in Figure 4(b,c), respectively. Some intrinsic Raman peaks appeared at 772, 862, 952, 1041, 1075, 1181, 1300, 1398, and 1625 cm$^{-1}$ and their intensities are almost as strong as those of solid MB [17]. It is pointed out that the minimum detected concentration of MB on the Ag$_2$W$_2$O$_7$ NRs is only 1.0 \times 10^{-6}$ M, whereas its counterpart is 1.0 \times 10^{-12}$ M on the Ag/Ag$_2$W$_2$O$_7$ NRs. The SERS intensity of the Ag/Ag$_2$W$_2$O$_7$ NRs at 1625 cm$^{-1}$ is 28.8 times
that of the Ag$_2$W$_2$O$_7$ NRs when concentration of MB come to 1.0 $\times$ 10$^{-6}$ M. The strongest SERS peak at 1625 cm$^{-1}$ was selected to determine the lowest possible concentration at which the MB molecule could be unequivocally detected by observing its Raman spectrum. This concentration was found to be 1.0 $\times$ 10$^{-12}$ M, as shown in inset of Figure 4(c). It is obvious that the characteristic Raman bands of MB are too weak at MB concentration of 1.0 $\times$ 10$^{-12}$ M, because its concentration is so low [17] that they are buried by the Raman scattering arisen from the Ag$_2$W$_2$O$_7$ NRs. But the vibration frequency of MB at 1625 cm$^{-1}$ is still observable.

The detection of limit is a significant important parameter for evaluating the overall performance of SERS substrates. We choose the peak at the 1625 cm$^{-1}$ to assess the LOD. Figure 4(d) shows the calibration curve of average peak intensities at the 1625 cm$^{-1}$ against the logarithmic concentration of MB for Ag$_2$W$_2$O$_7$ NRs with a correlation coefficient ($R^2$) of 0.993 and $I = 1517.15 + 106.44 \log |C|$. According to the definition of LOD, the detection limit is calculated to be about 8.91 $\times$ 10$^{-13}$ M. Meanwhile, the LOD on the Ag$_2$W$_2$O$_7$ NRs is 8.4 $\times$ 10$^{-7}$ M, which is six orders larger than that on the Ag$_2$W$_2$O$_7$ NRs.

The MB molecule contains 108 normal modes [18]. Here, we give a preliminary assignment for only a small part of the Raman frequency. The most intense peaks are the ring stretch ($\nu$ (C–C)) at 1625 cm$^{-1}$ and the symmetric C–H stretches at 1398 cm$^{-1}$. The peak at 1041 cm$^{-1}$ originates from C–H inplane bending mode [18]. The peaks at 1075 cm$^{-1}$ is assigned to C–H stretching mode. The peaks at 1181 cm$^{-1}$ is assigned to C–N stretching mode.

To extend the SERS application of the Ag$_2$W$_2$O$_7$ NRs, Raman spectra of Rh B on the Ag$_2$W$_2$O$_7$ and Ag$_2$W$_2$O$_7$ NRs substrates are also examined, as displayed in Figure 5(a,b). The peak at 1284 cm$^{-1}$ is attributed to the C=C=C stretch mode, while the peaks at 1363, 1435, 1509, 1533 and 1650 cm$^{-1}$ are assigned to the aromatic C=C stretching mode [19]. Their corresponding minimum detected concentrations are 1.0 $\times$ 10$^{-6}$ and 1.0 $\times$ 10$^{-11}$ M. Similarly, there is a good linear relationship ($I = 3595.68 + 312.54 \log |C|$, $R^2 = 0.92$) in Figure 5(c). The SERS intensity of the vibration frequency at 1650 cm$^{-1}$ for Ag$_2$W$_2$O$_7$ NRs, the corresponding LOD is 8.71 $\times$ 10$^{-12}$ M. And the LOD of pure Ag$_2$W$_2$O$_7$ NRs is 8.12 $\times$ 10$^{-7}$ M.

For practical application, the enhancement factor is another important parameter, its definition is as follows:

$$EF = \frac{I_{\text{SERS}}N_{\text{NR}}}{I_{\text{NR}}N_{\text{SERS}}}$$

where $N_{\text{SERS}}$ is the number of molecules covering the array within the laser spot area, and $N_{\text{NR}}$ the number of molecules excited in the reference sample. $I_{\text{SERS}}$ and $I_{\text{NR}}$ are the integrated intensities of the same band for the absorbed probe molecule in the SERS spectra and unabsorbed probe molecules in the SERS spectra of Ag$_2$W$_2$O$_7$ NRs, respectively [20]. The EF values of our samples are listed in Table 1. In order to compare them with

FIGURE 4 Raman spectra of the samples. (a) Ag$_2$W$_2$O$_7$ and Ag$_2$W$_2$O$_7$ NRs; (b) MB with different concentrations on the Ag$_2$W$_2$O$_7$ NRs; (c) MB with different concentrations on the Ag$_2$W$_2$O$_7$ NRs; (d) Linear calibration plot of MB at concentrations of 1.0 $\times$ 10$^{-9}$-1.0 $\times$ 10$^{-12}$ M on the Ag$_2$W$_2$O$_7$ NRs.
other substrate, we also list them in Table 1. It is seen that our experimental results are even higher than those obtained from other more complicated experiments.

We further evaluate the SERS stability of MB at a concentration of $1.0 \times 10^{-6}$ M on the Ag/Ag$_2$W$_2$O$_7$ NRs substrate. 30 points are randomly selected on the substrate to capture the Raman spectra as shown in Figure 6(a), with the intensities of peaks 1300, 1398 and 1624 cm$^{-1}$ are extracted for a more intuitive comparison in Figure 6(b–d). The RSD values obtained are <19%. It exhibits that their corresponding RSDs are 18.84%, 17.97% and 17.95%, indicating that the Ag/Ag$_2$W$_2$O$_7$ NRs substrate is suitable for actual detection.

4 MECHANISM

The generally accepted SERS enhancement mechanism includes electromagnetic mechanism (EM) and the chemical mechanism (CM) [26]. The former mainly involves the enhancement of the local electric field at the metal surface, which is the surface plasmon resonance (SPR). The latter originates from the polarizability due to chemical interactions between metals and molecules [27, 28]. For the Ag/Ag$_2$W$_2$O$_7$ NRs, the SERS enhancement is obtained from two aspects, one of which is the localized surface plasmon resonance (LSPR) can form very large field enhancements at the junctions between adjacent Ag NPs. The other is the charge transfers between Ag NPs and Ag$_2$W$_2$O$_7$ NRs under the induction of incident light, resulting in a resonance-like phenomenon, which greatly increases the polarization rate of the adsorbed molecules, resulting in signal enhancement.

5 CONCLUSION

In summary, we prepared 1D Ag$_2$W$_2$O$_7$ NRs by hydrothermal method. Subsequently, sodium borohydride was used to reduce the silver particles on the surface of Ag$_2$W$_2$O$_7$ NRs to improve its stability and activity, which resulted in the formation of Ag/Ag$_2$W$_2$O$_7$ NRs. We use two different cationic dyes Rh B and MB as target molecules for evaluate SERS performance. The Ag/Ag$_2$W$_2$O$_7$ NRs as effective SERS substrate to detect MB and Rh B dye molecules, and the observed mean SERS enhancement factor are $2.78 \times 10^7$ and $4.34 \times 10^6$, respectively. And their corresponding LODs are $8.91 \times 10^{-13}$ and $8.71 \times 10^{-12}$ M. The Ag/Ag$_2$W$_2$O$_7$ NRs exhibited better SERS activity than Ag$_2$W$_2$O$_7$ NRs. Although the fluorescence method has high sensitivity, it has problems such as fluorescence quenching effect and scattered light interference [29]. Compared with the fluorescence method, the detection of SERS has a narrower spectral band, which can provide more useful information, which helps to reduce signal overlap. It shows that SERS has wide applicability [30]. This is the first observation of Ag$_2$W$_2$O$_7$ nanoribbon in SERS detection. Our Ag$_2$W$_2$O$_7$ NRs provide a potential application for the determination of MB and Rh B in food colorants, disease treatment and environmental pollution, etc.

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**FIGURE 6** SERS stability of MB at a concentration of $1.0 \times 10^{-6}$ M on the Ag/Ag$_2$W$_2$O$_7$ nanoribbon. (a) 3D Raman spectrum from 30 random spots; (b–d) RSD values of the characteristic peaks at 1300, 1398, and 1625 cm$^{-1}$ at 30 random spots.

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