The improvements on TiO₂ catalyzed AgNPs based SERS substrate and detection methods

Huaizhou Jin[a,b], Qipeng Lu[a,*], Shangzhong Jin[c], Haiquan Ding[a], Hongzhi Gao[a], Xingdan Chen[a], Yanqiu Zou[c]

[a] State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin, China
[b] University of Chinese Academy of Sciences, Beijing, China
[c] Key Laboratory of Zhejiang Province on Modern Measurement Technology and Instruments, Jiliang University, Hangzhou, China

ARTICLE INFO

ABSTRACT

Using TiO₂ on slides to facilitate photo-catalysis of silver nano-particles (AgNPs) is a simple and versatile way of making silver based solid SERS substrates. However, due to the difficulty of getting optimal surface AgNPs structure, it is difficult to reach optimal enhancement factor or measurement uniformity with this method. In this research, production conditions and setups, ranging from dip-coating to photo-catalysis are investigated. Spectral analysis show that some conditions, such as time of calcination and the purity of UV light used in photo-catalysis, affect the resulting SERS substrates more significantly. The overall performance of substrates made using this method is increased; sensitivity is increased so that the limit of detection for Rhodamin 6G (R6G) is as low as 10^{-8} M, and the signature peak of R6G at $1650\,cm^{-1}$ measured from different spots on substrates has a standard deviation of less than 20%.

1. Introduction

Raman spectroscopy is a well-established analytical technique based on the inelastic scattering of monochromatic light by the vibrating atoms constituting the sample. It is widely used in fields such as materials, food, medicine, chemistry and so on [1–5].

One of Raman spectroscopy's main disadvantages is its relatively weak signal strength. The discovery of Surface enhanced Raman scattering (SERS) can be used to overcome this disadvantage. SERS was discovered by Fleischmann et al. in 1974 and later confirmed by Van Duyne et al. in 1977 [6–8]. SERS enhancement factor ranges from 10^8 to 10^{14}, so trace amounts of molecules become detectable [4,8–10].

For SERS to take effect, the sample molecules must be adsorbed on to the surface of metal nano-particles, most notably silver (AgNPs) or gold nano-particles (AuNPs) [3,4,11]. Multiple metal nano-particles aggregated together can increase the SERS enhancement factors [3,4,11,12], which is essential for the detection of trace substances. Ordered nano-structures can further enhance

Raman signals because of possible long-range ordering coupling effect [13].

There are usually two types of SERS substrates: a) nano-particle colloidal made from Lee and Miesal or similar methods [14] and b) solid substrates that come from various methods, such as deposition of nano-particle colloidal, reduction of silver nitrate (AgNO₃) or chloroauric acid (HAuCl₄), or nano-rod array structures made through self-assembly, deposition methods or Lithographic and Template Synthesis [15–21]. This study focuses on solid substrates, which show advantages when used to enhance certain types of samples, such as samples that contain large protein molecules [3,5].

One method of making AgNPs based solid substrates is using TiO₂ as a catalyst to facilitate the reduction of AgNO₃ under UV light [12,22,23], and then have the AgNPs adsorb on to TiO₂ [24,25]. This method takes relatively short time, is inexpensive and can be used to produce multiple substrates at once. As a chemical self-assembly method, its control over the surface structure and morphology of AgNPs is limited, when compared to methods such as glancing angle deposition (GLAD) physical vapor deposition [26], Lithographic and Template Synthesis [20,21], and it can be difficult to achieve optimal enhancement factor and uniformity.

* Corresponding author at: State Key Laboratory of Applied Optics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun, Jilin, China.
E-mail addresses: 18367198456@163.com (H. Jin), luqipeng@126.com (Q. Lu).

2. Materials and production of TiO$_2$ photo-catalyzed AgNPs substrates

Analytically pure Tetrabutyl titanate, acetylacetonate, nitric silver (AgNO$_3$), Rhodamin 6G (R6G), nitric acid, ethanol, as well as glass and quartz slides are purchased from Hangzhou Mike Chemical Instruments Co., Ltd.

Method for making TiO$_2$ photo-catalyzed AgNPs substrates are derived and improved on the basis of methods by Li et al. and Mazzocut et al. [12,22]. The steps of the production process are as follows:

2.1. Making TiO$_2$ sol-gel

The first step is to make TiO$_2$ sol-gel. Two solutions, solution A and solution B are prepared. Solution A is made by mixing 50 mL of Tetrabutyl titanate with 3 mL of acetylacetonate. Magnetically stir solution A for 10 min. Solution B is made by mixing 110 mL of 95% ethanol, 1.4 mL deionized water and 0.2 mL nitric acid. Solution B is also magnetically stirred for 10 min after mixing the three reagents.

After solutions A and B are made, solution B is added into solution A drop by drop, under magnetic stir. After all of solution B is added into solution A, continue magnetic stirring for 30 min.

2.2. Deposition of TiO$_2$

Before coating, the glass or quartz slides are washed using ethanol and then deionized water and then oven dried at 50 °C.

Then, coat TiO$_2$ on the slides using dip coating techniques. Different dipping speed would affect the thickness of TiO$_2$. Dipping speeds ranging from 100 mm/min to 300 mm/min have been tested. The slide stays in the solution for 2 min during dip coating. Then, the slide rests on a flat surface for 30 min before calcination.

2.3. Calcination

The goal of the calcination step is to turn the amorphous TiO$_2$ sol-gel on the slides into anatase form, which will act as the catalyst as the photo-catalysis step, as well as the spots for AgNPs to adsorb on to. Thus, the surface structure of TiO$_2$ on the slides will become an important factor in determining the surface structure of AgNPs, which determines the enhancement factor, as well as uniformity.

Around 400 °C, TiO$_2$ starts transforming into anatase form; however, around 550 to 600 °C, part of TiO$_2$ would begin transforming into rutile form, which is not as effective as catalyst or adsorbent for the deposition of AgNPs [12,27]. Therefore, temperature needs to be kept within the range between 450 and 550 °C.

The coated glass or quartz slide is calcined in a muffle furnace. After the slides are inside the furnace, the furnace is heated to around 500 °C in 30 min and stays at that temperature for 60 min. Different temperatures from 450° to 550° (at this range of temperature, amorphous TiO$_2$ began morphing into anatase form) are used and compared. After heating for 60 min, the heat is turned off and the furnace cools down naturally.

After the temperature in furnace drops to 300°, open the furnace hatch to let it cool down faster. Then, remove the calcined slides from the muffle furnace.

2.4. Photo-catalysis

The AgNO$_3$ solution is made by mixing 0.2548 g of AgNO$_3$ powder with 500 mL deionized water. Magnetically stir for 10 min.

The slides, after calcination, are cut into 5 × 5 mm pieces and put inside a culture dish. Pour AgNO$_3$ solution slowly into the dish, and make sure all slides are immersed in the solution instead of floating on the surface. Different immersion depths from 3 mm to 10 mm (meaning the how much the AgNO$_3$ solution level is higher than the top surface of the slides) are used and compared.

A 24W UV lamp is used for the photo-catalysis of the substrates. Two different wavelengths of UV light are used for photo-catalysis: 254 nm and 365 nm. A filter is also used to block most of the visible light emitted from the UV lamp during photo-catalysis for comparison. The time of photo-catalysis ranges from 30 min to 90 min for comparison.

After photo-catalysis, the resulting substrates are washed with deionized water and then oven dry at 50 °C for 10 min.

2.5. Gold deposition

Normally, silver based SERS enhancement substrates are unstable and are vulnerable to oxidation when exposed in air. Coating a protective film is a common way to separate silver from air; for example, methods that coat Al$_2$O$_3$ or SiO$_2$ on silver substrates are developed [28]. In this research, a gold deposition method is used on the substrates so that a thin layer (around 3 nm think) of gold are deposited on the substrates, and are compared to substrates without gold deposition.

3. Measurement instrumentation and methods

3.1. TiO$_2$ and AgNPs morphology measurement

Before photo-catalysis, the thickness and refractive index of TiO$_2$ on glass would be measured using a Horiba Jobin-Yvon Uvisel ellipsometer, both before and after calcination. Then, TeScan Vega3 scanning electron microscope (SEM) was used to observe the morphology of AgNPs on the substrates.

3.2. SERS measurement

Raman measurement was carried out using Horiba LabRAM Evolution, with a 50 mW 532 nm laser module. R6G (1.0×10^{-5}M to 1.0×10^{-7}M) is used to test the effectiveness of our SERS substrates. First, a small piece (5 × 5 mm) of substrate is immersed into the Rhodamin 6G solution for 30 min, and then the substrate is oven dried (50 °C) for 10 min before testing. 5% laser power is used for measurement to avoid damaging the substrate or the samples and measure for 5 s as a standard measurement. The average of standard measurements on 10 different spots on 5 substrates made using the same production setup (a total of 50 measurements) is used to compare the performance between different production setups.

Table 1
Thickness as a factor of dip speed on glass slide, measured by ellipsometry.

Dip speed(mm/min)	170	180	190	200	210	220	230
Thickness (nm, BC)	564.1	643.6	758.9	696.3	723.2	770.1	795.9
n(BC)	1.671	1.633	1.630	1.634	1.637	1.631	1.630
χ^2 (BC)	2.41	0.63	0.59	0.55	0.61	0.68	0.58
Thickness (nm, AC)	229.5	295.2	318.2	305.9	294.3	215.1	375.4
n (AC)	2.003	1.924	2.042	2.008	2.107	1.891	2.899
χ^2 (AC)	5.83	10.30	10.28	15.11	13.98	37.00	36.34