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# Recyclable three-dimensional Ag nanoparticle-decorated $TiO_2$ nanorod arrays for surface-enhanced Raman scattering

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## ABSTRACT

Multifunctional Ag nanoparticle-decorated $TiO_2$ nanorod arrays were prepared by two simple processes. $TiO_2$ nanorod arrays were first fabricated by the hydrothermal route and then Ag nanoparticles were decorated on the nanorods by the chemical reduction impregnation method. Three-dimensional Ag/$TiO_2$ arrays were used as an active substrate for surface-enhanced Raman scattering (SERS). The results show that the detection limit for rhodamine 6G (R6G) was as low as $10^{-7}$ M and the Raman enhancement factor was as large as $10^5$. After calibrating the Raman peak intensities of R6G, it could be quantitatively detected. More importantly, the photocatalytic activity of $TiO_2$ provides a self-cleaning capability to the SERS substrate, which can be recycled and used to degrade many Ag surface adsorbates such as R6G, methyl orange, Congo red, and methylene blue after exposure to visible light. The absorbed small molecules can all be rapidly and completely removed from the SERS substrate, which has been successfully reused four times without a decrease in accuracy or sensitivity. Our results reveal that the unique recyclable property not only paves a new way to solve the single-use problem of traditional SERS substrates but also provides more SERS platforms for multiple detections of other organic molecular species.

## 1. Introduction

Surface-enhanced Raman scattering (SERS) is one of the most sensitive and powerful analytical techniques, which could increase the scattering cross-section of a given molecule up to a billion-fold, enabling single molecule detection (Nie and Emory, 1997; Zhang et al., 2013; Li et al., 2009). High enhancement along with high selectivity and nondestructive detection make SERS widely used in analytical chemistry, biosensing applications, and medical science (Michaels et al., 1999; Zheng et al., 2012; Tabakman et al., 2011). For example, SERS has great potential in the fields of Raman labeling, *in situ* monitoring of chemical reactions, and even homeland security (Kustner et al., 2009; Heck et al., 2008; Golightly et al., 2009). To date, the primary SERS mechanism has been widely confirmed as a combination of electromagnetic enhancement (EM) associated with surface plasmon resonances on noble metallic nanostructures and chemical enhancement (CM) from the photo-induced dynamic electron transfer between probe molecules and proximal metallic nanostructures (Kneipp et al., 2002; Arenas et al., 2000; Otto et al., 1992). It is widely believed that in SERS enhancement long-range EM enhancement (of the order $10^4$–$10^6$) plays a much greater role than CM enhancement (of the order $10^2$) (Kneipp et al., 1997; Li et al., 2010). Noble metal Ag, in particular due to its nanostructures with strong and tunable surface plasmon responses from visible to near-infrared spectral regions (Song et al., 2010; Lee et al., 2012), has spurred efforts to fabricate more effective SERS active substrates. For example, Ag nanotriangle arrays fabricated with nanosphere lithography have exhibited high reproducibility, stability, and large field enhancement (Camden et al., 2008). Our group has prepared $SiO_2$ nanofilms covered Ag dendrites as SERS substrates for rapid, sensitive, stable, and quantitative detection of organic molecules (Chan et al., 2013). We have also synthesized Ag@$SiO_2$ core–shell nanoparticles (NPs) on Si nanowire arrays via simple chemical etching and metal reduction processes to act as ultrasensitive and ultra-stable SERS substrates with an enhancement factor (EF) as large as $10^{14}$ (Zhang et al., 2013). However, most of the substrates are one-off, which has greatly limited SERS applications because of the waste of noble metal and the high cost. Therefore, a recyclable SERS active substrate based on Ag nanostructures could effectively save

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resources and offer economic saving in addition to avoiding environmental problems.

$TiO_2$ is one of the most widely investigated semiconductor oxide materials in the fields of clean energy resources and environmental remediation owing to its photocatalytic properties, chemical stability and nontoxic nature (Hagfeldt and Gratzel, 1995; Gratzel, 2003; Mills and LeHunte, 1997; Stafford et al., 1996). However, because of the large band gap of $TiO_2$ (3.2 eV for the anatase phase and 3.0 eV for the rutile phase), the photocatalytic processes mediated by $TiO_2$ can only be activated by ultraviolet light (Kochuveedu et al., 2012). Additionally, the high electron–hole recombination rate of $TiO_2$ results in a low photocatalytic efficiency (Liu et al., 2013). To overcome these limitations of $TiO_2$, significant effort has been made to enhance the electron–hole separation and extend its absorption into the visible range through dye sensitization (Chen and Mao, 2007; Kim et al., 2009; Fuldner et al., 2010), incorporation of metal ions (Pian et al., 2011; Anpo and Takeuchi, 2003; Yamashita et al., 2002; Sakthivel and Kisch, 2003), or doping with nonmetals (Park et al., 2009; Chen et al., 2011; Zhang et al., 2010; Khan et al., 2002). In particular, visible-light-assisted active $TiO_2$ incorporated with metal ions has attracted increasing attention as it can maximize photocatalytic efficiency and importantly be further extended to a SERS substrate (Liu et al., 2013). $TiO_2$ nanostructures loaded with noble Ag NPs should have many advantages over other photoreaction methods because Ag could not only enhance $TiO_2$ photocatalytic efficiency under visible light irradiation, owing to the strong interaction between the incident light and electrons in noble metal, but Ag deposits also have higher surface plasmon resonance to provide high SERS activity. Deposited Ag NPs would act as traps to capture photo-induced electrons and holes, reducing electron–hole recombination in photocatalytic processes (Kochuveedu et al., 2012). Recent attempts to improve the SERS effect have focused on the construction of three-dimensional (3D) nanoarchitectures with nanogap rich metal NPs, which could generate more effective and adequate ‘hot spots’ for the creation of a strong and tunable electromagnetic fields within the detection volume. Compared with several typical previous reports (Table S1), the result indicates that our substrate has a much shorter photodegradation time under vis irritation and can provide more ‘hot spots’ with 3D array with low cost. Based on these peculiar properties of Ag and $TiO_2$, 3D Ag NP-decorated $TiO_2$ nanostructure arrays would be excellent candidates for molecular sensing with high SERS sensitivity and good recyclability.

Herein, a 3D, durable, reusable, highly stable and sensitive SERS-active substrate of highly ordered, rutile $TiO_2$ nanorod arrays (TRA) decorated by Ag NPs was prepared. The recyclable substrate was fabricated first by the hydrothermal method for $TiO_2$ nanorod (NR) growth based on fluorine-doped tin oxide (FTO) and second Ag NPs were deposited on $TiO_2$ NRs by chemical reduction impregnation. The hierarchical nanostructure could produce potential SERS ‘hot spots’ at the formed 3D arrays and was used to detect rhodamine 6G (R6G) at concentrations as low as $10^{-7}$ M. More importantly, the SERS substrates are recyclable and can be used for many Ag surface adsorbates such as R6G, methyl orange (MO), Congo red (GR) and methylene blue (MB). R6G is a xanthene dye while the other three are azo dyes. These four adsorbates were all widely used as organic dyes in the dye industry, which usually cause dyestuff pollution during the manufacturing processing. In this paper, these two types of dyes can be rapidly and completely removed from the Ag doped TRA (Ag/TRA) surface with visible light irradiation, which reveals that the unique recyclable property not only paves a new way to solve the single-use problem of traditional SERS substrates but also provides more SERS platforms for detecting of other organic species.

## 2. Experimental

### 2.1. Materials and instruments

Tetrabutyl titanate, $NaBH_4$, R6G, MO, GR, MB, $AgNO_3$, HCl, and $HNO_3$ were of analytical grade and supplied by Aladdin, Shanghai, China. FTO substrates (F: $SnO_2$, Tec 15, 10 Ω/cm) were supplied by OPV Tech., Yingkou, China. Other reagents used in the experiments were of analytical grade and used as received.

The typical morphologies of samples were characterized by field emission scanning electron microscopy (FE-SEM) (JEOL JSM-6700F, Japan), transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) (Phillips CM200 FEG-TEM), and X-ray diffraction (XRD) (Rigaku Ultima III). The ultraviolet-visible (UV–vis) diffuse reflectance/absorption spectra (DRS) of $TiO_2$ and Ag/TRA were monitored by a Shimadzu UV-3600 UV–vis spectrophotometer.

### 2.2. Synthesis of $TiO_2$ NRs

$TiO_2$ NRs of rutile crystal were prepared in a manner similar to that described in previous papers (Liu and Aydil, 2009), employing a hydrothermal method. The FTO substrate was ultrasonically cleaned for 60 min in a mixed solution of deionized water, acetone, and 2-propanol with volume ratios of 1:1:1. In brief, 30 mL of deionized water was mixed with 30 mL of concentrated hydrochloric acid (38% by weight) in a Teflon-lined stainless steel autoclave (100 mL volume; Parr Instrument Co.). The mixture was stirred at ambient conditions for 5 min following the addition of 1 mL tetrabutyl titanate (purity 98%). After stirring for another 5 min, one piece of FTO substrate was put parallel to the bottom of the Teflon liner with the conducting side facing down through a Teflon frame. The hydrothermal synthesis was conducted at 150 °C for 15 h in an electric vacuum drying oven. Finally, the FTO substrate with TRA was rinsed extensively with deionized water and dried in ambient air.

### 2.3. Synthesis of Ag/TRA

Ag NPs were deposited on $TiO_2$ NRs by chemical reduction impregnation method. 0.01 M $NaBH_4$ ethanol solution and 0.01 M $AgNO_3$ aqueous solution were prepared as reactant solutions. The $TiO_2$ NRs were first immersed into the $NaBH_4$ solution, shaken for 5 s, then it was taken out and immersed into the $AgNO_3$ solution and shaken for another 5 s. After repeating the process four times, Ag/TRA was obtained. The sample was rinsed thoroughly with deionized water several times to remove residual ions and molecules and then dried by a $N_2$ flow to avoid some of the oxidation. The entire process was conducted at room temperature.

### 2.4. SERS measurements

Raman measurements were performed at room temperature on the LabRAM ARAMIS Raman system with a HeNe 633 nm line laser as the excitation source. The diameter of the light spot area was ~1 μm and the spectral resolution and the incident power were 1 $cm^{-1}$ and 9 mW respectively. The spectra were recorded with an accumulation time of 15 s. Using R6G stock solution of $10^{-2}$ M, we prepared solutions with concentrations down to $10^{-7}$ M via successive dilution by factors of 10. The SERS substrates were pre-immersed in corresponding solution for 30 min to ensure that adsorption equilibrium was reached, then rinsed with deionized water and dried in a vacuum chamber for 5 min at 40 °C before each SERS measurement. Unless otherwise stated the accumulation times and the laser power are the same for all