



Highly sensitive surface-enhanced Raman scattering detection of hexavalent chromium based on hollow sea urchin-like TiO₂@Ag nanoparticle substrate

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ABSTRACT

As one of the most toxic heavy metals, hexavalent chromium (Cr(VI)) has long been a concern due to its threats to human health and the environment. In this work, we develop a sensitive surface-enhanced Raman scattering (SERS) sensor for highly specific detection of Cr(VI) using hollow sea urchin-like TiO₂@Ag nanoparticles (NPs). The TiO₂@Ag NPs are functionalized with glutathione (GSH) and used as substrates with 2-mercaptopyridine (2-MPy) as a Raman reporter for a recyclable SERS-active sensor, enabling ultrasensitive detection of Cr(VI). Excellent SERS signals of 2-MPy reporters are detected when GSH complexation with Cr(VI) causes aggregation of the TiO₂@Ag NPs. The developed sensor exhibits good linearity in the range from 10 nM to 2 μM for Cr(VI) with a detection limit of ca. 1.45 nM. It features excellent selectivity to Cr(VI) over other interfering metal ions, and good application for quantitative analysis of Cr(VI) in water samples. Moreover, the proposed SERS sensor can be fully regenerated when exposed to UV light as a result of the self-cleaning ability of the substrates. In contrast to the traditional SERS detection, the present work shed new light on the design and synthesis of hierarchically self-assembled 3D substrate for SERS, catalysis and biosensor development.

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1. Introduction

Contamination by heavy metals ions has become a serious threat to the environment and living organisms. Among various heavy metals, chromium has been widely used in various industries and has become a major environmental contaminant (Gomez and Callao, 2006; Jakubowska, 2010; Pellerin and Booker, 2000; Sun and Liang, 2008). The physicochemical and toxicological properties of chromium depend entirely on its oxidation state (Katz and Salem, 1993). Trivalent chromium (Cr(III)) is known as an essential trace element for maintaining normal physiological function, whereas hexavalent chromium (Cr(VI)) is highly carcinogenic and mutagenic, about 100 times more toxic than Cr(III) (Wang et al., 2004), and it universally exists as an oxyanion (CrO₄²⁻) in aqueous solution (Saha et al., 2011). Therefore, the reduction of Cr(VI), which exist as the chromate anion (Cr₂O₇²⁻) in

weakly acidic and basic aqueous solution, to Cr(III) is a crucial process for the detoxification of Cr(VI)-contaminated water and wastewater. According to the United States Environmental Protection Agency (USEPA), the concentration of the total chromium content in drinking water is regulated with a maximum limit of 100 μg/L (Sarkar et al., 2014). Due to the increasing threat of Cr(VI) exposure in the environment, there is a clear unmet need for accurate and reliable method for the determination of Cr(VI). Detection of Cr(VI) has been carried out by a wealth of traditional analytical techniques, including atomic absorption spectrometry (Gardner and Comber, 2002; Kiran et al., 2008), spectrofluorometry (Paleologos et al., 2001; Tsuyumoto and Maruyama, 2011), spectrophotometry (Themelis et al., 2006; Wu et al., 2013), electrochemistry (Jin et al., 2014; Li et al., 2009), inductively coupled plasma-mass spectrometry (ICP-MS) (Wang et al., 2010). While many of these methods are sensitive and accurate, they are also costly, time-consuming and require tedious sample pretreatments.

As a result of the integration of extraordinary sensitivity, unique spectroscopic fingerprint, and non-destructive data acquisition, surface-enhanced Raman scattering (SERS) has emerged as a promising spectroscopic tool for the identification and detection of the chemical and biological molecules located near/at

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nanostructured metal surfaces (Dasary et al., 2009; Graham et al., 2008; Lee and Moskovits, 2010; Lim et al., 2011; Liu et al., 2012; Shi et al., 2015; Smith, 2008; Zheng et al., 2015). SERS has the potential to achieve high sensitivity as well as selectivity toward Cr(VI) (Du and Jing, 2011; Ji et al., 2015; Mosier-Boss and Lieberman, 2003; Mosier-Boss and Putnam, 2013; Xiao et al., 2012). However, because metal ions including Cr(VI) do not exhibit Raman signals, their detection using the SERS technique can only be achieved either via indirect methods that correlate changes in the absolute SERS intensity of a Raman label in the presence of the analyte (Krpetic et al., 2012; Zhang et al., 2013) or by direct detection, in which the nanoatomic ions coordinate an organic chemoreceptor whose SERS spectrum is sensitive to the presence and extent of complexation (Tsoutsis et al., 2013, 2011).

Most SERS-based Cr(VI) sensing studies use SERS active metallic nanoparticles (Du and Jing, 2011; Mosier-Boss and Lieberman, 2003; Mosier-Boss and Putnam, 2013; Xiao et al., 2012). However, the SERS signal of a single nanomaterial (Au or Ag) is too weak for wide application in ultrasensitive detection. In recent years, researchers have found that a SERS substrate with metallic nanostructure dominate the SERS signal enhancement due to the strong local electromagnetic (EM) field coupling effect of adjacent metal nanostructures (Anker et al., 2008; Genov et al., 2004; Lee et al., 2006; Wang et al., 2005). In addition, it is widely accepted that Raman signals are also closely related to the morphology of SERS substrates. Therefore, metals with different architectures have been widely constructed to obtain effective SERS active-substrate (Shen et al., 2008; Yoon et al., 2008). Among various architectures, 3D nanostructures (such as flower-like (Wang et al., 2011), star-like (Kumar et al., 2007), sea urchin-like (Bakr et al., 2006; Lu et al., 2008) and dendritic morphologies (Ren et al., 2012)) are far superior because their 3D spatial structures can generate more active “hot spots” (Ko and Tsukruk, 2008; Zhang et al., 2008), and several novel properties. In particular, a new family of 3D substrates, sea urchin-like hollow nanostructure decorated with metal NPs, possess a high surface-to-volume ratio, and rich surface tips. Their open morphology preserves the large active surface area and the interstitial channels for diffusion of probe molecules into the structure, thereby improving the efficiency of surface reactions (Zhu et al., 2008). Therefore, they are very appropriate for assembling as a SERS sensor. Despite these amazing advances, it should be emphasized that most of these SERS substrates are discarded after one detection because they cannot be recycled. The combination of noble metals and semiconductor materials as recyclable SERS substrates has been proved to be an effective way of solving the problem described above (Esmailzadeh Kandjani et al., 2014; Shan et al., 2015; Zhang et al., 2015).

Recently, due to its remarkable physical and chemical properties, TiO₂ has been applied in photocatalysis, pollutant degradation and even analytic detection (Es-Souni et al., 2010). It has been reported that TiO₂ can be exploited as a potential candidate for the fabrication of SERS substrates (Ji et al., 2011; Musumeci et al., 2009). Furthermore, efforts have also been dedicated to fabricate hybrids consisting of TiO₂ and Ag/Au NPs to obtain a synergic effect of electromagnetic (EM) and charge transfer (CT) enhancements, also to exploit high surface area with increasing amount of adsorbed molecules (Lamberti et al., 2015; Tan et al., 2012), and these hybrids can serve as recyclable SERS-active substrates for photocatalysis under UV light irradiation (Li et al., 2010; Zou et al., 2013).

In the present work, we use the characteristics of sea urchin-like TiO₂@Ag nanostructures to prepare a multifunctional SERS-active substrates (Li et al., 2015; Su et al., 2014), which can be applied to the recyclable SERS detection. We propose a simple and efficient protocol for the synthesis of sea urchin-like TiO₂@Ag

nanostructures, and demonstrate their application as novel SERS-active substrates for Cr(VI) detection based on a “signal-amplification” strategy capable of generation for multiple sensing events. The design and fabrication of stable, homogeneous, reproducible and recyclable TiO₂@Ag hybrids is achieved via a hydrothermal reaction of SiO₂@TiO₂ core-shell microspheres in the presence of NaOH to form hollow sea urchin-like TiO₂ NPs. Then, Ag NPs are deposited on the TiO₂ surface, resulting in a strong local surface plasmon resonance (LSPR) absorption strength and highly sensitive SERS enhancement. The sensitivity and reproducibility of the substrate were investigated by applying Rhodamine 6G (R6G) as a Raman reporter molecule. Quantitative determination of Cr(VI) was achieved using a portable Raman spectrometer, based on the functionalization of the hollow TiO₂@Ag NPs with glutathione (GSH) and 2-mercaptopyridine (2-MPy). When moderate amount of GSH and 2-MPy are present, the TiO₂@Ag NPs keep in a state of suspension. However, the presence of Cr(VI) would lead to the aggregation of TiO₂@Ag NPs to form many SERS “hot spots”, and significant SERS enhancement signals of the Raman reporter molecule, 2-MPy. Our proposed SERS sensor features high sensitivity, reproducibility and selectivity, and exhibits a limit of detection (LOD) for Cr(VI) of ca. 1.45 nM. The practicality of this proposed method was further validated through the detection of Cr(VI) in water samples.

2. Materials and methods

2.1. Chemicals and reagents

Tetraethyl orthosilicate (TEOS, 99%), tetrabutyl titanate (TBOT, 99%), Glutathione (GSH, 98.0%) and silver nitrate (AgNO₃, 99.8%) were purchased from Sigma-Aldrich; Anhydrous ethanol, polyethylene glycol (PEG, MW 6 000), ammonium hydroxide (NH₃ · H₂O, 28%), hydrochloric acid (HCl, 36.5%), sodium hydroxide, trisodium citrate, potassium dichromate (K₂Cr₂O₇) were of analytical grade and obtained from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Rhodamine 6G (R6G) and 2-mercaptopyridine (2-MPy) were purchased from Solarbio and were used without further purification. Milli-Q water produced by a Milli-Q system (Millipore, Bedford, MA) was used in all experiments. The real samples of river water were collected from East China University of Science and Technology, Shanghai, China.

2.2. Instrumentation

To demonstrate the overall uniformity and morphology of the particles, the samples were examined by transmission electron microscopy (TEM, JEM-1400) and high-resolution transmission electron microscopy (HRTEM, JEM-2100). The samples for the TEM measurements were suspended in ethanol and supported onto a Cu grid. The crystalline structure was investigated by X-ray powder diffraction (XRD; Rigaku D/max 2550 VB/PC, Japan), in a 2θ range from 10° to 80°, using Cu Kα radiation. The optical absorption spectra were acquired on a UV–vis spectrometer (Shimadzu UV-1800, Japan). During the photocatalytic processes, a 15 W mercury lamp with maximum emission of 365 nm was used as the UV light source. Raman spectra were collected on a portable Raman spectrometer (B&W Tek Instruments, USA) equipped with a 785 nm laser, a charge-coupled device (CCD) detector and a 40 × objective lens with numerical aperture (NA) 0.65. The acquisition and analysis of Raman data were performed by using the BWSpec4 software.

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