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Photochemical decoration of magnetic composites with silver nanostructures for determination of creatinine in urine by surface-enhanced Raman spectroscopy



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ABSTRACT

In this study, silver nanostructures decorated magnetic nanoparticles for surface-enhanced Raman scattering (SERS) measurements were prepared via photoreduction utilizing the catalytic activity of ZnO nanostructure. The ZnO/Fe₃O₄ composite was first prepared by dispersing pre-formed magnetic nanoparticles into alkaline zinc nitrate solutions. After annealing of the precipitates, the formed ZnO/Fe₃O₄ composites were successfully decorated with silver nanostructures by soaking the composites into silver nitrate/ethylene glycol solution following UV irradiations. To find the optimal condition when preparing Ag@ZnO/Fe₃O₄ composites for SERS measurements, factors such as the reaction conditions, photoreduction time, concentration of zinc nitrate and silver nitrate were studied. Results indicated that the photoreduction efficiency was significantly improved with the assistance of ZnO but the amount of ZnO in the composite is not critical. The concentration of silver nitrate and UV irradiation time affected the morphologies of the formed composites and optimal condition in preparation of the composites for SERS measurement was found using 20 mM of silver nitrate with an irradiation time of 90 min. Under the optimized condition, the obtained SERS intensities were highly reproducible with a SERS enhancement factor in the order of 7. Quantitative analyses showed that a linear range up to 1 μM with a detection limit lower than 0.1 μM in the detection of creatinine in aqueous solution could be obtained. Successful applying of these prepared composites to determine creatinine in urine sample was obtained.

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1. Introduction

Creatinine is a metabolite of creatine and is eliminated from the human body through urinary excretion [1]. The concentration of creatinine in urine and serum can reveal the status of renal, muscular, and thyroid functions [2–6]. It also serves as a marker of metabolic abnormalities, neuroendocrine activation, and vascular diseases [7]. A large number of methods have been proposed to analyze the levels of creatinine in urine samples, including enzyme-based colorimetric [8–11], chromatographic [12,13], electrochemical methods [14,15] and others [16–18]. These methods generally suffer in one of the weakness such as tiresome sample preparation steps, complicated reagents, skillful operators, and interferences from drug and indigenous species from biological fluids. On the other hand, surface-enhanced Raman spectroscopy (SERS) has gained much attention in recent years owing to its potential to be an extremely sensitive means for analytical applications [19–21]. The treatment of creatinine sample is largely simplified in SERS type of measurements while promising results have

been obtained in the analyses of creatinine in urine [22–25]. For example, Premasiri et al. [22] studied the potential of the SERS method for analyzing creatinine in artificial urine using gold colloids as the SERS active substrate. Gold colloids have been prepared and used alone [23] or decorated on nanostructured poly(chloro-p-xylylene) [24] for quantitatively analyzing the creatinine level in urine. However, due to the small cross section of creatinine in Raman measurements, a highly sensitive SERS active substrate is essentially needed to enlarge the analytical signals. By improving the sensitivity in SERS measurements, the strong interferences from the urine sample can be largely reduced by a dilution method, which is a common method used for analytical technique with enough sensitivity. Therefore, to improve the sensitivity and to minimize the steps in the preparation of highly sensitive SERS substrates, a photochemical method to prepare composite composed of silver, ZnO and magnetic nanostructure is proposed in this work and targeted for sensitive detection of creatinine in urine samples by SERS.

Multifunctional hybrid structures have received great attention because these composites exhibit properties that would not have been obtained only from a single component counterpart. Among the various functional nanomaterials, ZnO-based hybrid materials containing silver give rise to a significant local field amplification

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that results from the accumulated electrons created by Ag/ZnO heterojunction [26,27]. This property makes the Ag/ZnO composites applicable in the field of SERS measurements [27–31]. Isolation and recovery of the Ag/ZnO (or Au/ZnO) composite with the adsorbed analyte's molecules from the aqueous suspension for SERS measurement, however, are not easy [26,32]. Tiresome procedure to deposit metal nanoparticles onto ZnO using linker agents that may compromise the cleanliness of the substrate for SERS measurement is an additional problem [33,34]. Moreover, accessibility of ZnO nanorods for uniform deposition of Ag nanostructures is challenging [35]. Here, these difficulties are circumvented by introducing magnetic particles as a platform for the Ag/ZnO hybrid structure where the composites are readily collected from the reaction mixture using an external magnet that needs no centrifugation or filtration. Most importantly, the enrichment effect acquired from the magnetic property of the composite is intensively pronounced and helps decrease the detection limit by using a small amount of Ag nanostructures-decorated magnetic particles, which allows complete saturation of a low concentration of analytes that enables detection of a minute amount of analytes.

In this work, ZnO is initially incorporated into magnetic nanoparticles to render magnetic and photocatalytic properties for the composite. UV light exposure of the mixture containing AgNO₃ solution (dissolved in ethylene glycol) and ZnO/Fe₃O₄ composite resulted in the formation of silver nanostructures onto the composite. Therefore, the composite exhibits a multifunctional advantage of optical, magnetic and photocatalytic properties given by the nanostructures of Ag, Fe₃O₄ and ZnO, respectively. The schematic diagram for the preparation of the hybrid structures in this work is shown in Fig. 1a. As can be seen in this diagram, the magnetic particles of Fe₃O₄ are first prepared from coprecipitation of Fe (II) and Fe (III) with a hydroxide solution. By dispersing magnetic particles into zinc nitrate solution, a hydroxide solution is used to form precipitates of Zn(OH)₂ on the magnetic particles. After annealing, ZnO/Fe₃O₄ composites were formed. By soaking ZnO/Fe₃O₄ composites into silver nitrate/ethylene glycol solution, Ag nanostructures-decorated ZnO/Fe₃O₄ composites with high SERS effect are formed. A series of pictures taken in each of the above steps is also plotted in Fig. 1b for reference.

2. Experimental

2.1. Chemicals

Iron (II) sulfate heptahydrate, iron (III) sulfate n-hydrate and sodium hydroxide were obtained from Showa (Tokyo, Japan). Ammonium hydroxide (28–30% (w/v)) was purchased from Acros

(Phillipsburg, NJ, USA). *p*-Nitrothiophenol (pNTP) was obtained from TCI (Tokyo, Japan). Methanol was obtained from Echo chemical (Toufen, Taiwan). Silver nitrate was purchased from J.T. Baker (Phillipsburg, NJ, USA). Oleic acid was purchased from Wako pure chemicals (Osaka, Japan). Creatinine, uric acid and zinc nitrate hexahydrate were purchased from Acros Organics (New Jersey, USA). Urea was purchased from Riedel-de Haën (Seelze, Germany). Ethylene glycol was obtained from Scharlau Chemie (Barcelona, Spain). All the chemicals were reagent grade and used without further purification. Deionized Milli-Q water was used throughout the study.

2.2. Preparation of ZnO/Fe₃O₄ composite

To prepare the composite, magnetic nanoparticles were first prepared by the coprecipitation method with some modification [36]. Briefly, 100 mL of 125 mM FeSO₄ and 62.5 mM of Fe₂(SO₄)₃ aqueous solutions were prepared. In this solution, 10 mL of ammonium hydroxide (28–30%, w/v) was added rapidly with vigorous stirring for 20 min to form magnetic precipitates. After addition of 4 mL of oleic acid, the precipitate was kept in an 85 °C water bath for 1.5 h. After cooling to room temperature, the magnetic precipitates were isolated from the solvent by magnetic decantation and washed several times by deionized water. These precipitates were further washed at least two times by ethanol.

In the synthesis of ZnO/Fe₃O₄ composites, 50 mg of Fe₃O₄ was soaked into a 50 mL solution of 45 mM zinc nitrate solution. After stirring and sonicating to form a well-dispersed solution, this mixture was dropped slowly into 50 mL of 90 mM NaOH solution at 70 °C with vigorous stirring within 40 min. This solution was kept in 70 °C water bath for 2 h and aged at room temperature for another 15 h to complete the reaction. The resulting composites were then separated with a magnet and washed with deionized water several times. After keeping in an 80 °C oven for 3 h, these particles were subsequently annealed at a temperature of 350 °C for 1 h. Once they are prepared, the composites were stored at room temperature and used for subsequent preparations of the SERS substrate by taking the required amount throughout the study.

2.3. Photochemical deposition of silver nanostructures on ZnO/Fe₃O₄ composite

To decorate silver nanostructures on the ZnO/Fe₃O₄ composite, 20 mg of the composite particles was taken and dispersed in 5 mL of AgNO₃ solution (in ethylene glycol) with the concentration ranging from 1 mM to 40 mM. The reaction mixture was then sonicated for 2 min to disperse the ZnO/Fe₃O₄ uniformly and placed into UV box for different lengths of irradiation times. The formed Ag@ZnO/Fe₃O₄ composite was cleaned with methanol or water using magnetic decantation and subsequently used as SERS substrate.

2.4. SERS measurements

To examine the performance of SERS activity of the prepared Ag@ZnO/Fe₃O₄ composites, 20 mg of the particles were soaked into 1 mL of 10 ppm methanolic pNTP solution and kept for 1 h. A Teflon protected cylindrical magnet (10 mm in diameter) was used to attract the Ag@ZnO/Fe₃O₄ composites. After being rinsed in methanol and air-dried, the composites were subsequently scanned by a Raman microscope as shown in Fig. 2. For detection of creatinine, 4 mg of the substrate was dispersed into 10 mL of an aqueous solution of creatinine, shaken for a while and kept for 30 min. Then, the particles were collected with a 3 mm iron bar attached with a permanent magnet. After being rinsed in water

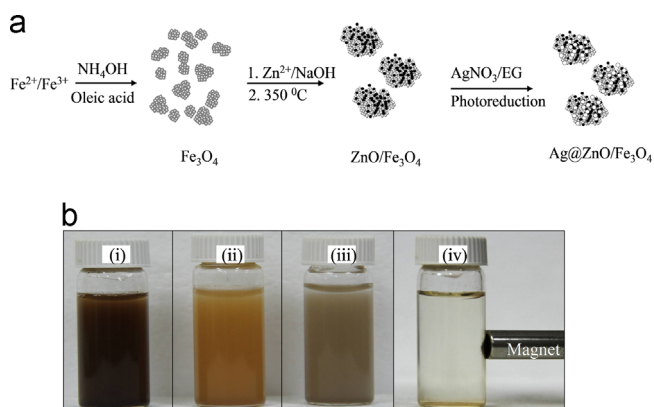


Fig. 1. (a) Schematic diagram for preparation of silver nanostructures-decorated ZnO/Fe₃O₄ composites. (b) Pictures for the corresponding synthesized Fe₃O₄ (i), ZnO/Fe₃O₄ composites (ii), Ag@ZnO/Fe₃O₄ composites (iii), Ag@ZnO/Fe₃O₄ composites assembled with permanent magnet (iv).

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