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Photochemical decoration of silver nanoparticles on magnetic microspheres as substrates for the detection of adenine by surface-enhanced Raman scattering

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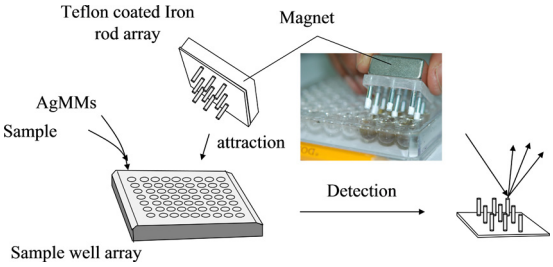
HIGHLIGHTS

- We have successfully prepared Raman active silver nanoparticles (AgNPs) on magnetic microspheres (MMs) for Raman applications.
- Photochemical reduction method has been used in this work to significantly simplify the preparation procedures.
- The prepared particles offer enhancement effect in Raman measurements and enrichment effect in concentration by MMs.
- Prepared AgMMs have been successfully applied in determination of the important biospecies of adenine in aqueous solution.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, silver nanoparticles (AgNPs) decorated magnetic microspheres (MMs) are prepared as surface-enhanced Raman scattering (SERS) substrate for the analysis of adenine in aqueous solutions. To prepare these substrates, magnetic particles were first synthesized by coprecipitation of Fe(II) and Fe(III) with ammonium hydroxide. A thin layer of cross-linked polymer was formed on these magnetic particles by polymerization through suspension of magnetic particles into a solution of divinyl benzene/methyl methacrylate. The resulted polymer protected magnetic particles are round in shape with a size of 80 μm in diameter. To form AgNPs on these MMs, photochemical reduction method was employed and the factors in photochemical reduction method were studied and optimized for the preparation of highly sensitive and stable AgNPs on MMs substrates (abbreviated as AgMMs substrates). By dispersing the AgMMs in aqueous samples, cylindrical magnet was used to attract the AgMMs for SERS detections. The observed enhancement factor of AgMMs reached 7 orders in magnitude for detection of adenine with a detection limit approaching to few hundreds of nanomolar.

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1. Introduction

Adenine plays a significant role in biological system as it has widespread effect to coronary and cerebral circulation, energy transduction, enzymatic reactions as cofactors, and even in cell signaling [1–5]. Abnormal changes of its concentration may indicate the presence of various diseases. Quantitation of adenine is, therefore, critically needed for the studies of a wide variety of biological issues. To determine adenine, a large number of analytical methods based on electrochemistry [6–9], separation technology [10–12], colorimetric [13], fluorescence [14], Rayleigh scattering [15], and chemiluminescence [16,17] have been proposed to

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provide fast and sensitive means for detections. Alternatively, surface-enhanced Raman scattering (SERS) has started to gain attention in the analysis of nucleobases or nucleotides as the technique in applying and handling SERS substrate is gradually matured [18–25]. This technique offers the advantages of no memory effect as in electrochemical methods, no tedious pre-cleaning steps as in separation methods, and no need of labeling or enzymatic reactions as in fluorescence or colorimetric methods.

In the past, magnetic nanoparticles with plasmonic properties have been reported as SERS substrate by different groups due to their nontoxic nature and ease of assembling of particles from reaction mixture [26–30]. For examples, the combination of AgNPs decorated magnetic nanoparticles with solenoid embedded microfluidic device simplifies the SERS detection [26]. The development of magnetic nanoparticles-based barcode materials enables rapid SERS determination [29]. With SERS-encoded magnetic nanoparticles, specific cancer cell can be identified by SERS measurements [30]. Surfaces of magnetic nanoparticles are usually chemically modified to limit the growth of the magnetic core and to form a coating on their surfaces for intended purposes. Surface modification also prevents aggregation and oxidation of magnetic particles. Silanization has been most commonly used for surface modification [29–32]. Copolymerization of divinyl benzene with other monomers to form cross-linked polymer has also been used to modify magnetic particles and largely used in concentration of environmental unfriendly species through the tuning of the composition in the copolymers [33–36]. The cross-linked nature of the polymer in this type of MMs provides better stability for the magnetic particles than Si based and, therefore, is selected in this work to prepare cross-linked polymer based AgMMs for decoration of AgNPs on their surfaces. The resulted polymer protected magnetic microspheres are stable because the protecting polymer layer prevents any reaction of the bare magnetic particles with surrounding chemicals and aggregation of magnetic particles themselves. Moreover, the attached silver nanoparticles (AgNPs) are not directly contacting with iron oxide, which prevents any reaction between iron oxide and AgNPs.

In this work, to improve the performance of SERS detection of adenine, the concentration ability of magnetic microspheres (MMs) is integrated with the enhancement ability of AgNPs in SERS measurements. Thus, to grow AgNPs on the MMs surfaces, photochemical reduction method was modified and applied in this work. According to the literature, photochemical reduction is feasible to prepare AuNPs or AgNPs colloidal solutions [37–40]. Therefore, to assist and simplify the formation of AgNPs directly on the MMs a simple photochemical reduction method is proposed and examined. Fig. 1A shows the schematic diagram for the preparation of AgMMs in this work.

2. Experimental

2.1. Chemicals

Fe(II) sulfate heptahydrate and Fe(III) sulfate n-hydrate were obtained from Showa (Tokyo, Japan). Methyl methacrylate and ammonium hydroxide (28–30% (w/v)) were purchased from Acros (Phillisburg, NJ, USA). Para-nitrothiophenol (pNTP), divinyl benzene, and α-α'-azobisisobutyronitrile (AIBN) were obtained from TCI (Tokyo, Japan). Poly vinylalcohol (PVA, MW:$1.24 \times 10^5 \sim 1.86 \times 10^5$), Polymethylmethacrylate (PMMA, MW:1.2×10^5) and uracil were obtained from Sigma (St. Louis, MO, USA). Methanol and toluene were obtained from Echo chemical (Toufen, Taiwan). Silver nitrate was purchased from J.T. Baker (Phillisburg, NJ, USA). Citric acid trisodium salt dehydrate was purchased from Janssen Chimica (Beerse, Belgium). Sodium chloride was obtained from USB Corporation (Cleveland, OH, USA). Adenine, cytosine and thymine were purchased from Alfa Aesar (Ward Hill, MA, USA). Guanine was obtained from MP Biomedicals (Eschwege, Germany). Oleic acid was purchased from Wako pure chemicals (Osaka, Japan). All the chemicals were reagent grade and used without further purification. Deionized Milli-Q water was used throughout the study.

2.2. Instrumentation

The Raman spectra were measured by Triax 320 Raman system (Jobin-Yvon, Inc., Longjumeau, France), equipped with 632.8 nm He/Ne laser line as excitation source (JDS Uniphase Corporation, Milpitas, CA) and a liquid-nitrogen cooled Ge array detector (Jobin-Yvon, Inc.). The laser power was 35 mW, and exposure time was 0.2 s for measurement of pNTP and 1 s for nucleobases. Scanning electron microscopy (SEM) images were obtained with JSM-6500F (JEOL, Ltd., Tokyo, Japan), field emission scanning electron microscope (FE-SEM) operating with accelerating voltage of 10 kV. UV box (TS-UV, De-Yun, Ltd., Taipei, Taiwan) operated at 30 W with a wavelength range of 320–400 nm was used as a UV light source for photo-reduction process. X-ray diffraction (XRD) patterns were obtained on a D2 phaser XRD-300 W powder diffractometer (Bruker, AXS GmbH, Karlsruhe, Germany) for a 2θ range of 30–80° at scan rate of 0.05 degree/sec using Cu Kα radiation at 40 kV and 100 mA. A Spectrum One FT-IR spectrometer (PerkinElmer 100 series) was used to measure the infrared spectra. Spectra were collected at a resolution of 4 cm^{-1} using a deuterated triglycine sulfate detector.

2.3. Preparation of polymer protected MMs

To prepare MMs, magnetic particles were first prepared by coprecipitation method with some modification [36]. Briefly, 100 mL of 125 mM $FeSO_4$ and 62.5 mM $Fe_2(SO_4)_3$ 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 oleic acid, the precipitate was kept in 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. 2 g of the formed magnetic precipitates were added into an organic solution containing methyl methacrylate, divinyl benzene, and toluene in volume of 10.6, 0.8, and 3 mL, respectively. In the meantime, an aqueous solution prepared by mixing 2.5 g PVA, 3 g NaCl and 100 mL deionized water was mixed with the organic solution prepared above. After ultrasonication of the mixture to form emulsion, the solution was transferred to reflux glassware. After stirring for another 30 min, 0.2 g AIBN was added to initiate the polymerization and subjected to reflux at a temperature of 70 °C for 5 h. Brown magnetic emulsion was separated by magnetic decantation. After washed with deionized water and methanol several times separately, a polymer protected MMs were obtained.

2.4. Preparation of silver nanoparticles on polymer protected MMs

To form AgNPs on the MMs (shortly AgMMs), 50 mg of MMs was dispersed in a 5 mL solution containing $AgNO_3$ and trisodium citrate. After sonicating the reaction mixture for 5 min to disperse the MMs, it was placed into UV box for different lengths of time. The formed AgMMs were cleaned with deionized water and methanol several times by magnetic decantation. For the simplicity of the discussion, the conditions used for the preparation of AgMMs, were

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