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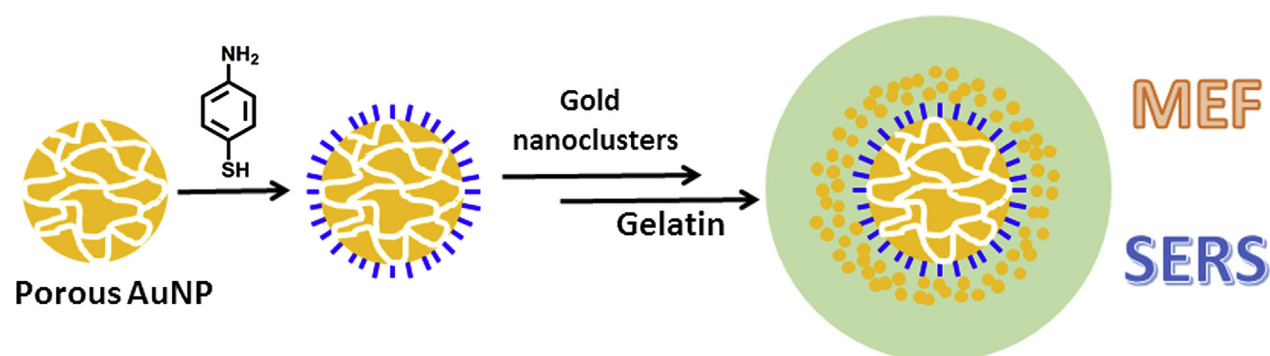
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## Synthesis and application of bifunctional gold/gelatin nanocomposites with enhanced fluorescence and Raman scattering

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### GRAPHICAL ABSTRACT



### HIGHLIGHTS

- A bifunctional gold/gelatin nanocomposite was fabricated with core-shell structure.
- Enhanced fluorescence and Raman scattering signals were observed in this particle.
- It shows good performance for fluorescence and SERS imaging of HeLa cells.

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### ABSTRACT

In recent decades, the preparation of multi-functional nanoplateforms that integrate two or more abilities into a single nanocomposite has attracted increasing interest and potential applications in many fields. Here, we report a novel hybrid core-shell structured nanocomposite integrating the capabilities of metal-enhanced fluorescence (MEF) and surface-enhanced Raman scattering (SERS). The nanocomposite consists of porous gold nanoparticle as a magnifying material for both MEF and SERS, 4-aminothiophenol (ATP) molecule as Raman probe, gold nanocluster as the fluorescent emitter, and gelatin as the protecting outer shell. In this nanocomposite, the fluorescence intensity of the gold nanoclusters was enhanced by about four times, while the Raman signal of the ATP molecules was increased by 4 orders of magnitude. Additionally, the nanocomposite shows low cytotoxicity and good performance for fluorescence and SERS imaging of HeLa cells.

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## 1. Introduction

The development of multifunctional core-shell nanoparticles that integrate individual functions into a single system has become one of the most important developing trends for many nanotechnology fields [1,2]. Combining the superior advantages of each function, possible synergistic effects, and increased suitability for complex biological environments, multifunctional nanoparticles have been extensively studied and applied in biological fields including drug delivery, biosensing, bioimaging, and theranostic [3–6]. Among them, gold nanoparticles (AuNPs) are excellent scaffolds for the fabrication of hybrid nanocomposites and have attracted particularly intense interest because of their distinct physical and optical properties [7–13]. These include localized surface plasmon resonance, surface-enhanced Raman scattering (SERS), metal-enhanced fluorescence (MEF), catalytic ability, photochemical effects, aggregation-induced colorimetric effects, and nonlinear optical properties [14–20].

In recent years, SERS technology has attracted much research interest and has thus developed very rapidly. Compared to other analysis methods, SERS shows superior advantages, such as offering fingerprint vibrational information on analytes, non-destructive analysis, and less interference in aqueous environments. More importantly, the acquired enormous enhancement factor of SERS, which is up to  $10^{14}$ , makes it possible to make detections at the level of single molecule or nanoparticle [21]. Consequently, SERS has already become a powerful spectroscopic technique for chemical and biological analysis with high sensitivity and selectivity [22–26]. While its application to cellular imaging has also attracted some interest [27,28], a limited imaging resolution and long measurement time are still barriers to its practical use for cellular imaging.

Apart from the Raman scattering signal, the fluorescence emission of a fluorophore can also be enhanced if it is placed in close proximity to plasmonic nanostructures, caused by interaction with the resulting enhanced electromagnetic field. This phenomenon is known as MEF [29,30]. Because fluorescence techniques are widely used for labeling, sensing, and imaging in many fields, the design of novel MEF-based fluorescent nanocomposites with enhanced emission properties shows specific meanings for practical application. To date, several different types of fluorescent species have been reported to be suitable for constructing MEF-based nanocomposites, including organic fluorophores [31,32], conjugated polymers [33,34], semiconductor quantum dots [35,36], and lanthanide-based upconversion nanoparticles [37,38], the fluorescence of which were enhanced by nearby plasmonic nanostructures. In recent years, sub-nanometer-sized metal nanoclusters have emerged as novel promising fluorescent emitters, and have attracted enormous attention owing to their good photostability and size-dependent photoluminescence from the near infrared to ultraviolet regions [39–42]. However, their use as a component of MEF-based fluorescent nanocomposites has rarely been reported.

To further improve the sensitivity of spectroscopic investigations, it is highly desirable to integrate MEF and SERS effects in a single plasmonic nanoparticle [43,44]. To maximally realize MEF and SERS, it is better to choose AuNPs with anisotropic shapes, which would have abundant hot spots around their edges or corners where the localized electromagnetic field would be significantly concentrated. It has been demonstrated that both MEF and SERS show a strong distance dependency, but the optimal distance for each is quite different. SERS effects decrease exponentially with increasing distance away from the plasmonic surfaces, and thus the Raman reporters must be very close to the metallic surface [45]. In contrast, fluorescence quenching often occurs if the fluorophore is placed close to the metallic surface, and only the fluorescence signals of fluorophores at certain distances can be enhanced [46,47]. Thus, to design such a dual-modal plasmonic platform, it is crucial

to find a suitable assembly method to place the Raman/fluorescent probes at reasonable distances from the metal nanoparticles. Additionally, an ideal fluorescent nanocomposite always requires good reproducibility and stability. Therefore, a shell layer is always needed to be coated on the Raman reporter and fluorescent emitter-labeled metallic nanoparticles to protect the probes and improve their dispersability and stability.

In this work, we fabricated a novel plasmonic platform providing dual-modal enhanced spectroscopic properties via SERS and MEF. As shown in Scheme 1, the proposed bifunctional nanocomposite was composed of four components. The inner core was a gold nanoparticle, which served as the magnifying substrate for both MEF and SERS. Gold nanoclusters and 4-aminothiophenol (ATP) were selected as the fluorescent species and Raman reporter molecule, respectively. Finally, gelatin biomacromolecules were coated on the outside of the shell, to ensure the stability and biocompatibility of the nanocomposite. As expected, both the fluorescence and Raman signals of the nanocomposite were found to be enhanced, by factors of 4 and  $3.1 \times 10^4$ , respectively. Finally, the good fluorescence and SERS imaging performance of the nanocomposite was demonstrated by co-culture with HeLa cells.

## 2. Experimental

### 2.1. Materials

Gelatin from cold water fish skin, chloroauric acid tetrahydrate ( $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ ), 4-aminothiophenol (ATP), glutathione (GSH), L-ascorbic acid (AA), (1-hexadecyl)-trimethylammonium chloride (CTAC), glutaraldehyde, sodium borohydride ( $\text{NaBH}_4$ ), and phosphate buffered saline (PBS) tablet were purchased from Sigma-Aldrich. All chemical reagents were used as received without further purification. Ultrapure Millipore water ( $18.6 \text{ M}\Omega$ ) was used throughout the experiments.

### 2.2. Synthesis of porous gold nanoparticles (AuNPs)

Porous AuNPs were prepared by a seed-mediated growth method according to a procedure reported in the literature [48]. First, gold nanoseeds were made by the addition of a freshly prepared, ice-cold aqueous  $\text{NaBH}_4$  solution (10 mM, 0.30 mL) to an aqueous mixture of  $\text{HAuCl}_4$  (10 mM, 0.25 mL) and CTAC (0.1 M, 10 mL) under magnetic stirring. The seed solution was vigorously stirred for 1 min and kept at room temperature for 2 h, after which it was diluted 1000-fold with 0.1 M CTAC and used in the following growth process. The growth solution was prepared by mixing aqueous solutions of  $\text{HAuCl}_4$  (10 mM, 0.5 mL), CTAC (0.1 M, 10 mL), and AA (0.1 M, 0.1 mL). After gently mixing the growth solution for 30 s, 0.02 mL of the diluted Au seed solution was added. The reaction solution was immediately gently mixed for another 30 s and then left undisturbed at room temperature for at least 4 h. The as-obtained AuNPs were washed with water three times by centrifugation/redispersion, and finally redispersed in 5 mL of water.

### 2.3. Synthesis of gold nanoclusters (AuNCs)

AuNCs were synthesized according to a previously reported method [49]. In brief, 1 mL of 20 mM  $\text{HAuCl}_4$  was added to 8.7 mL of water followed by addition of GSH solution (9.2 mg in 0.3 mL of water). The mixture was gently stirred for 5 min at room temperature, and then stirred at  $70^\circ\text{C}$  for 24 h. The AuNCs were obtained as a yellow solution.

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