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Facile and Green Synthesis of SERS Active and Ferromagnetic Silver Nanorods

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Silver nanorods with increased surface-enhanced Raman scattering sensitivity and detection have been synthesized in a novel, facile, and eco-friendly way through a simple chemical reduction method using 2,3-dihydroxyfumaric acid in aqueous solution under aerobic conditions. The structure and composition of the silver nanorods were characterized by UV/Vis spectroscopy, powder X-ray diffraction, transmission electron microscopy (TEM), and field emission scanning electron microscopy (FESEM). Simple hard washing agglomerates the nanorods. The agglomerated nanorods consist of several "hot spots", easily replaceable capping agents and an anisotropic shape, which are all responsible for its high sensitivity and trace detection (picomolar level) of different adsorbate molecules (thiophenol, Rhodamine 6G) in surface-enhanced Raman scattering. Rarely observed, but theoretically established, unpaired s-electron-based ferromagnetism is the other interesting aspect of these nanorods.

Introduction

Metal particles in the nanometer size range have attracted much attention because of their size, shape, and composition-dependent phenomena.[1–4] Coinage metal nanomaterials show size-dependent tuning of their electrical,[5] optical,[6–8] magnetic,[9,10] and catalytic properties,[11] which are related to the confinement of delocalized electrons. The novel properties are different from the isolated atom or bulk phase due to the "quantum size effect".[12] However, the challenge in nanoscale syntheses is the creation of pure and perfect nanometer-scale materials with a definite size and shape,[13,14] which can identically be replicated in unlimited quantities. Conventionally silver nanoparticles are synthesized by citrate or borohydride reduction.[15,16] But stronger reducing powers of the reductant and high-temperature requirements provide constraints for the in situ generation in a temperature-sensitive, mild system. Apart from these two methods there are several other methods; sol–gel techniques, thermal decomposition, and laser ablation have been reported in the literature.[17] With enormous growth in multidisciplinary nanoscience research, material scientists, biologists, and engineers are trying to develop easy, sustainable, and "green" methods for the synthesis of nanomaterials having multiple functionalities. Such a "green chemistry"[18] environmentally viable approach would be beneficial for application in biologically relevant systems and hence more practicable. Recently, we have exploited the two-electron oxidation of 2,3-dihydroxyfumaric acid (dhfa) for the synthesis of a number of Cu^I and mixed-valent porous $Cu^{I/II}$ coordination frameworks in aqueous solution under aerobic conditions.[19] This facile and green approach has been extended to the synthesis of novel metal nanostructures in aqueous solution in open atmospheres. In this contribution we report a novel, environmentally benign, and more advantageous method for the synthesis of silver nanorods (NRs) in aqueous solution without any external capping agent. Here, dhfa acts as both reducing agent[20,21] and capping agent [methyl ester of 2,3-diketosuccinic acid (dksa)]. Among various probable applications we have unveiled properties such as increased SERS sensitivity and trace detection up to picomolar levels of thiophenol (TP) and Rhodamine 6G (R6G) molecules, as well as ferromagnetism of the newly synthesized silver NRs.

Results and Discussion

Characterization of Nanorods

A potentiometric titration suggests that 1 equiv. of dhfa can reduce 2 equiv. of silver(I) ions to silver (Scheme 1). Mass spectra of the reaction solution, solid-state ^{13}C NMR, solid- and solution-phase ^{1}H NMR, and IR spectroscopy unequivocally suggest that dimethyl diketosuccinate, the rearranged product of dhfa after oxidation, acts as a capping

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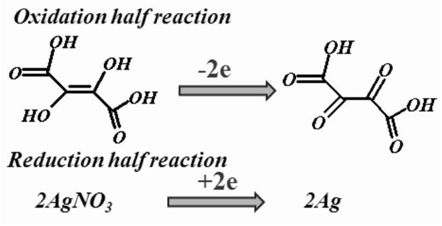
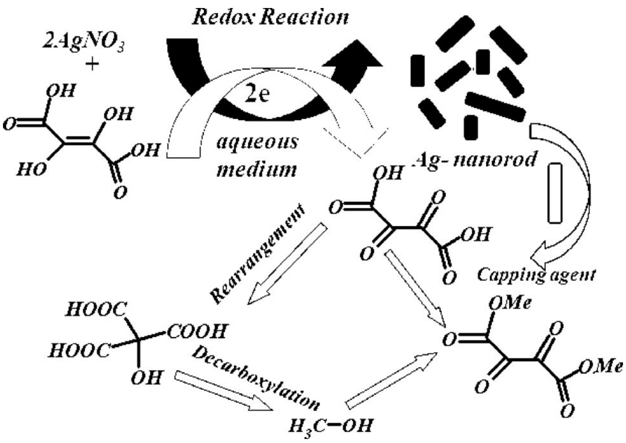
agent (details are given in the Supporting Information).[22] The mechanism for the formation of the silver NRs and corresponding capping agent is shown in Scheme 2. It is worth mentioning that the IR spectra of the solid NRs do not contain any peak that corresponds to α-diketone suggesting the existence of a Ag···O interaction with the carbonyl oxygen, which is further supported by the Raman spectral band (ν_{Ag}···O) at 220 cm^{-1} (Figure S4).



Scheme 1. Oxidation–reduction reaction equation for the formation of silver NRs.



Scheme 2. Mechanism for the formation of silver NRs and corresponding capping agent.

The morphology of the as-synthesized silver nanostructure is rod shaped as shown by a TEM image (see part a of Figure 1 and Figure S5 in the Supporting Information).

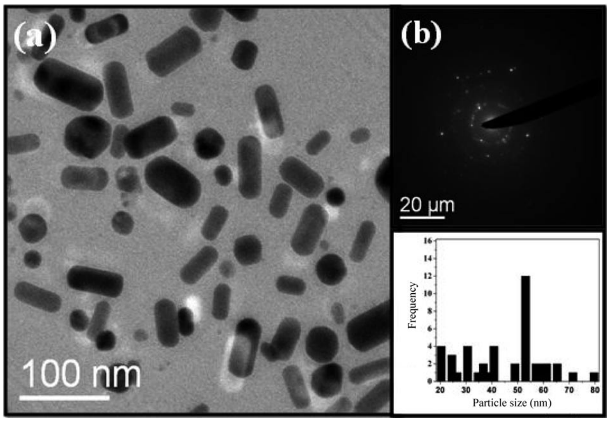


Figure 1. (a) TEM image for the as-synthesized silver NRs; (b) Electron diffraction (ED) pattern showing crystalline nature of the silver NRs and the histogram of particle size distribution based on 40 particles.

The size distribution is found to be 20–80 nm. Most of the rod-shaped nanostructures formed have an average length of 53 nm and a width of 25 nm. The distribution of the size with respect to its frequency of occurrence is calculated considering 40 and 194 nanoparticles, and the histograms are shown in Figure 1 and Figure S5, respectively. To clarify the crystallinity of the silver NRs, electron diffraction (ED) measurements were carried out. The diffraction rings of the silver NRs in the ED pattern (Figure 1, b) confirm the crystalline nature of these silver NRs.

The powder X-ray diffraction (PXRD) pattern (2θ = 30–80°) of the silver NRs is presented in Figure 2, in which the diffraction peaks for (111), (200), (220), and (311) lattice planes appear clearly. The diffraction planes of silver nanorods correspond well to the crystalline planes of the face-centered-cubic (fcc) structure of Ag, which is consistent with the ED pattern.[13]

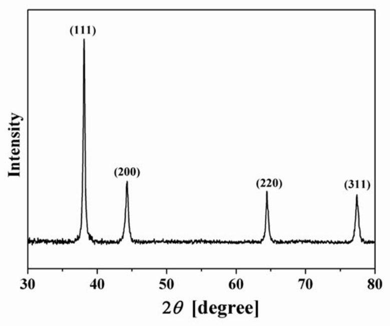


Figure 2. X-ray powder diffraction pattern (PXRD) for the as-synthesized silver NRs.

UV/Vis Spectroscopic Study of the Nanorods

The UV/Vis spectrum (Figure S10) of the silver NRs shows two surface plasmon resonance (SPR) bands; one at 420 nm and the other at 582 nm. The first band at 420 nm corresponds to the transverse SPR band, which is common for all silver nanostructures. The band at 582 nm corresponds to the longitudinal SPR band. The UV/Vis spectra of the colloids clearly supports the obsevation that nanostructures are anisotropic in shape.[23] Since the as-synthesized silver NRs have far less zeta potential and the capping agents are weak, they have a very high tendency to agglomerate. The change in color of the solution over a three-hour interval is shown in Figure 3 and a clear layer of NRs at

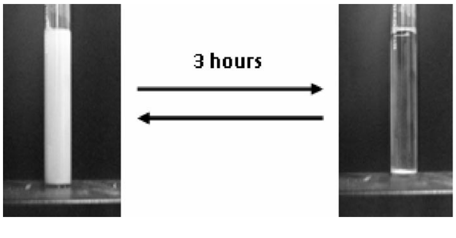


Figure 3. Photograph of the as-synthesized grayish-yellow colored silver NRs in an aqueous medium (left side) and after 3 h the NRs settled with a clear upper solution (right side).

the bottom of the vial indicates sedimentation due to agglomeration or inefficient dispersion in aqueous media. The UV/Vis spectra of washed NRs show a broad band starting from 416 nm that merges with the second SPR band (Figure S10, b). This is due to the agglomerations and the formation of nanoclusters with different sizes and shapes after removal of the capping agent. It is worth mentioning that particle size and shape depends on the concentration ratio of dhfa to silver nitrate.

SERS Activity of Nanorods

One of the most common properties of silver nanoparticles is its SERS sensitivity with the possibility of trace detection of molecules. Because of a very broad UV/Vis absorption and tendency to agglomerate (Figure 4) these NRs encourage us to employ them for trace detection of different substrate molecules. The advantage of a nearly flat response of the washed NRs in UV/Vis spectra is that there is no restriction on the excitation source to be used for SERS (Figure S9). To demonstrate this we have chosen an excitation source of 632.8 nm, which is far away from the UV/Vis absorption peak of 420 nm and 582 nm for a single silver NR. In order to take advantage of agglomeration of NRs, the molecule could be incubated with NRs, which would trap the molecule among the NR agglomerates leading to a hot spot-like environment (see inset of Figure 4). In order to test this, we have taken thiophenol (TP) as the test molecule and incubated it with washed silver NRs on a glass substrate. The SERS spectra of the incubated TP with NRs and free TP molecules have been shown in Figure 5. The spectral features agree well with the reported values. The enhancement factor G was calculated by the procedure given by Yu et. al.[24]

$$G = (I_{\mathrm{SERS}}/I_{\mathrm{norm}})(N_{\mathrm{bulk}}/N_{\mathrm{surf}})$$

where I_{SERS} and I_{norm} are the intensities of a specific band in SERS and normal Raman of the test molecule, respectively. N_{bulk} and N_{surf} are the number of probe molecules under laser illumination in the bulk and SERS experiments, respectively. We have chosen two bands at 1069 $\mathrm{cm^{-1}}$ and 1572 $\mathrm{cm^{-1}}$ to calculate the G factor for TP. N_{surf} is given by CA, where C and A are surface densities of TP (6.8×10^{14} molecules $\mathrm{cm^{-2}}$) and area of the laser spot on the sample, respectively.[25] On the other hand, N_{bulk} is given by $Ah\rho/m$, where h, ρ, and m are the penetration depth (100 µm), the density (1.079 $\mathrm{g\,cm^{-1}}$), and the molecular weight (110.18 $\mathrm{g\,mol^{-1}}$) of TP, respectively. In the present experiment we obtained a value of $G \approx 10^5$ for TP.

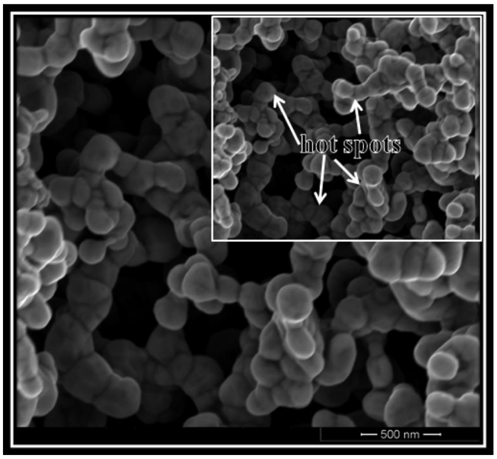


Figure 4. FESEM image for the agglomerated silver NRs after washing with water and methanol; inset showing the “hot spots” in the agglomerated silver NRs.

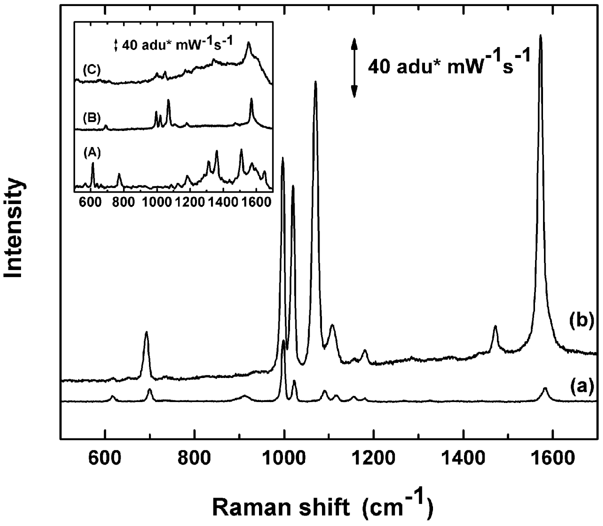


Figure 5. SERS spectra of Thiophenol (TP): (a) without and (b) with NRs. Inset: SERS spectra of (A) Rhodamine 6G (R6G, 1 pM), (B) Thiophenol (TP, 1 pM), and (C) L-Phenylalanine (1 µM).

The enhancement factor G (10^5 for TP) is similar to the reported values for the monolayer of silver nanorods and for silver nanospheres.[26] Similar enhancement factors have also been reported for gold nanorods and spheres. However, the dielectric constant indicates that silver has a more efficient scattering to absorbance ratio compared with gold and also has more polarizable electrons. Therefore, in general, silver shows greater surface enhancement than gold.[27] It is also known that when the laser excitation frequency is closer to the surface plasmon frequency, a larger SERS enhancement is observed.[28] Since the washed NRs shows broadening in the plasmon bands the laser frequency must overlap with the plasmon band. In addition a lightning-rod effect can result in a large electric field near the sharpest surface, e.g. the ends of the nanorod.[29] Therefore, Raman enhancement is largest at the sharpest surface. The maximum enhancement is reached under a certain aspect ratio and it has been seen that rods give maximum enhancement followed by wires and spheres.[30]

The silver NRs were also employed for SERS of the Rhodamine 6G (R6G) and phenylalanine Raman probes as shown in Figure 5 (inset). It can be seen that NRs with both the adsorbates have very strong SERS activity. The spectral features obtained for TP, R6G, and phenylalanine are similar to earlier reports.[31–33] In the case of R6G some background fluorescence observed was subtracted for clarity. It is normally seen that R6G has a strong chemical interaction with metal nanoparticles, which results in fluorescence quenching. In our case strong chemical binding is absent but R6G adheres to the NRs giving a good SERS signal with some background fluorescence. In the case of TP, the thiol group helps in chemical binding leading to no residual background giving rise to stable SERS spectra. The large decrease in frequency of the in-plane breathing mode coupled to the $\upsilon_{(C-S)}$ mode from 1092–1069 cm^{-1} in the SERS spectra show that the TP molecule is bonded to the metal surface.[34] With the NRs as the substrate, the SERS detection of TP and R6G is down to a concentration of 10^{-12} M, much lower than the reported values,[35] whereas in the case of phenylalanine we could only go down to μM concentrations.

Sun et al. have reported that dissolution of capping agents like CTAB in ethanol results in the formation of aggregates.[36] Chen et al. have shown that the electromagnetic enhancement depends strongly on the degree of aggregation of silver nanoparticles.[37] 3D aggregation of nanoparticles strongly influences the SERS enhancements as shown by Pignataro et al.[38] For stronger SERS signals aggregating agents like NaCl, KCl, and KNO_3 are often used.[39] In our case washing with methanol reduced the density of the capping agents on the NR surface, facilitating the adsorbates to be adsorbed onto the surface. The reduction in the capping agents facilitates the creation of 3D structures resembling hotspots (Figure 4).[40] Hence, the present NRs have a preference for analytes with groups containing sulfur, π electrons, and nitrogen, which facilitate chemical binding or strong adsorption onto these NRs resulting in its ability for trace detection.

Magnetic Properties of the Nanorods

Preliminary magnetic studies of the capped silver NRs were found to be ferromagnetic at low temperature (2.5 K) as well as at room temperature (see Figure 6). The field-dependent magnetization plot at 2.5 K (black curve in Figure 6) shows a saturation magnetization of 0.2857 emu g^{-1} with a small hysteresis loop of remanent magnetization of 0.004 emu g^{-1} and a coercive field of 74 G. When the same measurement was performed at room temperature the saturation magnetization value dropped down to 0.224 emu g^{-1} and the hysteresis loop became narrower, i.e the ferromagnetic interaction became weaker.

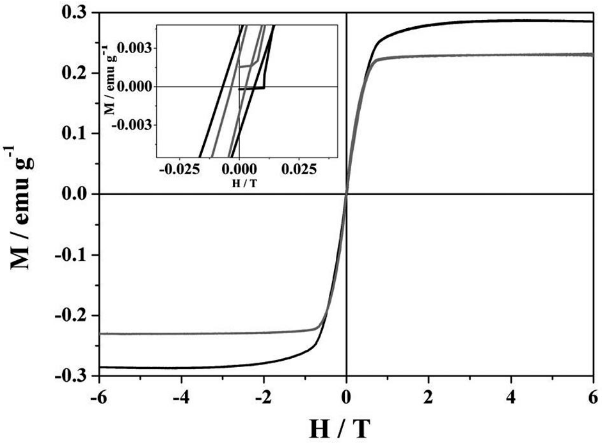


Figure 6. Field-dependent magnetization of silver NRs (black at 2.5 K and gray at room temperature). Inset: Low-field region showing small hysteresis for the NRs (black at 2.5 K and gray at room temperature).

It is a well-known fact that silver is diamagnetic in nature even on the nanometer scale. As reported earlier, magnetic properties occurring in a nonmagnetic element (Ag, Au) that is of nanometer size may arise from two possibilities; either by surface defects from a low coordination number of surface atoms or by the generation of unoccupied density of the d state from strong charge-transfer interactions between surface atoms and the organic capping agent (mainly sulfur-containing).[41,42] But here the NRs are capped with oxygen-containing organic molecules. In order to establish that the magnetic property of this nanostructure is not arising from the inorganic–organic layer as a result of strong charge transfer, we performed magnetic measurements on the NRs after complete removal of the capping agents. The NRs were found to behave similarly to the capped ones. The complete removal of the capping agent was peformed by heating the NRs at 700 °C under N_2 for 3 h at a heating rate of 5 °C min^{-1} (Figure S11 for TGA). This is confirmed by the disappearance of the Ag···O band in the Raman spectra. This observation clearly demonstrates that the magnetic property is not chemically induced but is inherent. As has been studied earlier, almost all nanostructure materials with one, two, or three components have deficiencies on the surfaces.[43] This is from the reduced coordination of the surface atoms of the nanostructure component. In our case, since it is a single component system the reduced coordination of silver at the surface gives rise to unpaired (nonbonding) electrons, which provide ferromagnetic interactions in the Ag nanorod. Recently Luo et al.[44] established, by First-Principle DFT spin-polarized calculation, based on the "superatomic" model, that ferromagnetic interactions are possible in the case of silver or gold nanoclusters.

Conclusions

We have developed a novel method for the synthesis of silver NRs at room temperature in a facile way by using a new reducing agent. Properties of the NRs were found to be quite exciting compared with other silver nanostructures. NRs were found to exhibit a high SERS sensitivity and detection towards thiophenol and Rhodamin 6G adsorbates. A rare ferromagnetic behavior was also observed in these NRs, which arises from the reduced coordination of the surface atom as well as partially filled s orbital. Therefore this environmentally benign method is useful for synthesizing silver NRs for applications in multiple purposes. Considering the application point of view this method would be beneficial for the generation of magnetic silver nanostructures without any instrumental perplexity or toxic chemicals.

Therefore, these magnetic silver NRs with excellent SERS sensitivity may be useful in bio-diagnostics, food and textile application, medical imaging, etc. Currently we are involved in the synthesis of nanostructures with other metals (Au, Pd) with different morphologies using this novel synthetic procedure by optimizing different conditions.

Experimental Section

Materials and Methods: $AgNO_3$, 2,3-dihydroxyfumaric acid, thiophenol (TP), and Rhodamine 6G (R6G) were obtained from Sigma–Aldrich chemicals and used without further purifications. Other reagents and solvents used were of AR grade.

Physical Measurement: For TEM analysis, the precipitate of silver NRs was dispersed on a carbon-coated copper grid. TEM images were recorded with a JEOL JEM 3010 instrument (Japan) operated at an accelerating voltage of 300 kV. Field emission scanning electron microscopic (FESEM) images were obtained by means of FEI (Nova-Nano SEM-600 Netherlands). UV/Vis absorption measurements were performed with a Perkin–Elmer Lambda 900 UV/Vis/NIR spectrometer. Magnetic measurements were carried out using 11.6 mg of the sample with a vibrating sample magnetometer using a physical properties measurement system (PPMS, Quantum Design, USA). IR spectra were recorded with a Bruker IFS 66v/S spectrophotometer with samples prepared using KBr pellets in the region 400–4000 cm^{-1}. X-ray powder diffraction (PXRD) patterns were recorded with a Bruker D8 Discover instrument using Cu-K_{α} radiation. The solid-state NMR spectra were recorded with a Bruker Avance-III spectrometer using a 2.5 mm-triple resonance probe. The pulses and the spectra were calibrated using a commercially available sample of adamantine without further purification. Mass spectra were measured with Bruker Ultraflex II MALDI/TOF spectrometers.

SERS Measurements: For micro Raman experiments,[45] the 632.8-nm laser excitation from a He–Ne laser (Model 25-LHR-151–230, Melles-Griot, USA) was used, which traversed a band pass filter (XL 12–633NB4, Omega Optical Inc., USA) and then launched into an epifluorescent microscope (Nikon 50i, Japan; axial resolution ca. 1 µm). A 50× dry objective (Nikon L Plan, NA 0.45) was used for focusing the laser beam and collecting the scattered light. The microscope was coupled to a spectrometer (IHR320 Triax, Horiba Inc.) attached to a liquid nitrogen cooled CCD detector (Andor, UK) by a 100 µm multi-mode single optical fiber cable. A resolution of 4 cm^{-1} was achieved by a holographic grating (1800 grooves mm^{-1}) in combination with a 500 µm entrance slit. The laser power measured at the sample was 5 mW. The NRs (1 µL) were dropped onto a clean glass slide. Molecules were adsorbed onto the NRs by dropping 1 µL of TP (1 mM) in ethanol followed by drying. Excess unadsorbed molecules were washed off with ethanol. For concentrations of µM and pM, the NRs and the solution were mixed and sonicated for 15 min prior to dropping onto the glass substrate.

Synthesis of the Silver Nanorods: The silver NRs were synthesized by the reduction of silver ions in the aqueous medium by dhfa and the approach is quite straightforward and novel. In a typical synthesis, an aqueous solution (50 mL) of $AgNO_3$ (0.5 mM, 0.085 g) was added dropwise (2 mL minute^{-1}) to an aqueous solution (30 mL) of dhfa (0.25 mM, 0.046 g) under constant stirring in a 250 mL conical flask. The pH of the solution was maintained at 5.0 by adding a KOH solution (1 M). Then the whole reaction mixture was stirred and sonicated for another 2 h. The color of the solution changed to grayish-yellow indicating the formation of silver nanoparticles. A grayish-yellow color suspension was centrifuged and the resultant as-synthesized product was characterized by TEM, UV/Vis spectroscopy, and powder X-ray diffraction studies. The as-synthesized grayish-yellow color product was washed several times with water and methanol to remove the excess capping agent and employed for UV/Vis, SERS, and magnetic property measurements.

Supporting Information (see also the footnote on the first page of this article): Characterization of capping agents, determination of the stoichiometry (potentiometric titration), mass (MALDI) spectra of the solution obtained after the potentiometric titration of $AgNO_3$ and dhfa, IR and Raman spectra of NRs, TEM image of the as-synthesized Ag NRs, solid-state ^{13}C and ^{1}H NMR spectra, solution-phase ^{1}H NMR spectra and UV/Vis spectra of silver NRs, thermogravimetric analysis (TGA) for the as-synthesized silver NRs.

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