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Hyaluronan-Assisted Photoreduction Synthesis of Silver Nanostructures: From Nanoparticle to Nanoplate

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In this work, a new photoreduction method is developed to fabricate different Ag nanostructures by using biopolymer hyaluronan (HA) as a reductant and stabilizing agent. In the experiment, a very interesting phenomenon is discovered that the shape of nanostructrues is highly dependent on the storage time of HA and AgNO₃ solution before their mixing for the photoreduction. With fresh and aged solution, spherical nanoparticle and triangular nanoplate can be simply synthesized in only 15 min, respectively. The nanostructures were characterized by UV−vis, SEM, HR-TEM, and XRD. The formation mechanism of the silver nanoplates from an aged solution is discussed and ascribed to the radicals generated from aged HA and small silver clusters generated from the aged AgNO₃ solution. This work maybe gives a new clue for fast photoreduction synthesis of silver nanoplates. The application of the nanostructures in surface enhanced Raman scattering (SERS) of HA was investigated, showing that the enhancement effect of the Ag nanoplate is much stronger than that of the Ag spherical nanoparticle. The enhancement efficiency is greatly dependent on the shape and the irradiation time. This work renders not only a fast photoreduction simple route for shape-controlling synthesis of Ag nanostructures, but also a facile approach to investigate the Raman spectra of HA by *in situ* generated Ag nanostructures.

Introduction

Metal nanostructured materials have been broadly used in catalysis, photonics, electronics, biosensing, and nanomedicines[1–6] of which silver (Ag) nanostructure provides an ideal system for investigation of their size and shape effects on surface plasmon resonance phenomenon such as surface enhanced Raman scattering (SERS) and its different applications.[7–13] Ag nanostructures are often used as a "template" to fabricate other metal or metal alloy nanostructures through metal replacement reactions.[14–16] Over the past decades, various methods have been used to make Ag nanostructures with different sizes and shapes. The most prevalent approach uses NaBH₄ and citrate as the reductant and protection agent respectively to fabricate Ag sphere nanoparticles in an ice bath. Different Ag nanostructures such as nanocubes, nanorods, nanowires, and nanoplates are also produced by using ethylene glycol as a weaker reducing agent and poly-(vinylpyrrolidone) (PVP) as a capping agent under controlled nucleation and growth conditions.[17,18]

UV initiated photoreduction is a simple and effective method to produce silver and gold nanostructures in the presence of citrate,[19] PVP,[20] poly(acrylic acid) (PAA),[21] and collagen.[22] Since adsorption of chemical species on a metal surface can change the Fermi level of both the metal and the reactant, a photoinduced reaction is developed to convert Ag nanospheres to nanoplates.[23–25] However, the method still needs preparation

SCHEME 1: Chemical Structure of HA

D- Glucuronic acid   N-Acetyl-D-glucosamine

HA
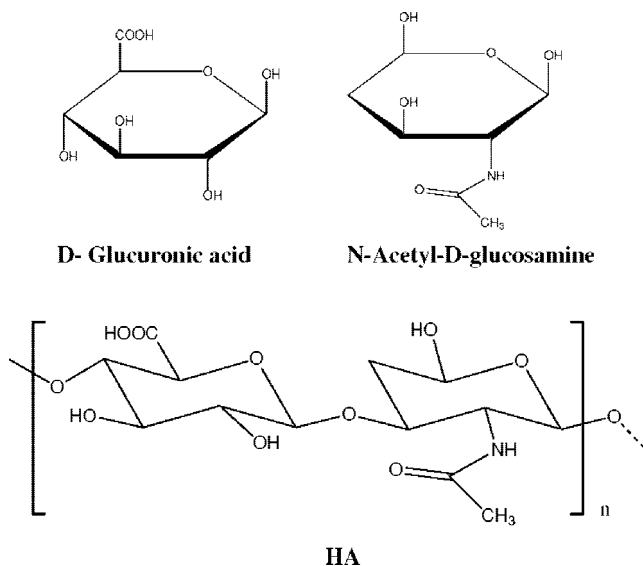
of seeds, in which a strong reducing agent such as NaBH₄, a nongreen chemical to the environment is required. In addition, a number of hours irradiation time is a main drawback for converting silver nanoparticles into nanoplates. There is a great need to explore a green chemistry-based and faster method to synthesize Ag nanostructures for broad applications such as SERS and biosensing.

HA is a natural polydisaccharide with a repeat unit of D-glucuronic acid and *N*-acetylglucosamine (as shown in scheme 1), existing in many connective tissues of mammals such as

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Photoreduction Synthesis of Ag Nanostructures

J. Phys. Chem. C, Vol. 112, No. 29, 2008 **10731**

cartilage, the central component for structuring the tissue,[26] and is a "green" chemical. It is used as a diagnostic indicator for many diseases such as tumor and liver diseases.[27] Thus, it is of great importance to study or detect HA in a biological system. Recently Raman spectroscopy has been employed to investigate the structure of HA;[28,29] however, it has only been used to detect and characterize a bulk HA film. It is known that a Ag nanostructure plays a critical role in SERS[8–10] for sensitive Raman detections. HA has abundant hydroxyl groups in D-Glucuronic acid units as reducing agents.[30–32] In a neutral solution, HA possesses negatively charged carboxyl groups, which can electrostatically interact with Ag^+ to form a complex to photoreduce Ag^{+33} favorably to a Ag nanostructure. In addition, HA can function as a capping agent on a metal surface to protect the newborn Ag nanostructures. HA impregnated in an Ag nanostructure with a fabrication approach is a good probe for SERS study. Thus, as a reductant, catalyst, and stabilizing agent in Ag^+ reduction, HA eventually plays a multifunctional role in fabrication of a Ag nanostructure. In this work, we present this simple and economic method to fabricate different Ag nanostructures, study the mechanism of the Ag nanoplate with aged solutions, characterize the synthesized nanostructures by SEM, HR-TEM, and XRD, and demonstrate the strong impact of the nanostructures on the SERS sensitivity. The work could provide a simple, fast and economic approach to fabricate a unique Ag nanostructure for highly sensitive SERS.

Experimental Section

HA (molecular weight = 30 000 Da) was purchased from Lifecore Biomedical (USA). Silver nitrate ($AgNO_3$) was supplied by Strem Chemicals. Ultra pure water was used to prepare the solutions.

To synthesize the Ag nanostructure, $AgNO_3$ (500 μL, 10 mM), HA (170 μL, 30 mM), and ultrapure water (330 μL) were mixed in a tube for a final concentration of 5 mM $AgNO_3$ + 5 mM HA in repeat units. The solution was then irradiated with UV light (wavelength at 365 nm with a electromagnetic radiation power of 75 mW/cm²) by UV Flood 4.1 system (Epoxy and Equipment Technology Pte Ltd., Singapore) for various exposure times.

The produced Ag colloids were purified by centrifugation for characterizations with scanning electron microscope (SEM) and transmission electron microscopy (TEM). The colloid was first centrifuged at 6000 rpm for 10 min and then the sediment obtained from removal of the supernatant was repeatedly purified three times by resuspending the sediment in water and recentrifuging for sediment by removing the supernatant.

UV–vis absorption spectra were examined by Hitachi U-2800 UV–vis spectrophotometer (Japan). The crystal structure of the product was characterized by X-ray diffraction (XRD, Bruker AXS X-ray diffractmeter). Field-emission SEM (FE-SEM) was performed with JEOL JSM-6700F at an acceleration voltage of 5 kV and a working distance of 8 mm. TEM images were measured by JEM 2100 (JEOL, Japan) with a working voltage at 200 kV. The sample for TEM characterization was prepared by directly dropping 5 μL of the reaction solution onto copper grids followed by a drying step at room temperature overnight.

For Raman investigation, 5 μL of the reaction solution was taken after different irradiation times and dropped onto glass slides followed by drying at room temperature. SERS studies of HA were carried out by an integrated confocal-Raman-microscope, three to one system (CRM 200, WITec, Germany).
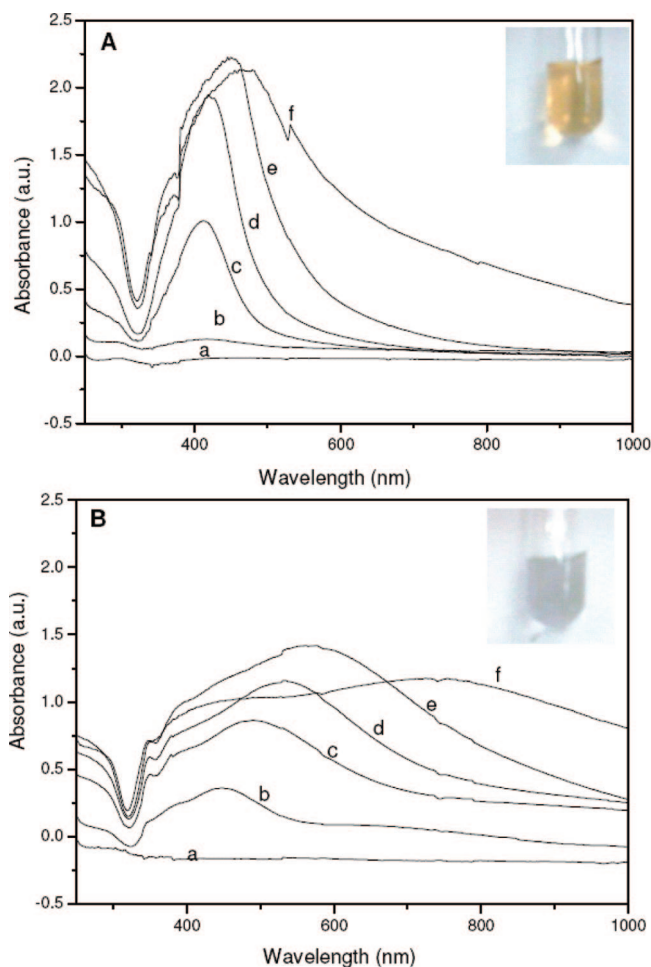

Figure 1. UV–vis spectrum of fresh (A, reaction time is 0, 8, 12, 15, 20, 30 min from a–f) and aged (B, reaction time is 0, 2, 5, 10, 15, 25 min from a–f) solution. Inset is the photo at 15 min reaction. The reaction solution contains 5 mM HA (repeat units) and 5 mM $AgNO_3$.

Results and Discussion

One of the advantages of using UV irradiation to fabricate a Ag nanostructure is to create a nonthermal, uniform reaction environment and to prevent formation of silver-mirror on the sides of the reaction vials or tubes. In our experiments, it was observed that a bright yellow solution was obtained after 15 min of UV irradiation of a freshly prepared precursor solution (as shown in the inset photo of Figure 1A). UV–vis absorption spectrum is a sensitive tool to monitor the formation of silver colloids.[20,22] Figure 1A shows an absorption peak at 409 nm after 8 min irradiation, indicating the presence of spherical Ag nanoparticles. With increased irradiation time, the peak intensity increases rapidly and finally reached a maximum at 20 min with a wavelength red-shifted about 20 nm, showing increase of both particle concentration and size of the nanoparticles in the reaction.[22] However, when the synthesis was carried out using an "aged" precursor solution mixed from silver nitrite solution and HA solution stored at least one month, of which the former was stored in dark, the color of the reacted solution was violet after 15 min of UV irradiation, which was different from that of the freshly prepared one as shown in inset of Figure 1B, indicating that the reaction in the aged solution was much faster than that in the fresh solution. A strong absorption peak at about 480 nm is observed after 2 min irradiation. With increased time, the intensity increases rapidly and reaches a maximum after
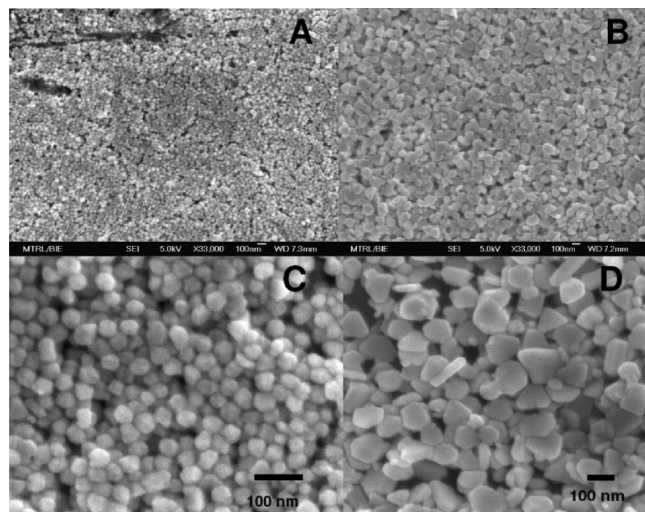
Figure 2. FE-SEM of Ag nanosphere particles obtained from fresh solution (A,C) and nanoplate obtained from aged solution (B,D) after 15 min UV irradiation. Panels A and B are low magnification, and panels C and D are high magnification, respectively. The reaction solution contains 5 mM HA (repeat units) and 5 mM AgNO$_3$.

Figure 3. (A) TEM of silver nanoplates after 15 min reaction time. (B) HRTEM image of silver nanoplate in the [111] orientation. Inside is SAED pattern. The circled spot corresponds to {220} diffraction, and squared spots could be assigned to the (1/3){422} reflection. (C) X-ray diffraction (XRD) of silver nanoplates.

about 15 min irradiation and at the same time the peak position shifts to around 600 nm. This indicates that both the size and morphology of the product obtained from the aged solution are different from that of product obtained from the freshly prepared solution (Figure 1A). For reactions in both aged and fresh precursor solutions, the control experiments conducted in the absence of HA in the reaction solution showed no UV−vis peaks observed after UV irradiation for more than 1 h. This strongly suggests that HA effectively catalyzes the reduction of Ag ions to produce Ag nanoparticles and the rate of reduction is dependent on the length of irradiation time.

The morphology of the product was investigated by FESEM. Figure 2A,C illustrates that a uniform silver nanosphere of about 25 nm forms after 15 min irradiation of the fresh solution. However, the products obtained from the aged precursor solution are triangular or truncated triangular nanoplates with each edge sized around 100 nm (Figure 2B,D). It is worthy to note that the reaction rate and the amount of triangular plates increases with the "age" increase when the solution is less than 1 month old (data not shown). Only after one month old at least, the main products turns to triangular nanoplates. The morphology difference is well in agreement with the UV−vis adsorption spectra presented above.[23,34] The mechanism for the formations of nanosphere and nanoplates from fresh and aged solution is not fully understood yet and is still under investigation in our laboratory. However, according to Xia's[17,18] and Maillard's[24] interpretations for shape controlled synthesis of Ag nanostructures, it is possible that during the photoreduction a freshly prepared precursor solution forms Ag seeds for nucleation in a homogeneous environment, in which HA uniformly covers the seeds surface, leading to formation of a spheric structure. In an aged solution, small Ag cluster could form to have anisotropic properties, while aged HA would produce radicals because of dissolved oxygen and hydrolysis of HA.[26] The radicals could anisotropically accelerate the photoreduction rate in the different crystal face of the small silver clustered seeds.[23,25]

High resolution TEM (HR-TEM) and electron diffraction (SAED) analysis of a single Ag nanoplate was conducted. Figure 3A shows that most of the products are triangular-shaped nanoplates. Figure 3B illustrates a high-resolution TEM image of [111] orientated nanoplate with a lattice spacing of 2.5 Å,
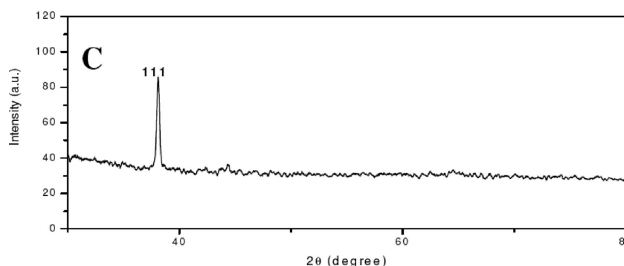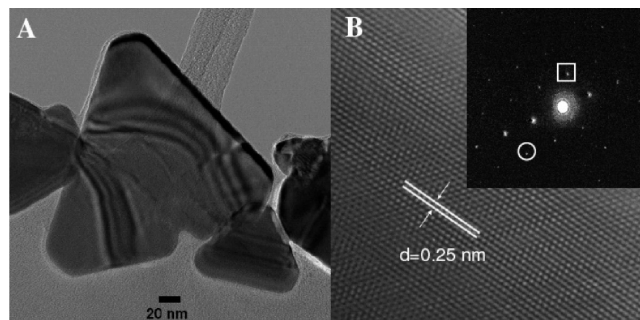
which can be ascribed to the (1/3) reflection that is generally forbidden for an fcc lattice.[35] The inset of Figure 3B shows typical region selected from the SAED pattern recorded by directing the electron beam perpendicular to the flat faces of a single nanoplate. The 6-fold rotational symmetry displayer by the diffraction spots implies that the nanoplate faces are presented by {111} planes. The circled and the boxed spots are indexed as {220} and formally forbidden (1/3){422} Bragg reflection, which is in agreement with HR-TEM image in Figure 3B and with the reported geometrical model of Ag nanoplates.[34,35] According to the growth rule of crystal faces described by Gilman et al., to reach thermodynamically steady state, only the crystal faces with low free energies can be exposed in large proportions, such as the {111} crystal face.[36] This is also confirmed by the results of X-ray diffraction (XRD) conducted by us. As shown in Figure 3C, the overwhelmingly intense diffraction peak is located at $2\theta = 38.34$, which is from the (111) lattice plane of fcc silver.

Photoirradiation time is a critical factor in the formation of Ag nanostructure. During the formation of both nanosphere and nanoplate structures, the clear reaction solutions became opaque after 20 min irradiation and sediment was observed after 30 min. This phenomenon is consistent with the observation from UV−vis spectra in Figure 1, in which the surface Plasmon resonance peak of Ag nanostructures reaches a maximum value at 20 min and then decreases sharply afterward. The decrease of the UV intensity after 20 min irradiation indicates that nanoparticles and nanoplates are precipitated from the solution. This could be expressed as the following equation: in which

$$2Ag^+ + \left(\!CHOHCHOH\!\right) \xrightarrow{h\nu} 2Ag + 2\ \underset{H}{\overset{}{\underset{|}{C}}}\!=\!O + 2H^+ \quad (1)$$
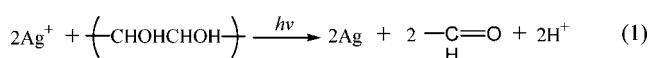
Ag$^+$ ions are reduced to Ag atoms by the hydroxyl groups of HA under UV irradiation and two protons are generated as byproduct. Therefore, the pH of the solution can decrease as
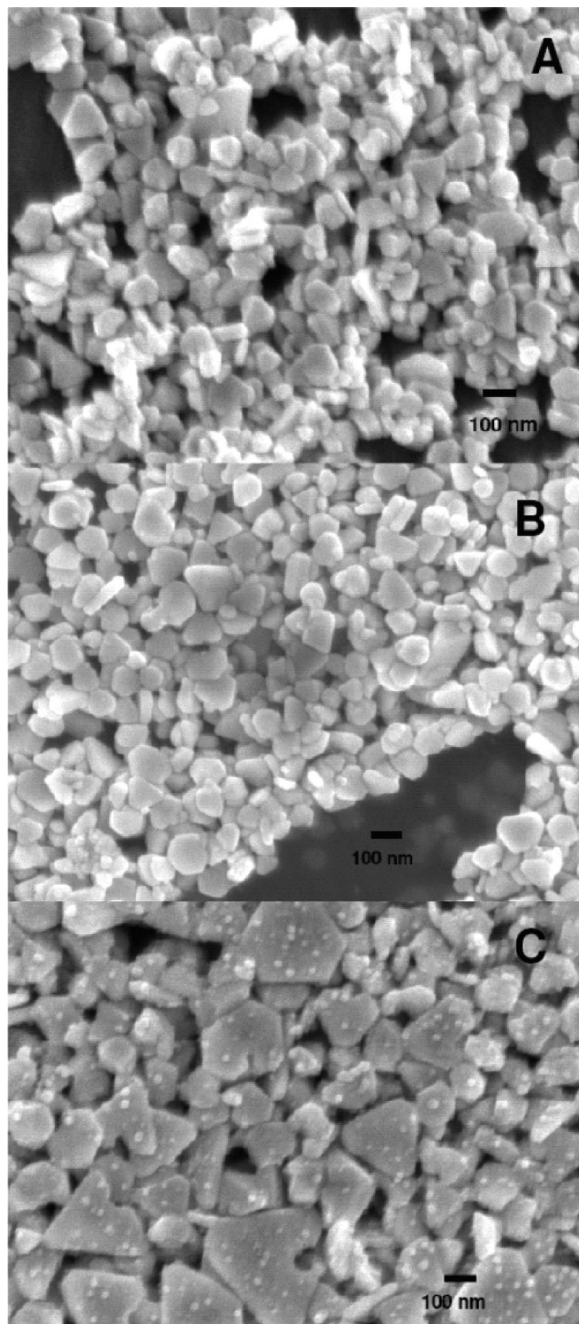
Photoreduction Synthesis of Ag Nanostructures

J. Phys. Chem. C, Vol. 112, No. 29, 2008 **10733**

Figure 4. FE-SEM of nanoplates with irradiation time of 5 (A), 15 (B), and 25 min(C). The reaction condition is same as Figure 1B.

Figure 5. SERS of HA enhanced by nanoparticle (A) and nanoplate (B) with different irradiation time. The reaction condition is same as Figure 1.

the reaction proceeds. This in turn would inhibit the hydrolysis of the carboxylic groups of HA. HA could lose its negative charge that is essential for stabilizing the Ag nanostructures. To prove this hypothesis, the pH value was monitored during the reaction, and was observed it decreased from about 7.0 to 3.0 after 30 min UV irradiation. This strongly supports the hypothesis.

The morphology change of the nanoplates with different irradiation times is clearly shown by FE-SEM images in Figure 4. With 5 min irradiation, the product is a mixture of nanoplates (the size smaller than 100 nm) and anisotropic nanoparticles (size about 30 nm) (Figure 4A). However, after 15 min irradiation more nanoplates are formed and most of them are larger than 100 nm with better size distribution (Figure 4B). With 30 min irradiation, their size is larger than that with 15 min irradiation, of which some reach about 400 nm in the edge
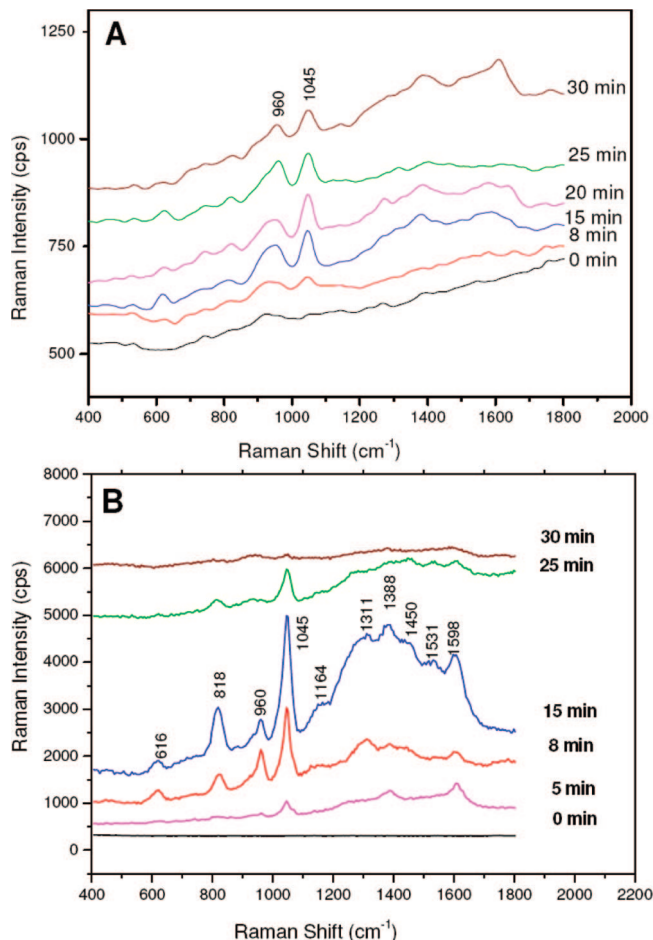
length of the triangles (Figure 4C). At the same time, lots of small nanoparticles (smaller than 20 nm) adhered on the large nanoplates and defects are observed at the edge of the nanoplates (Figure 4C). These defects could be ascribed to an etching process from HNO_3 generated during the reaction. It is likely that both photoreduction and etching reaction occur simultaneously, producing both large nanoplates and small particles.

Five microliters of reaction mixture was dropped onto glass slides during the photoreduction process to examine the Raman spectrum of HA contained in silver nanoparticles and nanoplates and are shown in Figure 5 panels A and B, respectively. It is can be seen that without the nanostructure formation, no detectable spectrum of HA could be observed using the same amount of HA solution. For both nanoparticles and nanoplates, the enhancement of Raman scattering effect is greatly dependent on the irradiation time, in which the maximum peak intensity of HA is reached with 15 min photoreduction while little or no peak was observed with irradiation more than 30 min. This may be due to the better uniform size distribution and good stability of Ag-HA particles formed with 15 min photoreduction and the particles aggregation and precipitation from drop of pH after longer reaction time. The spherical nanoparticle displays two obvious peaks at 960 and 1045 cm^{-1} (Figure 5A) while the nanoplate has 10 peaks, which is very similar with that of bulk HA reported in literature.[28,29] Table 1 summarizes the SERS bands of HA in Ag nanoplates. The SERS intensity of peak at 1045 cm^{-1}, corresponding to C−C and C−O stretching mode, is about 40-times stronger than that from the spherical Ag

TABLE 1: Assignment of Raman Bands for HA Obtained Using Ag Nanoplate at 15 Min Irradiation Time

peak position (cm^{-1})	assignment
616	
818	Skeletal vibrations associated with the β linkages
960	Skeletal vibrations associated with the β linkages
1045	C−C and C−O stretching
1164	
1311	Amid III
1388	C−H bend
1450	Symmetric stretch of the COO$^-$ group
1531	
1598	Amide I

nanoparticle (Figure 5B). Apparently, the Ag nanoplate structure has much stronger surface enhancement of Raman scattering than the Ag nanoparticle. This can be ascribed to the localized surface plasmon resonance adsorption of nanoplates in near-infrared region.[37,38] The decrease of solution pH with time and extent of Ag$^+$ photoreduction plays a key role in formation of the metallic Ag nanoplates and further studies of SERS of polymers. This discovery provides a new approach to control the shape of silver nanostructures during synthesis for SERS and may be useful for further investigation of the mechanism of surface enhancement of the Raman scattering.

Conclusion

In an *in situ* photoreduction of Ag$^+$, HA is discovered to function as reductant, catalyst, and stabilizing agent to produce Ag nanostructures. Different nanostructures, and spherical nanoparticle and triangle nanoplate are fabricated by simply using fresh and aged HA and AgNO$_3$ for reactants, solution, respectively. This phenomenon renders a new, simple, and economic strategy for shape-controlling photoreduction synthesis of a metal nanostructure. The formation mechanism of the silver nanoplate structure is ascribed to the radicals generated from the aged HA and small silver clusters generated from the aged AgNO$_3$ solution. The fabricated Ag nanostructures are well characterized by UV−vis, SEM, HR-TEM, and XRD and demonstrate that 25 nm silver nanosphere and 100 nm nanoplate obtained with 15 min irradiation have the best size distribution and excellent stability. Both Ag nanoparticle and nanoplate were used to characterize HA by SERS, showing that enhancement efficiency of the Raman scattering is dependent on the shape of the nanostructure and irradiation time of the synthesis. The *in situ* generated Ag nanostructures may also have potential applications in investigating HA biopolymer with highly sensitive SERS.

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