Materials Letters ∎ (∎∎∎∎) ∎∎∎–∎∎∎

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/matlet

Raman spectroscopy study of the effect of urea, uric acid and creatinine on steric configuration of bovine hemoglobin using SERS-active BN nanosheets/Ag nanoparticles hybrids

Q1 Shanshan Yang, Zhaochun Zhang*, Jun Zhao, Zhenwei Yu, Huiyi Jiang

School of Material Science and Engineering, Shanghai University, Shanghai 200444, China

ARTICLE INFO

Article history:
Received 5 January 2014
Accepted 17 May 2014

Keywords:
Bovine hemoglobin
Boron nitride
Nanoparticles
Raman
Biomedical

ABSTRACT

Herein surface-enhanced Raman scattering active boron nitride nanosheets/Ag nanoparticles hybrids (BN/AgNPs) has been synthesized by a wet chemistry procedure to study the effect of urea, uric acid and creatinine on steric configuration of bovine hemoglobin. XRD analysis indicates that BN/AgNPs hybrids have been successfully prepared. TEM analysis shows that as-prepared BN/AgNPs hybrids are layer-structure and the AgNPs are randomly distributed on the layered BN. Raman study shows that urea, uric acid and creatinine can destroy the steric configuration of bovine hemoglobin to some extent. The research results could be useful for biomedical application and may open an avenue to the exploration of factors affecting the demic protein structure.

1. Introduction

Surface-enhanced Raman scattering (SERS) has been proposed for various ultrasensitive chemical and biological sensing applications, such as the detection of organic (azaindole [1], 4-aminobenzenethiol [2]) and biological molecules (DNA/RNA, vesicles, proteins, pathogens and so on) [3,4]. It is now generally accepted that SERS mainly occurs as a combination of the two effects: the electromagnetic (EM) model associated with large local fields caused by surface plasmon resonance (SPR) of the noble metal nanoparticles (NPs) and charge transfer (CT) model between metal and adsorbate [5,6]. Recently, the SERS active substrates are focusing on the nanosheets/NPs, such as graphene/AgNPs [7], graphene/AuNPs [8], MoS_2/AgNPs [9] etc., which sometimes offer synergistic effects to the intrinsic properties of the NPs, making the composites much more attractive in applications of SERS in various materials than the NPs alone.

As a graphene analog, boron nitride (BN) nanosheet exhibits the unique physical, optical and electrical properties correlated with its 2D ultrathin atomic layer structure, which has distinct similarities compared to graphene and can be applied as a promising supporting material to stabilize metal NPs. In our previous study [10], the BN/AgNPs hybrids have higher SERS activity than graphene/AgNPs, making it more attractive to be used in biomedicine fields.

It is well known that there are many factors affecting the steric configuration of protein: temperature, ultraviolet light, organic solvent and diseases. Among them diseases seem to be rarely researched for the effect of urea, uric acid and creatinine on proteins. One of diseases may be the renal damage which could cause the increase of concentration of urea, uric acid and creatinine [11–13]. Hence, in this study, we first attempted to prepare SERS-active BN/AgNPs hybrids and adsorb the bovine hemoglobin (BHb) on BN/AgNPs hybrids by biological coupling and then studied the effect of higher concentration of urea, uric acid and creatinine on BHb.

2. Experimental Q2

Fabrication of BN/AgNPs: BN nanosheets were prepared from BN powder via liquid-phase exfoliation method in isopropanol solution. The BN/AgNPs hybrids were synthesized according to the chemical reducing procedure using $N_2H_4 \cdot H_2O$ and $AgNO_3$ solution. The specific process can be found in our previous experiment [10].

Fabrication of BN/AgNPs/BHb: The adsorption of BHb on BN/AgNPs hybrids was based on a biological coupling method. The buffered solution contained 25 mM trisaminomethane (Tris) and 75 mM NaCl. 1.25 g BN/AgNPs hybrids were diluted in 100 ml of buffered solution (marked as A). The solution B contained 750 mg BHb diluted in 10 ml of buffered solution while solution C contained 80.25 mM urea, 1.15 mM uric acid and 1.40 mM creatinine diluted in buffered solution. The normal BN/AgNPs/BHb was obtained by mixing A, B and buffered solution (the volume ratio of

* Corresponding author. Tel.: +86 21 56334810; fax: +86 21 56336270.
E-mail address: zhangzhaochun@shu.edu.cn (Z. Zhang).

http://dx.doi.org/10.1016/j.matlet.2014.05.120
0167-577X/

A, B and buffered solution is 2:2:1) while the contrast BN/AgNPs/BHb was obtained by mixing A, B and C (the volume ratio of A, B and C is 2:2:1).

Characterization: Morphological characterizations were performed by transmission electron microscopy (TEM, JEM-2010) and selected area electron diffraction (SAED) operated at 200 kV acceleration voltage. X-ray diffraction (XRD) date was collected on Rigaku D/max-rC using Cu Ka radiation (λ=1.5418 Å). The Raman spectrum and SERS spectra were obtained by using Renishaw inVia plus spectrometer equipped with an Ar^+ ion laser.

3. Results and discussion

The preparation process of BN/AgNPs and BN/AgNPs/BHb was interpreted in Fig. 1a and the XRD analysis was in Fig. 1b. The XRD pattern indicates that BN/AgNPs hybrids have the distinct characteristic peaks in 2θ regions of 38.2°, 44.3°, 64.5°, 77.5° and 81.8°, which are assigned to the (1 1 1), (2 0 0), (2 2 0), (3 1 1) and (2 2 2) crystallographic planes of face-centered cubic (fcc) AgNPs [JCPDS No. 04-0783]. Evidence of BN was shown by the obvious peak corresponding to the (003) diffractions of BN in XRD pattern, which confirmed the successful fabrication of the BN/AgNPs hybrids.

Fig. 2a shows the TEM images of two-dimensional sheet-like structure of BN nanosheets decorated by AgNPs, indicating that AgNPs are uniformly covered on the BN nanosheets and statistic data for the size of AgNPs which is about 50–100 nm. Nevertheless, the AgNPs agglomerate severely to form particles few hundred nanometers in size. The corresponding SAED pattern image of the AgNPs states clearly that AgNPs are single crystal. The interactions between the BN nanosheets and AgNPs are so strong that they cannot be destroyed even after a long time of sonication during the preparation of TEM specimen. Parallel fringes with the space of 0.234 (d_1) and 0.203 (d_2) nm (Fig. 2b) are consistent with the space of (1 1 1) and (2 0 0) lattice planes of fcc Ag.

To obviously evaluate the effect of urea, uric acid and creatinine on the steric configuration of bovine hemoglobin, we selected high SERS activity of the as-prepared BN/AgNPs substrate, which can dramatically increase the scattering signals of bovine hemoglobin molecule adsorbed on the NPs surfaces. It has been demonstrated that BN nanosheets combined with AgNPs have a strong Raman enhancing effect via EM field enhancement of the AgNPs associated with large local fields caused by SPR and CT between the energy levels of the molecule and Fermi levels of the AgNPs. Coupled surface plasmon is localized in the nanoscale junctions and interstices between AgNPs which play main role of EM hot spots, leading to the strong Raman enhanced signals [9]. When bovine hemoglobin molecule is absorbed on the AgNPs, SERS enhance the molecular Raman signal by many orders of magnitude owing to noteworthy increase in the scatting cross-section [14]. In addition, The CT from AgNPs to BN nanosheets would augment the CT from bovine hemoglobin molecule to AgNPs, which augment the chemical enhancement of SERS on BN/AgNPs [9].

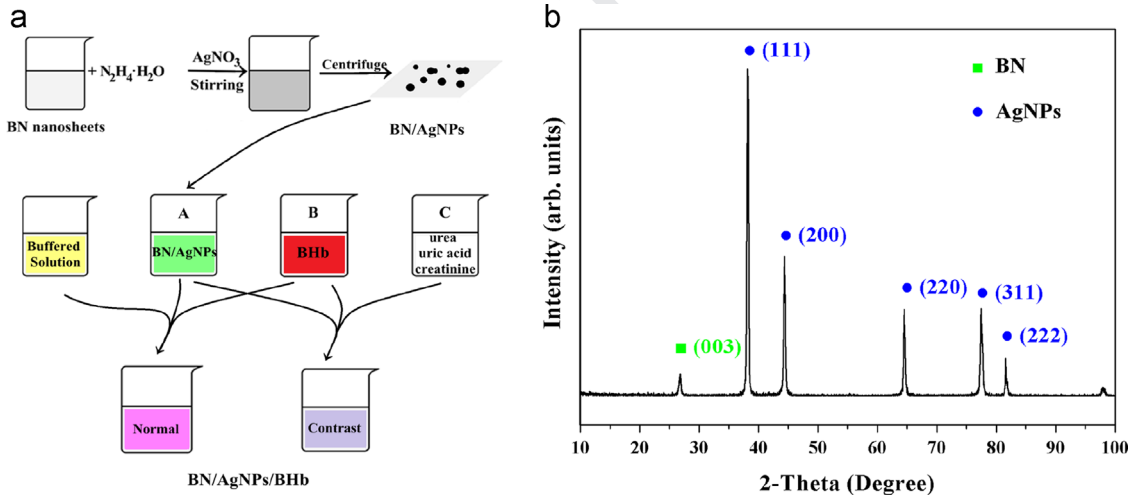

Fig. 1. (a) Schematic illustration of the preparation process; (b) XRD pattern of BN/AgNPs hybrids.

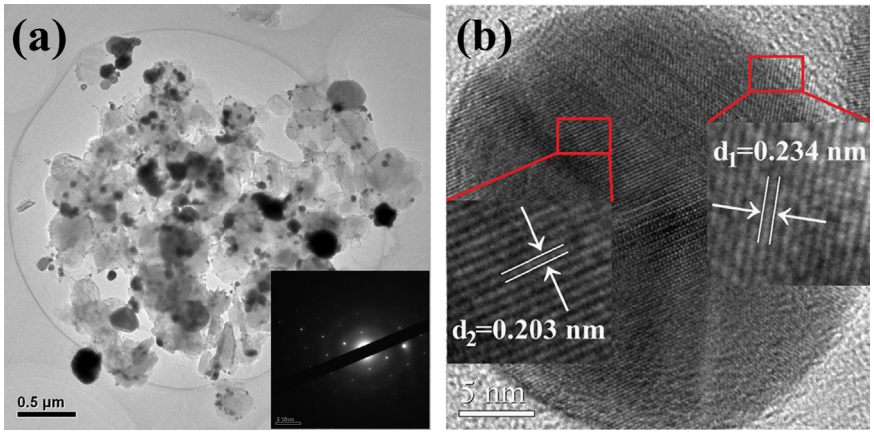

Fig. 2. (a) TEM images of BN/AgNPs hybrid; (b) HRTEM image of the AgNPs with enlarge images of fringe spacing.

Please cite this article as: Yang S, et al. Raman spectroscopy study of the effect of urea, uric acid and creatinine on steric configuration of bovine hemoglobin using.... Mater Lett (2014), http://dx.doi.org/10.1016/j.matlet.2014.05.120