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ARTICLE TYPE

Colorimetric Detection of Ag ion with Graphene Oxide in Dimethylformamide

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We report on the selective and sensitive colorimetric detection of Ag⁺ in Dimethylformamide (DMF) solution in the presence of graphene oxide based on the surface plasmon resonance absorption of Ag nanoparticles (NPs).

Recently, graphene oxide (GO), a 2-D sp²-bonded structure bearing oxygen functional groups, has been received much attention due to its possible application in flexible electronics including dielectrics,¹ optoelectronics,² flexible transparent electrodes,³ memories,⁴ and chemical sensing.⁵ Compared to graphene, however, the electrical properties of GO are somewhat reduced because of damage in the graphene lattice or the creation of point defects.⁶ To improve the electrical conductivity of GO, several attempts have been made to fabricate polymer-GO composites,^{7, 8} and a metal-GO nano-composites.⁶ For example, several groups reported on the use of GO or reduced graphene oxide (r-GO) as a template to synthesize metal NPs and metal NPs-GO composites.⁹⁻¹³ Zhou *et al.* reported the synthesis of Ag particles on GO and reduced-GO surface without any surfactant or reducing agent.¹¹ In addition, tunable oxygenous functional groups and a high solubility make graphene oxide a promising material for chemical sensing.¹⁴⁻¹⁶

The development of a quantification methods for Ag⁺ has been received much attention because silver ion can inactivate sulfhydryl enzymes, which leads to toxicity by bioaccumulation. The quantification of Ag⁺ is possible by using conventional analytical techniques including atomic absorption spectroscopy and inductively coupled plasma mass spectrometry. However, these methods require the complicated instrumentation and cannot offer the real time detection in environment. On the contrary, colorimetric measurement is a simple but powerful method to determine the concentration in environment.

Recently, the design and development of sensitive molecular sensors for Ag⁺ has been of considerable interest because of its possible application in real time monitoring in environments and medical diagnosis. However, most of the research efforts have been placed on developing molecular probes¹⁷⁻¹⁹ and oligonucleotides^{20, 21} with a specific Ag⁺ binding site via complicated synthesis procedures. Wen *et al.* demonstrated the selective fluorescent detection of Ag ion based on silver specific cytosine rich oligonucleotide and interaction between oligonucleotide and GO.⁵

Previously, Liz-Marzán *et al.* reported the formation of Ag NPs

without any surfactant using DMF as a reducing agent, which results in the colour changes from colourless to yellow.²²⁻²⁴ However, the disadvantage is that the size of Ag particle is ranging from a few tens of nanometers to 1 μm. It is difficult to apply their observation in quantification of Ag ion because of the nature of aggregation of synthesized Ag NPs in the absence of capping materials.

In the present paper, we report on the selective and sensitive colorimetric detection of Ag⁺ based on the formation of Ag NPs on GO surface using DMF as a solvent and reducing agent at room temperature. The facile detection of Ag⁺ was achieved based on the surface plasmon resonance absorption of Ag NPs. We found that the presence of GO facilitated the formation of Ag NPs without any aggregation of formed Ag NPs even in the absence of any surfactant. We also determined the activation energy for the formation of Ag NPs on GO in DMF.

GO was prepared by oxidizing natural graphite powder according to the method developed by modified Hummers' method.²⁵ In a typical experiment, the quantification of Ag ion were carried out in a DMF solution via reduction of Ag⁺ in the presence of GO at room temperature. Upon the reduction of Ag⁺ by DMF, the colour of the solution changed from colourless to yellow, indicating the formation of Ag NPs with distinct surface plasmon bands at 420 nm. Liz-Marzán *et al.* proposed the following mechanism to explain the role of DMF as a reducing agent in the synthesis of Ag NPs at room temperature.

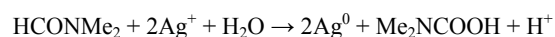


Figure 1 shows the absorption spectra of the DMF solution in the absence (dashed line) and in the presence (solid line) of GO upon addition of the Ag ion. For comparison, the absorption spectrum of the GO in DMF is also included. In the absence of GO, the absorption spectra gradually changed from yellow to black, implying the aggregation of formed Ag NPs. On the other hand, in the presence of GO, the reaction reached equilibrium condition within 1 hr at room temperature. The results indicated that silver NPs were deposited on GO sheets by chemical reduction of silver ions using DMF on GO at room temperature.

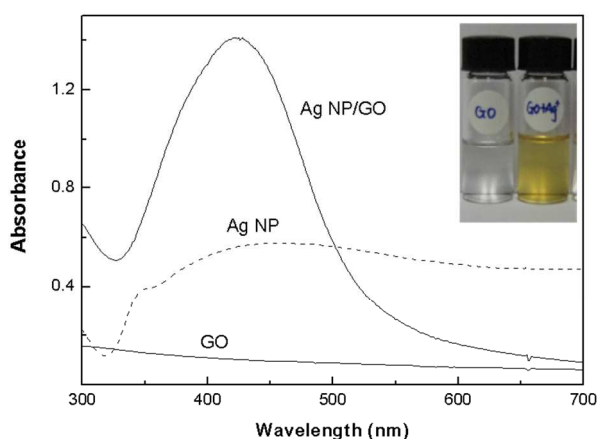


Figure 1. Absorption spectra of prepared Ag NPs in the absence (dashed line) and in the presence (solid line) of GO in DMF. The inset shows the photographs exhibiting the color changes upon addition of Ag ion.

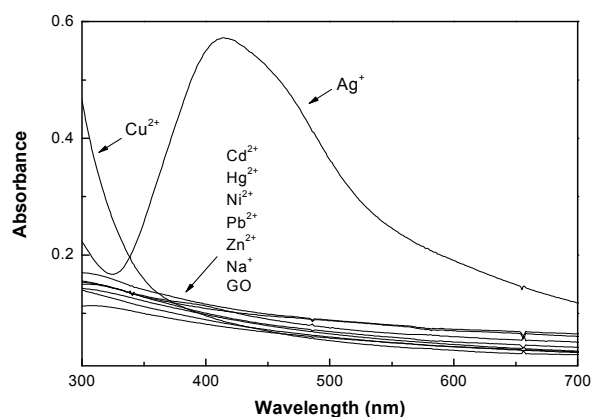


Figure 2. The Absorption spectra of GO in DMF solution in the presence of various metal ions.

We investigated absorbance changes to evaluate the selectivity property of GO in DMF toward Ag ion over other metal ions. Figure 2(A) shows the absorption spectra of GO in DMF solution upon the addition of various metal ions, including Ag⁺, Cd²⁺, Cu²⁺, Hg²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Na⁺ and K⁺. Absorption spectra were measured 30 min after addition of metal ions. Upon the addition of the tested metal ions, only Ag⁺ led to colour change from colourless to yellow due to the chemical reduction of silver ions by DMF on GO at room temperature. On the other hand, no significant absorption spectrum band was observed for the other metal ions including Cd²⁺, Cu²⁺, Hg²⁺, Ni²⁺, Pb²⁺, Zn²⁺, Na⁺ and K⁺. The detection limit was determined to be 65 ppm at room temperature. The results imply that GO in DMF has great sensitivity and selectivity for Ag⁺, indicating a potential use for Ag⁺ ion sensors.

To elucidate the role of GO on the formation of Ag NPs, the reduction properties of Ag ion in the presence of GO toward various solvents (Acetone, Toluene, CH₂Cl₂, CH₃CN, Ethanol, water, CHCl₃, THF, DMF) were investigated by UV/Vis absorption spectroscopy. Figure 3 represents the absorbance changes of Ag⁺ in various solvents of interest in the presence of

GO. For comparison, the absorbance of GO only in DMF was also included. When Ag⁺ was introduced to a DMF, significant absorbance enhancement was observed, a result of the formation of Ag NPs. On the other hand, little absorbance changes were observed for other solvents in the presence of GO. Although Pasricha *et al.* reported that hydroxyl group on GO played an important role in the reduction of Ag ion in alkaline condition,¹⁰ we could not observe any Ag NPs formation for other solvents even in the presence of GO. These results indicate that DMF plays more important role than GO in the reduction reaction of Ag ion.

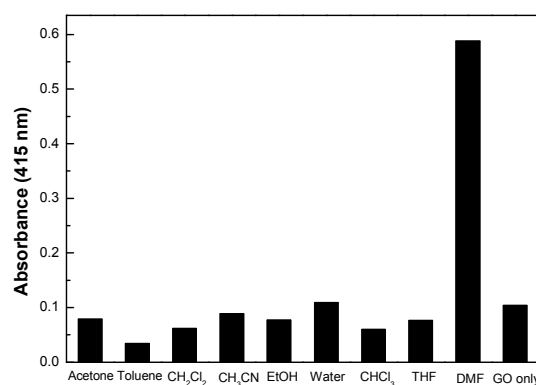


Figure 3. The absorbance changes of Ag ion in the presence of GO in various solvents.

Figure 4(A) shows the SEM images of the as-synthesized Ag NPs in the absence of GO, indicating the aggregation of formed Ag NPs. The result in the absence of GO is similar to the previously reported result by Liz-Marzán *et al.*,²²⁻²⁴ where the sizes of the Ag NPs ranged from a few tens of nanometers to 1 μm. On the other hand, the TEM images (Fig 4(B)) of as-synthesized Ag NPs on GO demonstrates the formation of Ag NPs with an average diameter of approximately 7 nm. The Ag NPs are well-dispersed on the GO surface without aggregation, indicating the GO plays an important role in prohibiting the aggregation of NPs.

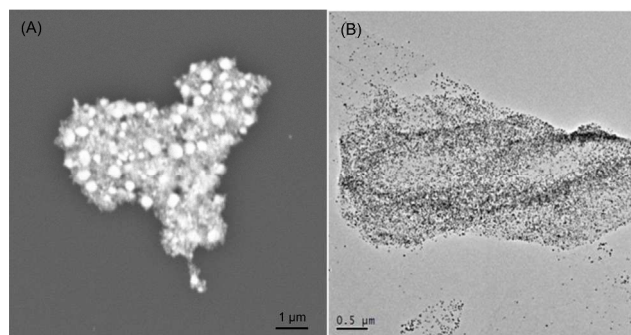


Figure 4. SEM images of the synthesized Ag NPs in the absence of GO (A) and TEM images of the synthesized GO-NPs (B).

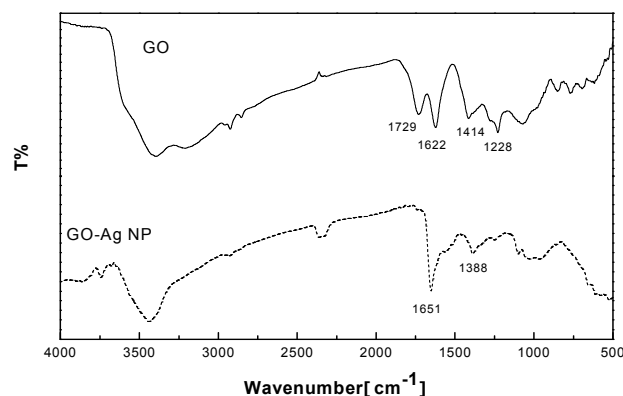


Figure 5. FT-IR spectra of GO (solid line) and GO-Ag NP (dashed line).

We also monitored the IR absorption spectra changes to clarify the adsorption mechanism of Ag NPs on GO surface. Figure 5 shows the IR spectra of GO and Ag-GO nano-composites. The most characteristic features in the FT-IR spectrum of GO are the absorption bands corresponding to the C=O stretching at 1729 cm^{-1} , the O-H deformation vibration at 1414 cm^{-1} , the C-OH stretching at 1228 cm^{-1} , O-H stretching at 3400 cm^{-1} , and the C-O stretching at 1069 cm^{-1} .²⁶ Upon treatment with Ag^+ , the C=O stretching vibration at 1729 cm^{-1} almost disappeared, whereas the O-H stretching at 3400 cm^{-1} did not significantly change. In addition, new peak at 1651 cm^{-1} attributing to the carbonyl stretching from the semiquinone moiety appeared.¹⁰ Oxygen functional groups are responsible for the initial attachment of the free Ag^+ in a solution by electrostatic interactions. The shift of carbonyl peak from 1729 cm^{-1} to 1651 cm^{-1} strongly indicates that the carbonyl groups importantly involve in the coordination with the Ag NPs. In addition, the interaction between Ag particles and oxygen-groups on GO sheets plays a significant role in the growth of silver NPs,^{27, 28} which prevents the aggregation of NPs to form larger particles.

To explore the effect of temperature on the formation rate of Ag NPs, we measured the absorbance as a function of time at different temperatures. Figure 6 illustrates the kinetic plot for the formation of Ag NPs in a DMF solution as a function of reaction temperature in the presence of GO in a DMF solution. The inset plot shows the activation energy for the formation of Ag NPs in DMF from the temperature-dependent kinetic measurements. The activation energy E_a for the formation of Ag NPs was estimated to be 33.5 kJ/mol in DMF using the expression $\ln k = \ln A - E_a/RT$. Since the GO was involved in the formation of Ag NPs, GO prohibited the aggregation between NPs. Presenting method takes advantage of the deposition of Ag NPs on GO surface and controls the size distribution of the NPs.

A colorimetric sensor for Ag^+ at sub ppm levels was developed based on the reduction reaction in DMF solution in the presence of GO at room temperature. The detection mechanism involved the reduction of Ag^+ by DMF in the presence of GO. GO is responsible for the initial attachment of the free Ag^+ ions and prevents the aggregation of NPs. We found that the activation energy for the formation of Ag NPs was determined to be 33.5 kJ/mol in DMF.

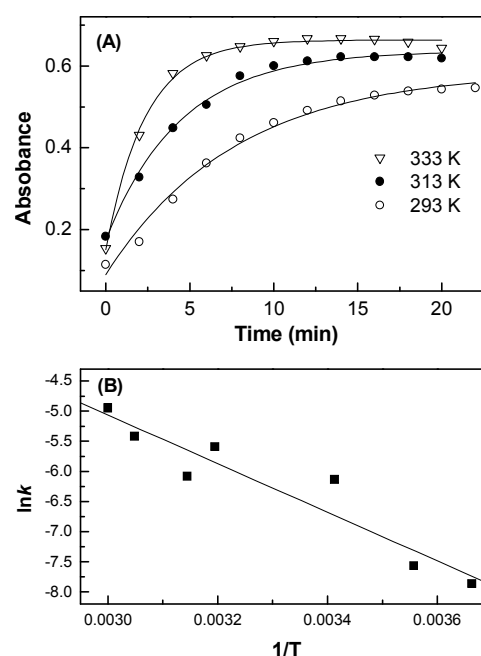


Figure 6. Kinetic plot for the formation of Ag nanoparticles in DMF solution as a function of reaction temperature in the presence of GO (A) and Arrhenius plot for the formation of Ag NPs (B).

Experimental Section

Chemicals. DMF (Fisher) were used as purchased without further purification. Natural graphite powder (325 mesh, Alfa Aesar)

Synthesis GO was prepared by oxidizing natural graphite powder according to the method developed by modified Hummers' method.²⁵ Briefly, Graphite (10 mg) was sonicated 3 hours in 10 mL DMF to give GO. Washed with DMF and hexane three times and dried under vacuum 50–60 $^{\circ}\text{C}$.

Characterization. FT-IR experiments were conducted on a JASCO FT/IR-4200 spectrometer. TGA data were collected with TGA Q5000 IR. UV-Vis absorption spectra were recorded on a Shimadzu UV-3100. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-2100F.

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Abstract

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