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Near infrared surface plasmon resonance of gold tabular nanostructures in the $HAuCl_4-Na_2S$ reaction

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The $HAuCl_4-Na_2S$ reaction is a common reaction for gold nanoshells and nanoparticles.[1–5] The typical reaction started when 2 mM bright yellow $HAuCl_4$ solution was mixed into 1 mM transparent Na_2S solution with a volume ratio of 1:2 while stirring, and the mixed solution turned to colloidal dark brown. There are certainly several alternative reaction pathways besides this one. Solid Au, S, and Au_2S nanoparticles and Au_2S/Au nanoshells formed when $HAuCl_4$ was mixed with Na_2S in the solution. The origin of the near infrared adsorption peak for this reaction is controversial. Some explanations claimed that this peak is due to the surface plasmon resonance of Au_2S/Au nanoshells,[1,2] while others insisted that gold nanoparticle aggregates should be responsible for the peak.[6,7] Our experiments show that the gold tabular nanostructures formed in the $HAuCl_4-Na_2S$ reaction can also be the origin.

Normally, the Na_2S solution is used one or two days after it was made to increase the HS^- activity. In our experi-

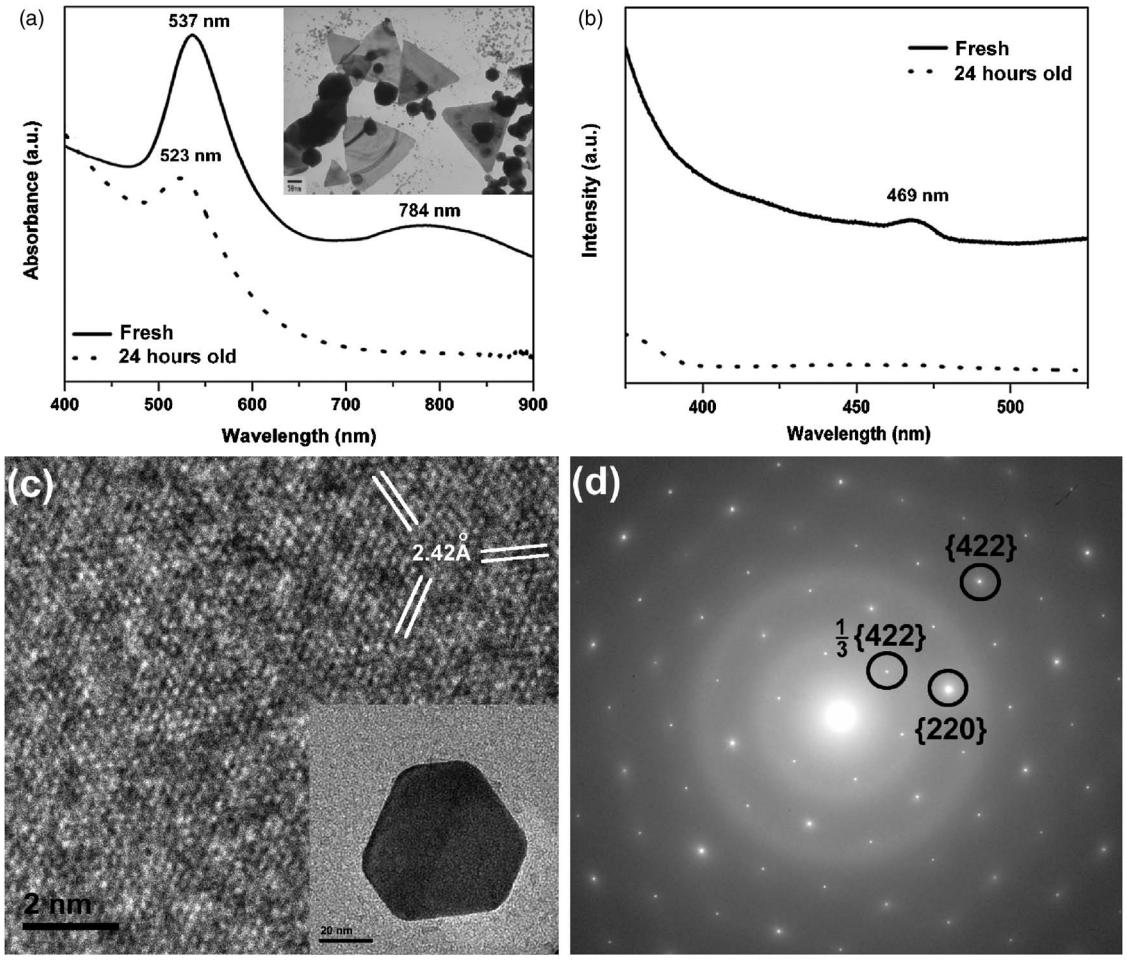

FIG. 1. (a) is the absorbtion spectrum and (b) is the the photoluminescence spectrum (exciting at 330 nm) of the final solutions for fresh and 24 h old Na_2S. The inset of (a) is TEM images of gold tabular nanoparticles with a 50 nm scale bar. (c) is the HRTEM image and (d) is the electron diffraction pattern of a hexagonal gold tabular nanoparticle shown by the inset of (c). The scale bar in (c) is 2 nm and in the inset is 20 nm.

ments, by using the fresh Na_2S solution for the typical reaction listed above, we got an unexpected product, gold tabular nanostructures. As shown in the inset of Fig. 1(a), those nanostructures are typically in the size of hundreds of nanometers and are in the shape of triangle or hexagon. The absorption spectrum of the final solution is shown in Fig. 1(a). The peak at 537 nm is due to the surface plasmon resonance (SPR) of spherical gold nanoparticles. According to the previous results of similar gold and silver tabular nanostructures,[8–13] we believe that the SPR of gold tabular nanostructures caused the near infrared peak at 784 nm. Based on comparisons of the adsorption peak position (λ) with the axial (A) ratios between the horizontal axis and the vertical axis, obtained form analysis of transmission electron microscopy (TEM) data, Kirkland *et al.* provided a relationship between the peak position and the axial ratio of gold tabular nanostructures as shown in the following formula:[8]

$$\lambda(\mathrm{nm}) = 487.29 + 36.413A. \quad (1)$$

The axial ratio of gold tabular nanostructures obtained from the above equation is about 8, which is consistent with our TEM observation. By using the same Na_2S after 24 h, we obtained gold nanoparticles as before,[4] and did not find near infrared adsorption peak. To verify that tabular nanostructures are gold, high resolution transmission electron microscopy (HRTEM) and electron diffraction were used. As shown in Fig. 1(c), the lattice spaces on $\langle 111 \rangle$ are all 2.42 Å. By comparing this with the electron diffraction pattern in Fig. 1(d), we found that this lattice space corresponded to the $\frac{1}{3}\{422\}$ (2.45 Å) of gold crystal. The presence of the formally forbidden $\frac{1}{3}\{422\}$ reflections observed in plan view is due to the presence of small numbers of parallel $\{111\}$ twin planes.[8]

Furthermore, Norman *et al.* also believed that Au_2S cannot form in the aqueous $HAuCl_4$–Na_2S reaction or at the room temperature.[6] As shown in Fig. 1(b), when we checked our reaction solution with fresh Na_2S by fluorescence spectrophotometer, we observed peak at 469 for 330 nm exciting. The energy of 469 nm photons (2.64 eV) is very close to the the calculated band gap of Au_2S: 2.6 eV.[2] This may be an evidence for the formation of Au_2S.

In conclusion, we provided another possible explanation for the near infrared adsorption peak of the $HAuCl_4$–Na_2S reaction caused by the SPR of the gold tabular nanostructures.

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