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## LETTER TO THE EDITOR

## A new optical absorption peak for Au/SiO<sub>2</sub> nanocomposite formed by sonochemistry

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### Abstract

An Au nanoparticle/monolithic mesoporous silica assembly was synthesized by means of ultrasonic irradiation. For this as-prepared Au/silica sample, exposure to ambient air (or ageing) at room temperature (10 °C) and subsequent drying at 120 °C induce a new optical absorption at 460 nm in addition to the normal surface plasmon resonance (SPR) of Au nanoparticles. Further drying results in diminishing and even disappearance of this new peak accompanied by enhancement of the normal SPR. Further experiments revealed that the exposure to ambient air for sufficient time at room temperature after irradiation plays a crucial role in the appearance of the new peak after subsequent drying at 120 °C. This new optical absorption peak may be associated with Au clusters with size less than 1 nm.

The optical properties of Au nanoparticles have been extensively studied [1–8]. For a spherical Au particle with size from 2 to 99 nm, its surface plasmon resonance (SPR) occurs in the visible band from 520 to 575 nm [4, 7]. For the Au particles with other shapes, such as prolates, rods [9–11], thin plates [12], and even aggregates [13, 14], there exists another absorption peak at lower energy down to the near-infrared region. Recently, in our laboratory, we synthesized a nanostructured Au/monolithic mesoporous silica assembly by means of ultrasound irradiation, and found a new absorption peak at higher energy induced by ambient exposure at room temperature and subsequent drying at 120 °C. The details are reported in this letter.

The monolithic mesoporous silica host (planar-like, about 1.5 mm in thickness) was prepared by a sol–gel process, drying, and finally annealing at 700 °C for 1 h, as described in detail elsewhere [15]. The mesoporous silica prepared in this way, whose pores are interconnected and open to ambient air, had a specific surface area of 600 m<sup>2</sup> g<sup>-1</sup> and pore

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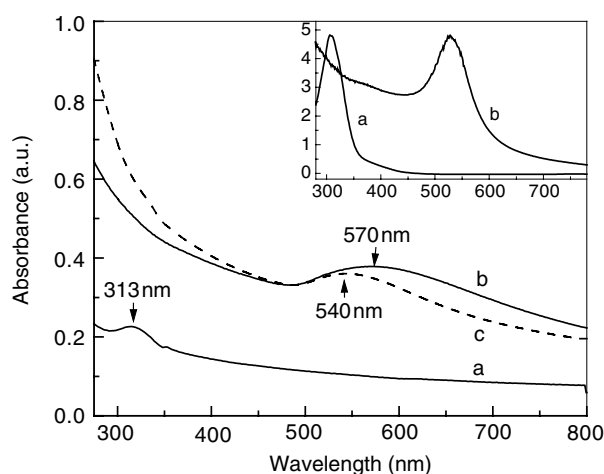
diameters mainly distributed in the range below 10 nm, as determined by isothermal N<sub>2</sub> adsorption measurement, as described previously [15]. The preformed monolithic mesoporous silica was immersed in a 0.8 mM HAuCl<sub>4</sub> aqueous solution (containing 0.2 M isopropanol) for three weeks, which is long enough to make the concentrations of AuCl<sub>4</sub><sup>-</sup> and isopropanol in the pores of the mesoporous silica the same as those in bulk solution [16]. After sufficient immersion, the HAuCl<sub>4</sub> aqueous solution (about 25 ml) together with the soaked mesoporous silica was transferred to a conical flask for ultrasonic irradiation.

Ultrasonic irradiation was accomplished in a KQ218 commercial ultrasonic cleaner (40 kHz, 100 W output power), as described previously [17, 18]. The ultrasonic generator is beneath the ultrasonic bath, where the conical flask containing the sample was placed. During ultrasonic irradiation, a water flow was utilized in order to keep the flask in the bath at room temperature (about 10 °C) and Ar gas was purged into the flask to eliminate oxygen from it. After ultrasonic irradiation for 2 h, the irradiated solid samples were taken out of the solution and their surfaces were wiped with filter paper; this was followed by exposure to ambient air (about 10 °C) for up to seven days and subsequent drying at 120 °C for different times.

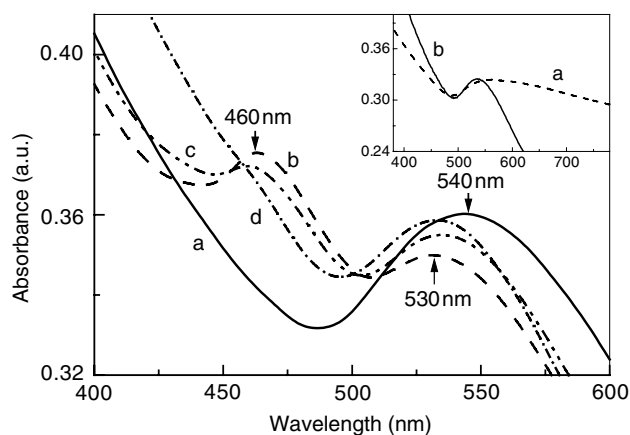
Optical absorption spectra were measured using a Cary 5E UV–visible–NIR spectrophotometer over the wavelength range from 200 to 800 nm. The irradiated solution was simultaneously transferred into a quartz cell with a 1 cm path length for optical study. Transmission electron microscopic (TEM) observation was conducted using a JEOL 2010 operating at an accelerating voltage of 200 kV after grinding the samples into powders.

Figure 1 shows the optical absorption spectra of a solid sample before and after irradiation for 2 h. For the soaked sample before irradiation, there is only one peak at 313 nm, attributed to AuCl<sub>4</sub><sup>-</sup> ions [19] within pores of silica, in the spectra. After irradiation for 2 h, the peak at 313 nm vanishes, indicating complete reduction of the AuCl<sub>4</sub><sup>-</sup> ions, and a broad peak around 570 nm appears, which relates to the well-known SPR of Au nanoparticles [7]. TEM examination shows nearly spherical Au nanoparticles dispersed in silica, as previously illustrated [17]. For comparison, the corresponding optical spectra of the solution are also shown in figure 1 (see the inset). The two are similar except as regards the width and position of the SPR. After the irradiated solid sample is exposed to ambient air (or aged) at room temperature (10 °C) for sufficient time (say, seven days), the SPR diminishes and blue-shifts to 540 nm.

Interestingly, the aged sample exhibits quite different optical spectra after drying at 120 °C, as shown in figure 2. After drying for 1 h, the SPR at 540 nm diminishes and blue-shifts to 530 nm, and an absorption peak at 460 nm appears. Although two-absorption-peak band-structure for Au nanoparticles has been reported in many references for non-spherical nanoparticles, such as prolates, rods [9–11], thin plates [12], and even aggregates [13, 14] (the absorption peaks occur at around 530 nm and at lower energy down to the near-infrared region), to our knowledge the peak at 460 nm has not been reported so far for this Au/SiO<sub>2</sub> system and hence is a new observation. With increase of the drying time at 120 °C, the new peak diminishes, and this is accompanied by a rise of the absorption in the edge region at higher energy, and the SPR at 530 nm is enhanced, but the positions of both peaks are basically unchanged. When the drying time is increased up to 20 h, the new peak disappears. Further experiments revealed that the exposure to ambient air (or ageing) for sufficient time at room temperature after irradiation plays a crucial role in the appearance of the new peak after subsequent drying at 120 °C. For the irradiated solid sample without ageing at room temperature before drying at 120 °C, we can only find the normal SPR peak around 530 nm, but on peak at 460 nm, as indicated in the inset of figure 2. After drying the aged sample at 120 °C for a short time, further ageing at room temperature induces a similar result to increased drying time at 120 °C, as shown in figure 3.

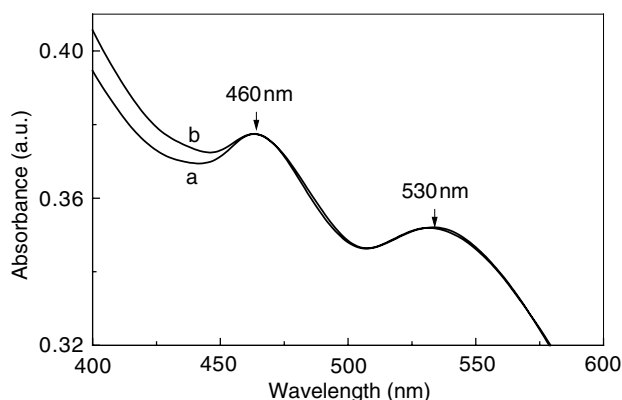


**Figure 1.** The optical absorption spectra for the monolithic mesoporous silica soaked with 0.8 mM  $\text{HAuCl}_4$  aqueous solution before (a) and after (b) irradiation for 2 h. (c) After a seven-day exposure to air at  $10^\circ\text{C}$  of the sample from (b). Inset: for  $\text{HAuCl}_4$  aqueous solution before (a) and after (b) irradiation for 2 h.



**Figure 2.** The optical absorption spectra of the irradiated mesoporous silica with seven-day exposure to air at  $10^\circ\text{C}$  and then drying at  $120^\circ\text{C}$  for different times. (a) Before drying at  $120^\circ\text{C}$  (the same as curve (c) in figure 1); (b) after drying for 1 h at  $120^\circ\text{C}$ ; (c) after drying for 3 h at  $120^\circ\text{C}$ ; (d) after drying for 20 h at  $120^\circ\text{C}$ . Inset: optical spectra for the irradiated solid sample. (a) Without ageing and drying (the same as curve (b) in figure 1); (b) after drying the sample from (a) at  $120^\circ\text{C}$  for 1 h.

Now let us give a brief discussion of the results above. Ultrasonic waves have been used extensively to generate novel materials with unusual properties [20]. The chemical effect of ultrasound is attributed to acoustic cavitation: the formation, growth, and implosive collapse of bubbles in a liquid irradiated with high-intensity ultrasound [20–23]. During the collapse of such bubbles, local hot spots are created with temperatures up to  $\sim 5000\text{ K}$  and pressure of 1800 atm. These extreme conditions have been exploited to generate metal carbide [24], metal oxides [25, 26], metal sulfides [27, 28], and metals [29, 30]. Noble-metal nanoparticles (Au and Pd) located inside the pores of monolithic mesoporous solid were also successfully



**Figure 3.** The optical absorption spectra of the sample from (c) in figure 2 exposed to air at 10 °C for 0 h (a) and 24 h (b).

synthesized by soaking preformed monolithic mesoporous silica host in noble-metal ionic solution and subsequent ultrasonic irradiation at room temperature [17, 18].

The disappearance of the peak at 313 nm after irradiation for 2 h indicates complete reduction of the  $\text{AuCl}^-$  ions in solution. Reduced atoms will form clusters and nanoparticles within pores of silica, leading to the appearance of the Au SPR. Subsequent exposure to ambient air at room temperature will result in evaporation of solvent inside pores of silica and increase of the effective dielectric constant of the Au nanoparticles' surrounding medium [31], which will lead to decrease and blue-shift of the SPR according to Mie theory [1] (see figure 1). Subsequent drying at 120 °C for 1 h induces further evaporation of the solvent in silica, which would lead to further decrease and blue-shift of the SPR. Increase of the drying time induces growth of nanoparticles within pores of silica and hence enhancement of the SPR, as shown in figure 2.

Some authors reported that Au clusters could produce an absorption peak around 500 nm. Palpant *et al* [2], found that  $\text{Au}_{300}$  (2 nm) clusters supported on silica exhibit a peak at 500 nm, which was still attributed to the SPR; Duff *et al* [3] and Marcus *et al* [8] also reported that  $\text{Au}_{250}$  (2 nm),  $\text{Au}_{170}$  (1.5 nm), and  $\text{Au}_{55}$  clusters displayed a peak at 500 nm (but no peak for  $\text{Au}_{34}$  (0.9 nm) clusters [3]), although El-Sayed *et al* [5] found no such peak for  $\text{Au}_{200}$  (1.9 nm) clusters. There is no report of the peak at 460 nm presented in this letter. For Ag oligomers in mesoporous silica, Bi *et al* [32] found that there exist two absorption peaks at higher energy than the peak of the normal SPR for Ag nanoparticles. Although some kind of Au complex with the host may be formed and be responsible for the 460 nm peak, here we suggest that this peak could be associated with Au oligomers or clusters with size less than 1 nm. After irradiation, there would be some reduced Au atoms in solution within pores, in addition to the Au nanoparticles which induce the normal SPR at 530 nm. Subsequent ageing at room temperature would result in evaporation of solvent inside pores, and formation of isolated ultrafine liquid (solution) drops (containing Au atoms) in the channels of silica. Drying at 120 °C would give rise to disappearance of the drops, and the Au atoms in a drop *in situ* would form a cluster or an oligomer with size <1 nm, leading to the peak at 460 nm. Further drying could induce growth of the oligomers and/or their diffusion onto the adjacent nanoparticles, which in turn would give rise to diminishing and even disappearance of this peak accompanied by enhancement of the SPR at 530 nm. As regards the origin of this new peak, more detailed work is in progress.

In summary, a nanostructured Au/monolithic mesoporous silica assembly was synthesized by sonochemical reduction. Exposure to ambient air at 10 °C and subsequent drying at 120 °C led to a new optical absorption peak at 460 nm, in addition to the normal SPR peak of Au nanoparticles. Further drying induced diminishing and even disappearance of this new peak accompanied by enhancement of the normal SPR. This new optical absorption peak may be attributed to Au clusters with size less than 1 nm.

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