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Localized surface plasmon resonance sensor by $PdCl_2$-GNPs for Hydrogen gas

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Abstract:
In this study gold nanoparticles (GNPs) with about 521 nm plasmonic peak were prepared by pulsed laser (Nd: YAG, λ=1064 nm) ablation (PLA) synthesis in DI water then different concentrations of $PdCl_2$ solution including Pd:Au ratio 2:1, 1:1 and 1:2 were added. After adding process, $PdCl_2$/Au core-shell agglomerations were observed on TEM images, which was attributed to a surface-charge-induced agglomeration effect. It was shown that the obtained $PdCl_2$-GNPs can detect very small amount of hydrogen through the surface plasmon spectral shift due to hydrogen reduction of $PdCl_2$ to metal Pd, which results in change in particles surrounding dielectric constants. In the gas calibration curves, a linear dependency vs. hydrogen concentration was observed.

Key words: Hydrogen sensor; Gold nanoparticles; Pd nanoparticles; pulsed laser ablation; localized surface Plasmon resonance.

Introduction

LSPR is a powerful tool for sensing due to its high sensitivity to the media refractive index change[1]. The LSPR arises from collective oscillations of free electrons in the metal nanoparticles in resonance with incoming light fields, resulting in strong local electromagnetic fields as well as an intense extinction band, So it occurs in materials that have a high charge carrier density like metals. But the most investigation focused on noble metals because they are stable under a wide range of conditions and create sharp spectral absorption in the visible range[2]. Wavelength of this peak depends on the particle size, shape, and dielectric properties of environment. Therefore, by maintaining the size, shape and changing the environment of nanoparticles, position and intensity of LSPR peak has been changed. Depends on changing the refractive index of environment we can see blue or red shift in the wavelength absorption spectra[3]. Hydrogen sensing is momentous for many applications because hydrogen is very explosive and dangerous when its concentration is between 4% (lower explosive limit) and 74.5% (upper explosive limit) at room temperature and pressure[4]. Hydrogen is a flammable gas without color, smell and taste and so cannot be detected by human senses. Therefore, for the safety reasons are needed to detect its presence and measure the concentration. Recently hydrogen gas has been used in various areas of the chemical industry either being one of the necessary components of chemical processes [5]. In this study, we use laser ablation for gold nanoparticles. Laser ablation of solid targets in liquid environment permit us to generate nanoparticles with good properties such as high purity, easily functionalize-able surface, metastable composition or complex structure. The main idea of this paper is to use LSPR properties of Au nanoparticles in the presence of $PdCl_2$ solution as dielectric medium that is sensitive to the presence of hydrogen[6,7]. Actually the synthesized $PdCl_2$-GNPs colloidal solution was successfully applied to detect hydrogen by LSPR sensing.

Materials and method

Gold nanoparticles were fabricated by pulsed laser ablation of a gold target in 200 cc deionized water using an Nd:YAG laser (wavelength=1064 nm) with 9 Hz repetition rate for 30 minutes. $PdCl_2$ solution was prepared by adding 0.02 g of $PdCl_2$ powder into a mixture of 99.9 cc DI water and 0.1 cc HCl. This composition was kept in ultrasonic bath until $PdCl_2$ was dissolved and a uniform yellowish solution of 0.2 g/l $PdCl_2$ was obtained after 1 hour. The samples were prepared by different Au:Pd ratios of 2:1, 1:1 and 1:2. For this purpose 20 cc of Au nanoparticles solution were added to various amounts of as prepared colloidal solution of $PdCl_2$ colloidal. The phase compositions of the Au-Pd colloidal samples were characterized by a Philips X-ray diffractometer (XRD) with Cu Kα radiation (k =

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0.15418 nm) in 2θ range of 10– 80°. The size and morphology of nanoparticles were observed on a Philips model CM120 Transmission electron microscope (TEM). Optical absorption behaviour (UV-Vis characterization) is done by PerkinElmer Lambda25 spectrophotometer in wavelength range 190-1100 nanometer.

Results and Discussion

XRD patterns of $PdCl_2$-GNPs are shown in Fig.1 (a). All the diffraction peaks agree well with the cubic crystal structure of gold (JCPDS no. 00-001-1172) and rhombohedral $PdCl_2$ phases (JCPDS no. 01-086-1888). TEM image of $PdCl_2$-GNPs (Fig.1 (b)) samples the spherical GNPs are covered with a thin layer of Pd. actually noble metal nanoparticles have negative surface charges, so palladium ions (Pd^{+2}) attracted and accumulated over the GNPs.

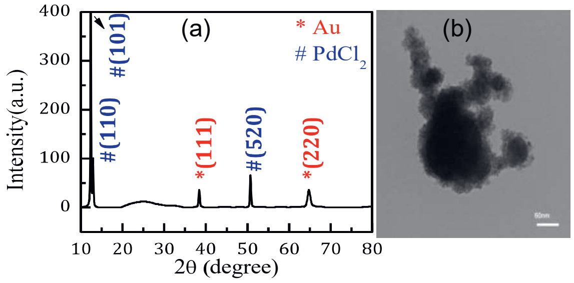

Fig.1. (a) XRD pattern and (b) TEM image of $PdCl_2$-GNPs (2:1)

For hydrogen gas sensing tests, first the air into the glass bottle was removed with a vacuum pump until the solution began to bubble (typically 30 s). Second the hydrogen was introduced by inserting a syringe filled with hydrogen 10% mixed with Ar into the glass bottle for 5 min under slow stirring to ensure a complete absorption. After the H_2 absorption the UV–Vis absorption spectrum of the solution was recorded. Fig.2 (a) shows the absorption spectra of different ratio of $PdCl_2$-GNPs colloidal solution when exposed to various concentrations of hydrogen gas (ppm in liquds). By applying hydrogen, palladium is reduced and since the refractive index decreases, the Au plasmon peak move to smaller wavelengths. In Fig. 3, variations of Au LSPR wavelength and intensity are plotted for the three samples in different concentrations of hydrogen. As seen for 2:1, 1:1 and 1:2 samples, the wavelength and intensity of the gold peak remain constant after 4.3, 8.5 and 26 concentration (ppm in liquid) of hydrogen gas respectively. In fact, by increasing the amount of palladium in the sample, we need more hydrogen to recover it, and it will be saturated to higher levels of hydrogen.

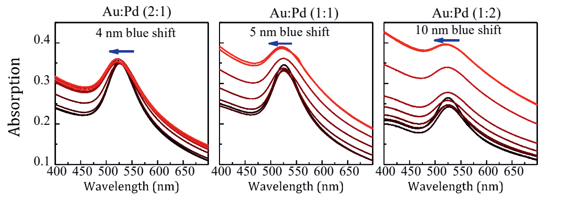

Fig.2. Absorption spectra of $PdCl_2$-GNPs after insertion of various hydrogen concentrations

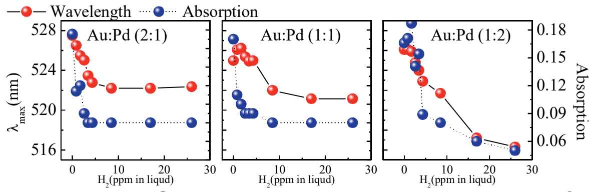

Fig.3. Au LSPR wavelength and intensity of absorption as a function of hydrogen concentration (ppm measured with respect to whole liquid) for different Au:Pd ratio

Conclusions

Gold colloids were prepared by PLA method and activated against hydrogen by adding $PdCl_2$ solution. We demonstrated that $PdCl_2$-GNPs colloids exhibit a significant ability for plasmonic detection of hydrogen gas, in which wavelength blue-shifts and intensity variations were recorded as detection factor. Sample with Au: Pd (1:2) ration showed an optimum spectral shift in the presence of 10% H_2. These results demonstrated that hydrogen gas can be detected optically both via plasmonic shift and intensity variations. From XRD metallic Au and $PdCl_2$ crystal phases were obtained also TEM image showed the bimetallic particles are spherical core Au NPs covered by a Pd (II).

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