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Hydrogen sensing by localized surface plasmon resonance in colloidal solutions of Au-WO₃-Pd

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Abstract

Nowadays, hydrogen has attracted significant attention as a next generation clean energy source. Hydrogen is highly flammable, so detection of hydrogen gas is required. Gold nanoparticle based localized surface plasmon resonance (LSPR) is an advanced and powerful sensing technique, which is well known for its high sensitivity to surrounding refractive index change in the local environment. We put particular focus on how LSPR of gold nanoparticles can be used to sense hydrogen gas. Additionally, metal oxides are generally used as materials for high sensitivity and fast response H₂ sensors. Therefore, we used both an Au and WO₃ colloidal with a PdCl₂ solution added as a hydrogen catalyst. In this work, colloidal WO₃ nanoparticles were synthesized by an anodizing method and Au NPs were obtained by pulsed Nd:YAG laser ablation. The gold NPs showed a LSPR absorption band over the visible and near infrared region. When Au nanoparticles were added to the mixture of WO₃ and PdCl₂, the plasmon peak of Au nanoparticles shifted to a longer wavelength in the presence of hydrogen gas. Structural, morphological and optical properties of colloids were investigated by using a XRD, TEM and UV-Vis spectrophotometer, respectively.

1. Introduction

Hydrogen sensing is important for many applications because hydrogen is very explosive in concentrations

between 4% (lower explosive limit) and 74.5% (upper explosive limit) at room temperature and pressure [1]. Hydrogen is a flammable gas without color, smell or taste and so cannot be detected by

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human senses. Therefore, it is necessary to be able to detect its presence and measure the concentration for safety reasons. Recently hydrogen gas has been used in various areas of the chemical industry as necessary components of chemical processes and medical applications; it is also used in the food industry [2, 3].

LSPR is a powerful tool for sensing due to its high sensitivity to the media refractive index change. LSPR occurs in materials that have a high charge carrier density like metals. It has also been recently reported in heavily doped semiconductor nanocrystals [4]. But most investigations are focused on noble metals because they are stable under a wide range of conditions and create sharp spectral absorption in the visible range. When an electromagnetic wave interacts with plasmonic metal nanoparticles, and if the frequency of light is equal to the plasmon frequency of the noble metal, a resonance occurs and we have an intense peak in the absorption spectra. The wavelength of this peak depends on the particle size, shape, and dielectric properties of the environment. Therefore, by maintaining the size and shape but changing the environment of the nanoparticles the position and intensity of the LSPR peak can be changed. Depends on the changes to the refractive index of the environment we see a blue or red shift in the wavelength absorption spectra [5]. On the other hand, tungsten trioxide (WO_3) is a metal oxide with good physical and chemical properties, making it suitable for a numerous spatial applications for optical gas sensors. In gas sensors, WO_3 covers a wide range of concentrations with a desirable response. However, noble metals (Pt, Au, and Pd) are required to reduce gases (CO , H_2 , ethanol, methanol, etc.). Most of the literature focuses its attention on the LSPR effect of thin films, but some have studied liquids. Some papers similar to our work include S. Kim et al. [6] who dealt with acetone sensing of Au and Pd-decorated WO_3 nanorod sensors. Decoration of WO_3 nanorods with Au/Pd bimetallic catalyst has a synergistic effect in enhancing the sensitivity of the WO_3 nanorod sensor to acetone gas. In another work, E. Filippo et al. [7] investigated the Ag-PVA

solutions used to realize a renewable, very fast and simple hydrogen peroxide sensor. These samples were also tested as LSPR-based optical sensor for the detection and determination of hydrogen peroxide.

The present work used properties of tungsten trioxide (WO_3) decorated with both Pd and Au nanoparticles as optical hydrogen sensors based on LSPR sensing. In this study, we used different methods to produce each component of our nanoparticles; anodizing for tungsten oxide nanoparticles and laser ablation for gold nanoparticles. Anodizing has many advantages. This method is cheap, easy, mass-productive and a safe process that is not harmful to human health. Nanoparticles of tungsten oxide dehydrate were fabricated by anodizing tungsten rods in diluted HCl. Laser ablation of solid targets in a liquid environment permitted us to generate nanoparticles with good properties such as high purity, easily functionalizable surface, metastable composition or complex structure. Au-Pd bimetallic catalysts have been used because of their superior catalytic activities [8]. The main aim of this paper is to use LSPR properties of Au nanoparticles in the presence of colloidal solutions of WO_3 -Pd as a dielectric medium that is sensitive to the presence of hydrogen.

2. Materials and methods

2.1. Preparation of samples

Gold nanoparticles were fabricated by pulsed laser ablation of a gold target in deionized water using an Nd:YAG laser (wavelength=1064 nm) with 600 mJ/pulse energy, 0.2 mm² spot size and 9 Hz repetition rate for 15 minutes (8100 Total number of pulses). The gold metal plate was placed on the bottom of a glass vessel filled with 50 ml of deionized water. The laser beam perpendicularly aligned with a prism 90 degree and was focused to the target by a 20-cm-focal-length lens. Nanoparticles of tungsten trioxide were synthesized by anodizing tungsten rods in diluted HCl. For this aim, two tungsten rods were

put into a 0.02 M HCl electrolyte and a 60 V DC bias voltage was applied to them for 5 minutes. By applying voltage, the anode surface began to corrode and was distributed into the electrolyte. A PdCl₂ solution was prepared by adding 0.02 g of PdCl₂ powder into a mixture of 99.9 cc DI water and 0.1 cc HCl. This composition was kept in an ultrasonic bath until the PdCl₂ was dissolved and a uniform yellowish solution of 0.2 g/l PdCl₂ was obtained after 1 hour. The samples were prepared by different WO₃:Au:PdCl₂ ratios of 5:1:1, 10:1:1, 15:1:1 and 20:1:1. For this purpose 20 cc of Au nanoparticles solution was added to various amounts of as prepared colloidal solution of tungsten dehydrate and then PdCl₂ colloidal added to them. Table 1 presents the sample codes and their ratio.

Table 1. Sample names and their relative concentrations

Sample code	Relative concentrations
5-1-1	WO ₃ :Au(5:1) and WO ₃ :PdCl ₂ (5:1)
10-1-1	WO ₃ :Au(10:1) and WO ₃ :PdCl ₂ (10:1)
15-1-1	WO ₃ :Au(15:1) and WO ₃ :PdCl ₂ (15:1)
20-1-1	WO ₃ :Au(20:1) and WO ₃ :PdCl ₂ (20:1)

2.2. Characterizations

The phase compositions of the WO₃-Au-Pd colloidal samples were characterized by a Philips X-ray

diffractometer (XRD) with Cu K α radiation ($\lambda = 0.15418$ nm) in a 2θ range of 10–80°. The transmission electron microscope (TEM) images were taken by a Leo 912 AB. Optical absorption behavior (UV-Vis characterization) was done by a PerkinElmer Lambda25 spectrophotometer in a wavelength range of 190-1100 nanometers. The hydrogen gas sensing tests were carried out by bubbling 10%H₂/Ar gases through a tiny pipe into a quartz cell containing the colloidal samples.

3. Results and Discussion

3.1. XRD and TEM

The Powder X-ray diffraction technique was used to investigate the phase structures. Fig. 1(left) shows a typical XRD pattern of sample 10-1-1. All the diffraction peaks agree well with the monoclinic tungsten oxide dehydrate (JCPDS 018-1420), WO₃.2(H₂O) and cubic (Fm-3m) Au (JCPDS 89-3697). However, no palladium phases have been detected for PdCl₂ probably due to its low concentration. The TEM image (right) shows that particles are spherical and their diameters are less than 20 nanometer. Because all the particles in our samples are spherical we cannot distinguish the type of particles.

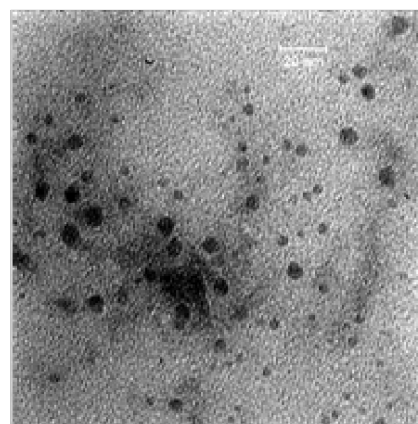
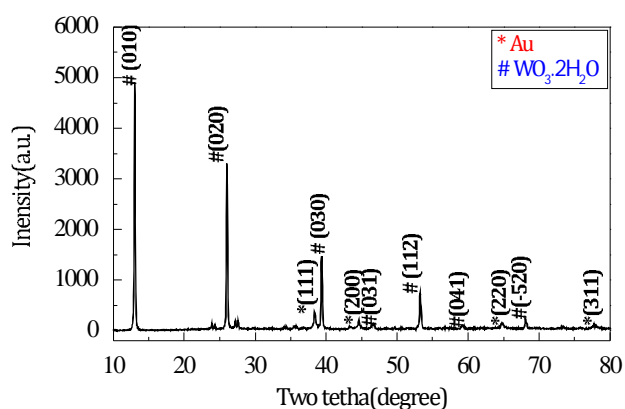


Fig. 1. XRD pattern (left) and TEM image (right) of sample 10-1-1.

3.2. Hydrogen sensing tests

For hydrogen gas sensing tests, samples were exposed to hydrogen gas (10% H₂/Ar) for 10 min. Fig. 2 shows the absorption spectra of WO₃-Au-PdCl₂ before (black line) and after exposure to hydrogen (red dashed line). For sample 5-1-1 no peak displacement was observed. In sample 10-1-1, however, this shift is about 9 nm; but in samples 15-1-1 and 20-1-1 the position of the plasmon peak changed about 1 and 5 nm, respectively. As can be seen for sample 10-1-1, the environment refractive index is much more changed and is more sensitive for hydrogen gas. Also, WO₃ shows gaschromic behavior, so the color of samples 15-1-1 and 20-1-1 changed from pink to blue after exposing to hydrogen. These peaks are shown in Fig. 2 with blue arrows.

To better visualize the gas effect, the optical absorbance change (OAC) parameter, defined as the difference between absorbance during gas exposure and absorbance in air (OAC = Abs Gas - Abs Air), is also reported. Fig. 3 shows the OAC spectra following exposure to 10% hydrogen at room temperature for

the four samples tested. As can be seen, all samples displayed clear optical responses to the presence of hydrogen, but several significant differences could be discerned. Sample 15-1-1 showed the ideal behavior.

3.3. Detection of hydrogen concentration

Fig. 4.a shows the dynamic responses of the WO₃ decorated with both Pd and Au nanoparticles for different concentration of hydrogen gas. Samples were exposed to mixed hydrogen (10%) and Argon gas by a mass flow controller (MFC). Hydrogen absorption experiments were performed, at room temperature, using a quartz cell containing 2mL volume of sample solution. The hydrogen was introduced by inserting a needle into the cell for 10 min. As can be seen, as the concentration of H₂ gas increases, color change of the colloidal solutions increases and the solution became light blue. In addition, the shift of the plasmon peak changed more as the concentration of hydrogen gas increased. Fig. 4.b shows the LSPR peak of Au and two peaks of WO₃ labeled WP1 and WP2 in the different concentrations. The intensity

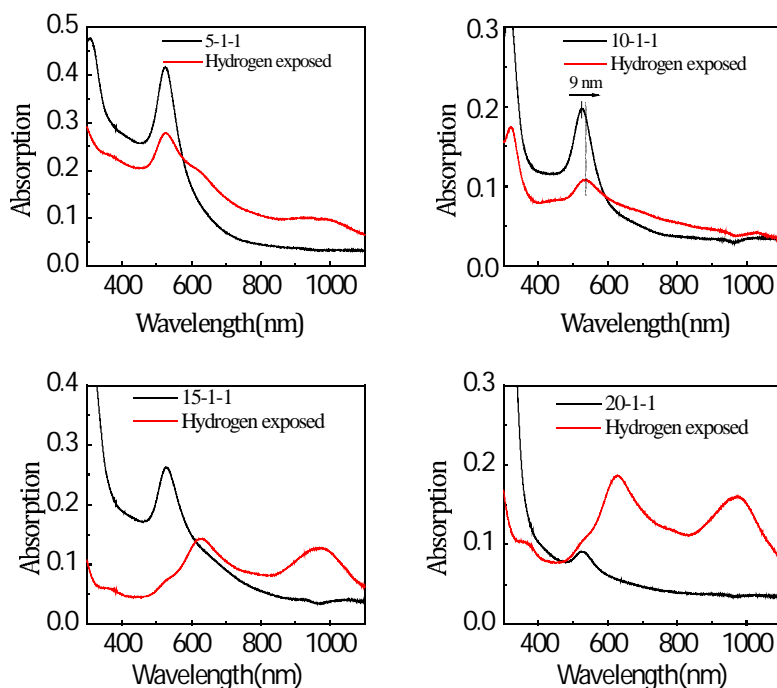


Fig. 2. Optical absorption spectra of initial colloids of Au, WO₃ and PdCl₂, and for samples before (black line) and after (red line) exposure to hydrogen.

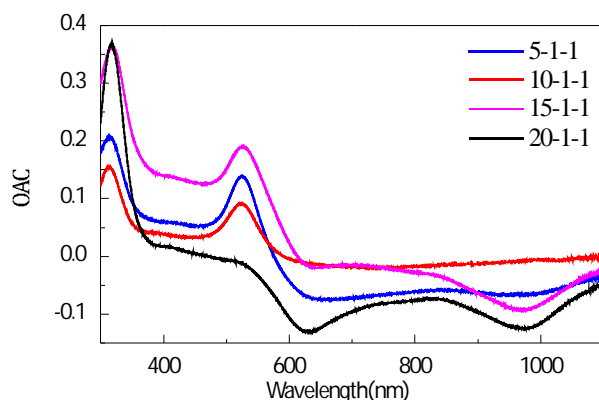


Fig. 3. Optical absorption change (OAC) of different samples.

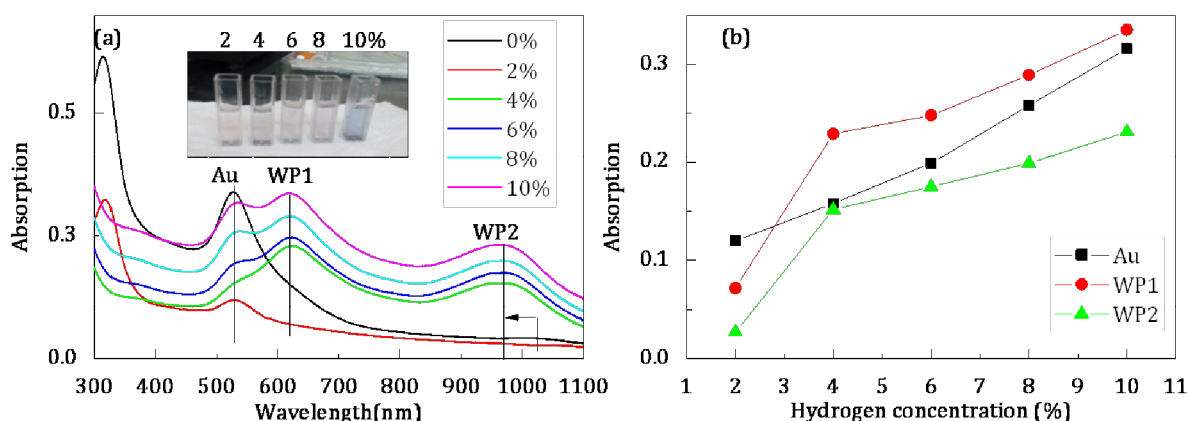


Fig. 4. a) Absorption spectra of 10-1-1 sample in different concentration of hydrogen and b) intensity of plasmon peak of Au and WO_3 peaks for the different concentrations.

of the plasmon peak increased linearly with the concentration of hydrogen gas for Au NPs. This behavior is similar for both peaks of WO_3 .

5. Conclusion

Tungsten oxide hydrate and gold colloids were prepared by anodizing and PLA methods, respectively. This mixing was activated against hydrogen by adding a $PdCl_2$ solution. We demonstrated that Au-Pd- WO_3 colloids less than 20 nm in size exhibit a significant ability for plasmonic detection of hydrogen gas, in which wavelength red-shifts and intensity variations were recorded as the detection factor. The sample with a 10-1-1 ratio showed an optimum spectral shift in the presence of 10% H_2 . When exposing this sample to different H_2 concentration it turned from pink to blue and at

the same time the peak absorption increased linearly with the H_2 percentage. These results demonstrate that hydrogen gas can be detected optically both via plasmonic shift and intensity variations.

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