THE CREATION OF AU@TIO$_2$ PLASMON-ACTIVE STRUCTURE FOR HYDROGEN PRODUCTION

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Abstract

In this work substrates able to efficiently perform so-called photo-electrochemical process are proposed. The hybrid substrates consist of a plasmon-active gold structure and a certain number of TiO_2 layers deposited by the atomic layer deposition (ALD) method. Above the influence of LED lamp irradiation (λ=850 nm) in the water splitting process, the enhancement of hydrogen production is observed (0.11 ppm/sec VS. 0.22 ppm/sec) which can be explained by creation of surface plasmon-polariton resonance (SPP), which occurs as a result of the excitation of collective electronic vibration on the periodical gold nanostructure under the incident light. Also, it is suggested that the combination of gold and titanium dioxide can lead to plasmon triggering of TiO_2 catalytic activity, which will lead to decreasing energy costs on the photolysis of water and to the overall acceleration of the process.

Keywords: Electrochemistry, plasmonic, atomic layer deposition, titanium dioxide, photolysis of water

1. INTRODUCTION

One of the most important global environmental problems nowadays is the search for sources of ecological "green" fuels [1-7]. This problem is closely related to the high amount of emission gases that cause global warming effect and creating of greenhouse effect. One of the most promising «green» fuels is hydrogen, which releases water vapor as a by-product when burned [8-11].

One of the richest sources of hydrogen is water. By cleaving water molecules under the influence of electric current, the so-called «green» hydrogen can be released. Today, there are many studies related to the cleavage of water by electrolysis. However, these methods have relatively high energy requirements [12–15]. Therefore, studying related to the increasing the rate of green hydrogen production at lower energy costs is very relevant [16–19].

The main goal of this work was to create a hybrid structure with a combination of plasmon-active gold structure and additional catalytic TiO_2 layer. The water splitting process proceeds under the simultaneous plasmon triggering and an electric field application. In perspective, proposed structures will be applied for the hydrogen production and generation of ecologically pure fuel in the future.

2. EXPERIMENTAL

2.1. Materials

Gold targets for metal deposition (purity of metal, 4 N) were purchased from Safina (Czech Republic). SU-8 2005 was purchased from Microchem (Newton, USA). Titanium chloride ($TiCl_4$, Vecton, Russia 99.99%) and deionized water were used as precursors, Rhodamine 6G was purchased from Sigma-Aldrich.

2.2. Sample preparation

The SU-8 polymer was deposited on a clean glass surface by using spin-coating method (1400 rpm for 20 minutes). The prepared samples then were dried at 60 °C for 24 hours and then irradiated with UV light for 30 minutes, followed by heat treatment at 90 °C for 2 hours (**Figure 1A**). Creation of periodic polymer structure was performed by excimer KrF laser with a wavelength of 248 nm (**Figure 1B**). Then, thin layers of gold were deposited on the periodically structured surface by vacuum sputtering (**Figure 1C**). In the last stage, a different number of TiO_2 layers were deposited on the gold surface using ALD equipment (**Figure 1D**). The atomic layer deposition was performed in the hot-wall, flow-type reactor Nanoserf having slot-type geometry (Nanoengineering Ltd, Russia). The temperature of the reactor was maintained at 200 °C. Nitrogen (99.9999%) was used as a carrier and purging gas. The total reactor N_2 flow rate at purge and pulse was 300 sccm (standard cubic centimeters per minute). The pulse and purge durations were 100 ms and 20 s respectively.

LED light source (λ=850 nm, FWHM=30 nm, irradiance=1450 μW/cm^2, current=1200 mA) was used for plasmon-polariton resonance excitation.

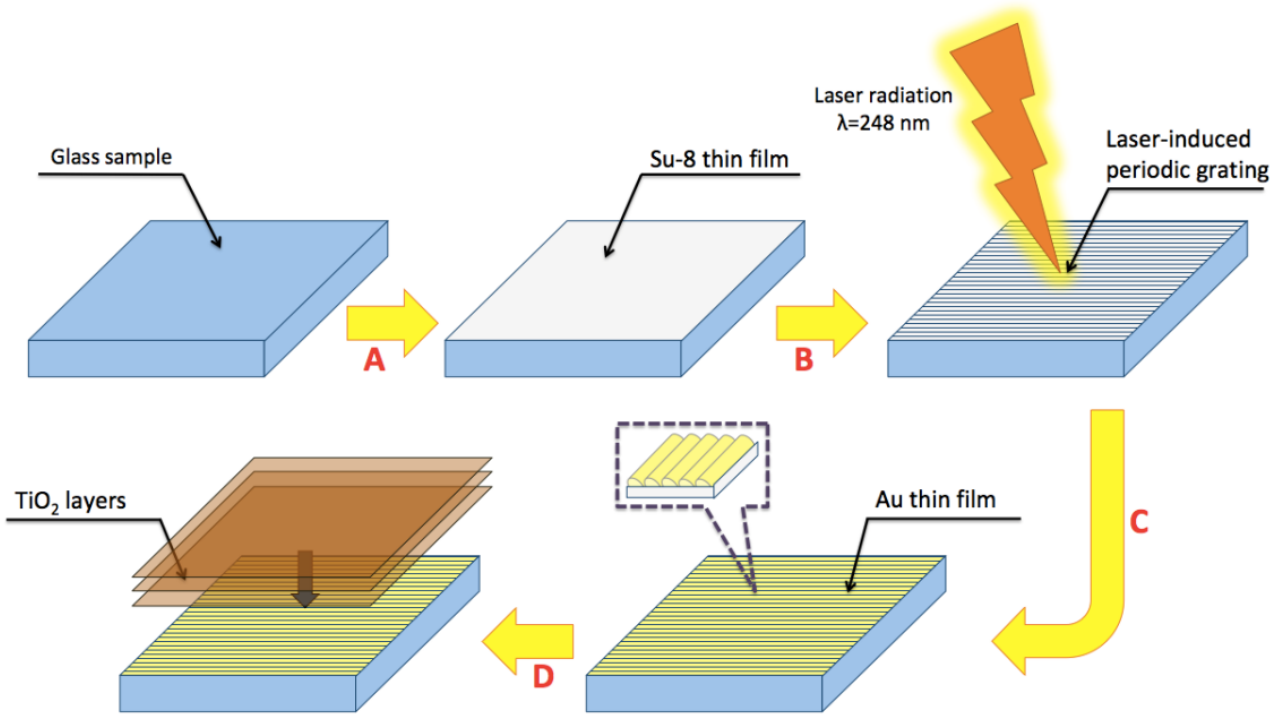

Figure 1 Formation of a combined plasmon-active surface based on TiO_2

A - Deposition of Su-8 polymer on the glass surface; B - creation of a periodic grating under laser irradiation; C - Deposition of the gold layer by vacuum sputtering; D - Deposition of monoatomic TiO_2 layers by ALD method

2.3. Measurement techniques

Raman scattering was measured by using ProRaman-L spectrometer (Laser power 30 mW) Raman spectrometer with 785 nm excitation wavelengths. SEM images and EDX mapping were obtained using energy dispersive spectroscopy (EDX, analyzer X-MaxN, 20 mm^2 SDD detector, Oxford Instruments). The amount of generated hydrogen was measured by gas chromatography (Tianmei GC 7900, TCD detector, N_2 as a carrier).

3. RESULTS AND DISCUSSION

Figure 2 shows results of SEM measurements and EDX element mapping for Au and Ti. **Figure 2A** shows that as a result of laser modification of the polymer, an even and straight periodic grating was formed. After the deposition of titanium oxide by atomic layer deposition, significant changes in the structure are observed (**Figure 2B**). Moreover, based on the results of the EDX analysis (**Figures 2C, 2D**), it can be seen that gold was evenly distributed over the surface of the periodic structure. The EDX element mapping for titanium (**Figure 2F**) also shows that atomic layer deposition process results in an uniform distribution of titanium over the gold surface, while no traces of titanium were found on pristine sample (**Figure 2E**).

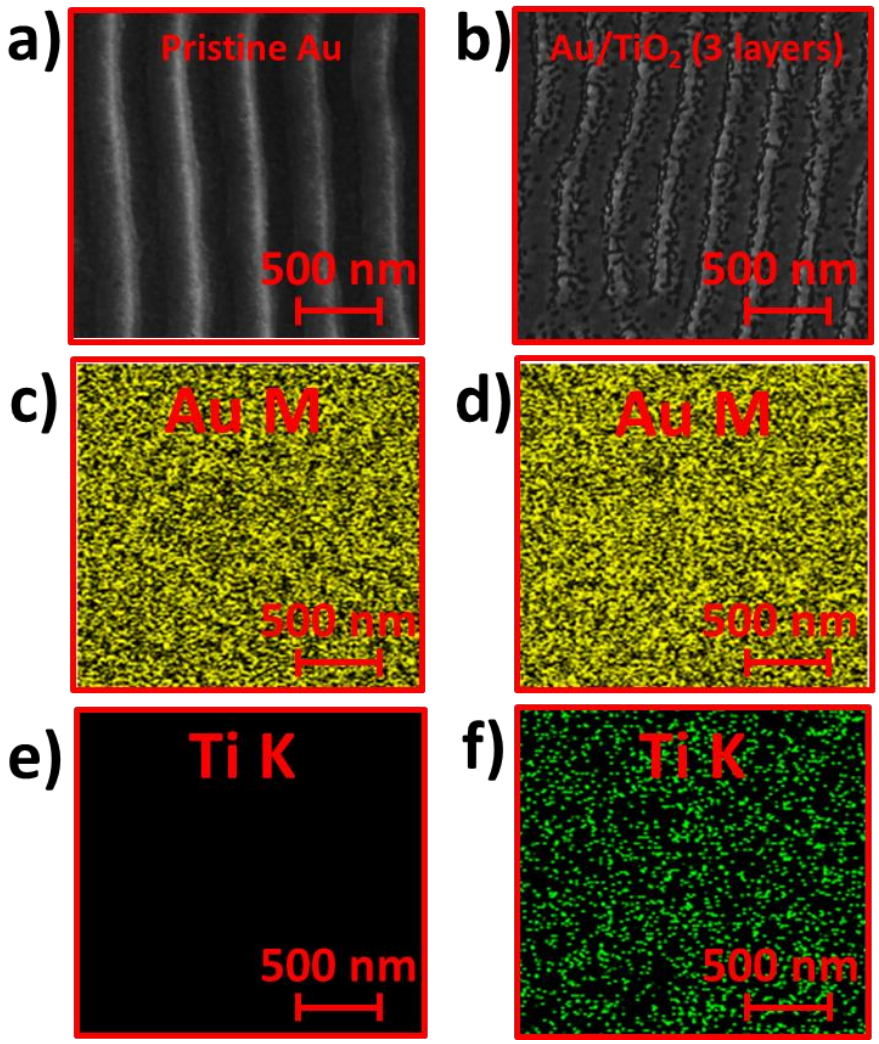

Figure 2 Results of SEM for (a) pristine grating covered by gold and (b) gold grating covered by 3 layers of TiO_2 and EDX element mapping (Au, Ti) for (c, e) pristine grating covered by gold and (d, f) gold grating covered by 3 layers of TiO_2

Figure 3 shows the results of the SERS measurements. No peaks were observed on the gold sample without a periodic grating. However, a sample containing a periodic lattice coated with gold is capable to generate surface plasmon resonance, resulting in the appearance of pronounced peaks of the dye (Rhodamine 6G – R6G). Also, according to the measurement results, it was found that a combined structure based on a gold periodic grating and titanium oxide contributes to a significant increase in the SERS signal due to the influence of surface plasmon-polariton resonance and significant amplification of the electromagnetic field.

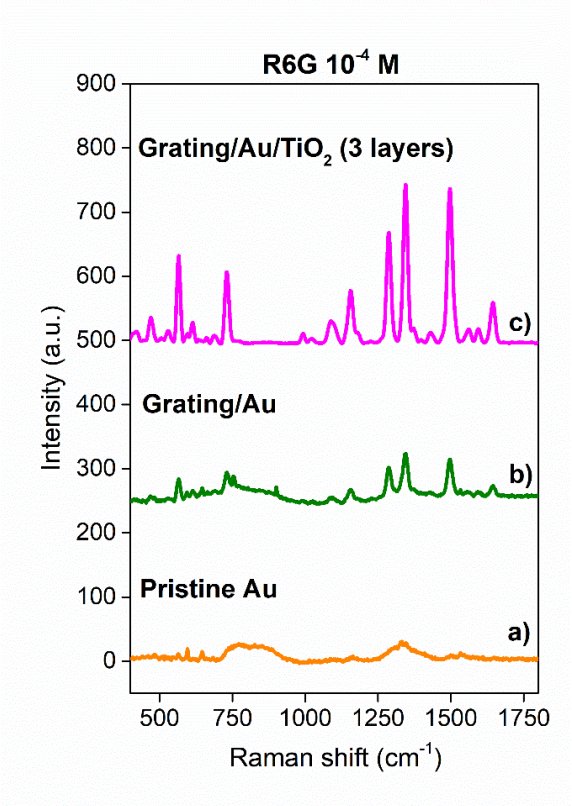

Figure 3 SERS measurements for a) pristine sample with Au without grating, b) pristine sample with Au on the periodic grating and c) sample with gold periodic grating covered by 3 layers of TiO_2

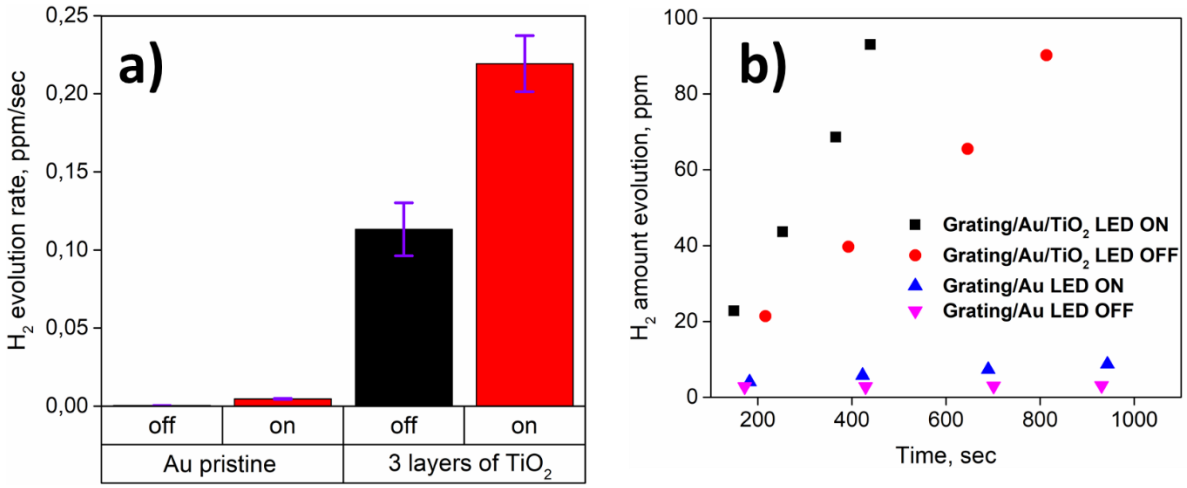

Figure 4 Results of hydrogen amount evolution: a) H_2 evolution rate production by using pristine gold grating and combination of gold grating with titanium dioxide layers with and without LED lamp; b) H_2 evolution amount of samples with and without LED lamp

Figure 4 shows the results of measuring the amount of hydrogen produced in the process of water splitting. **Figure 4A** shows a comparison of hydrogen evolution efficiency with applied voltage of 0.6V by using samples with and without titanium oxide on the gold grating. The measurement results show that the samples with titanium oxide on the surface generate more hydrogen than the original sample due to plasmon triggering of titanium dioxide. Moreover, the effect of an LED lamp switching is also well visible. **Figure 4B** shows the time dependences of the hydrogen concentration in the electrolytic bath, which allows estimating approximately the reaction kinetics.

4. CONCLUSION

In this work, we created a hybrid structure with a combination of plasmon-active component and photocatalytic component TiO_2. Grating was created in using excimer KrF laser with a wavelength of 248 nm. Gold was deposited by vacuum sputtering. TiO_2 layer was produced from titanium (IV) chloride and was deposited by using atomic layer deposition process (ALD). Experiments were performed in dark or under illumination with LED lamp (λ=850 nm, FWHM=30 nm, irradiance=1450 μW/cm^2, current=1200 mA) which corresponded to plasmon absorption band. It is shown that the combination of gold and titanium dioxide can lead to the triggering of catalytic activity of TiO_2 and enhanced generation of green hydrogen.

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