THE NEW METHOD OF SURFACE-ASSISTED COF SYNTHESIS FOR OPTICAL SENSOR MODIFICATION

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Abstract

Covalent organic frameworks (COFs) are an emerging class of crystalline networks that are covalently built from organic components and featured by merits of low density, well-defined pore aperture, large surface area, inherent porosity, facilely tailored functionality, and ordered channel structure. Among other applications, COF compounds can be utilized for CO_2 detection. It Is known that the preparation of COFs compounds is commonly associated with hard experimental conditions (high pressure, inert atmosphere, and high temperature). In this work, we suggest an alternative method of COFs under normal pressure and temperature. The experimental concept implements the surface-assisted COF growth. The created surface-immobilized COF structures were subsequently used for measurement of CO_2 presence.

Keywords: Optical fibers, COFs, plasmons, selectivity

1.   INTRODUCTION

Covalent organic frameworks (COF) are a new class of crystalline porous organic polymers with controlled porosity and highly ordered structure [1,2]. Today, COFs have found a wide range of applications in catalysis, separation and absorption gases [3]. However, the manufacture of COF requires difficult experimental conditions and is quite expensive [4,5]. In addition, the formation of COF layer on functional materil or devices surface still remain a challenging task [6,7]. So, the development of a technology for producing COFs on the solid surface(s) is urgently required. The main goal of this work is to develop the simple and scalable procedure for COF synthesis on directly the sensor surface and subsequent utilization of created hybrid materials for CIOs sensing.

2.   EXPERIMENTAL

2.1.   Materials

Gold targets for metal deposition (purity of metals, 4 N) were purchased from Deionized water, methanol (reagent grade, ≥ 99.8 %), acetone (97 %), were purchased from Sigma-Aldrich and used without further purification. 4-cyanobenzenediazonium tosylate (ADT-CN) was prepared according to published procedure [3]. CO2 gas was obtained from SIAD.

2.2.   Samples preparation

The deposition of Au was accomplished from Au target (purity of 99.99 %, provided by Safina, Czech Republic).

At the first stage, covalent organic structures of the CTF-1 (carbon triazine framework) type were obtained on the sensor surface (**Figure 1**). First, the samples were spontaneously modified by soaking in a 3 mM freshly

prepared aqueous solution of ADT-CN for 30 min. After modification, the samples were washed with water, methanol, and acetone for 20 minutes and dried in a desiccator for 2 hours. At the next stage, the COF building units were dissolved in chloroform with addition of activation agent and samples were immersed in this solution for 3 h.
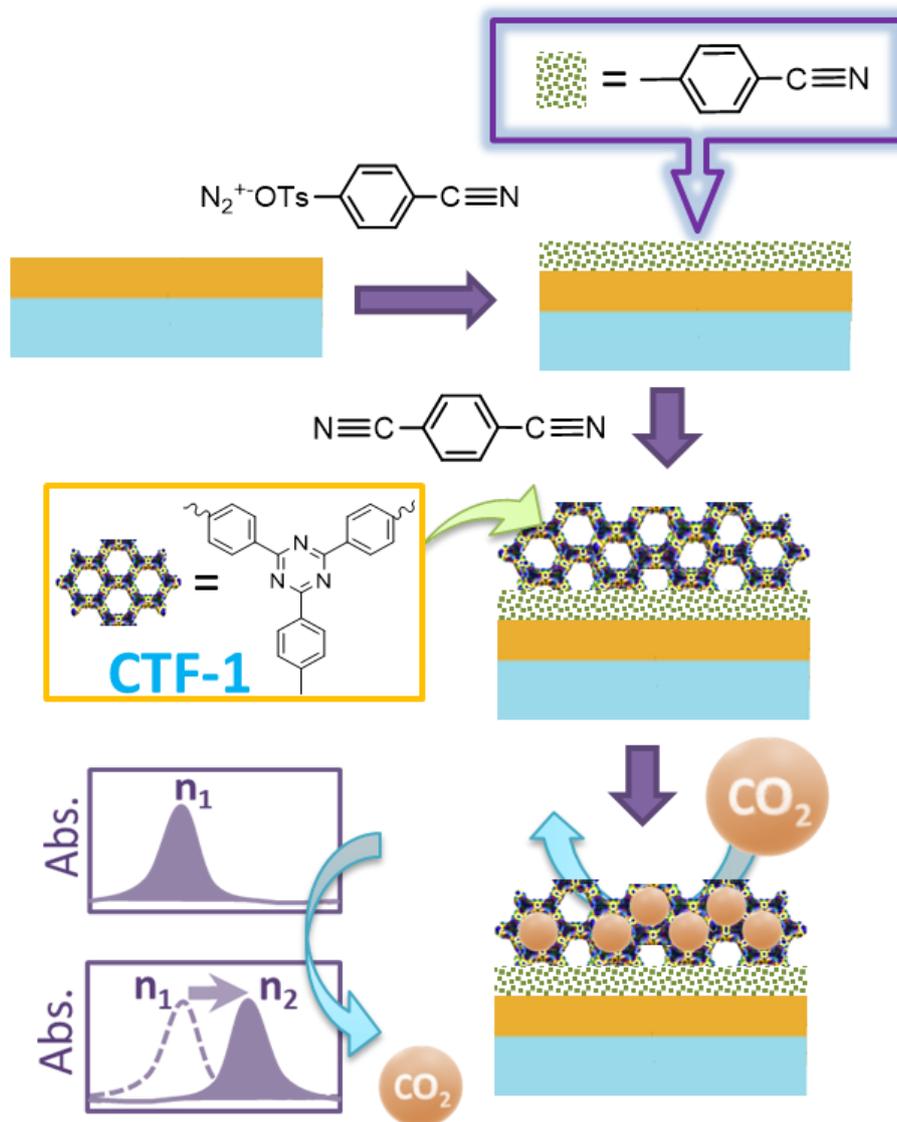
Figure 1 Schematic representation of the fabrication of a sensor with a sensitive surface in the form of CTF-1 covalent organic structures

2.3. Measurement Techniques

The X-ray photoelectron spectroscopy (XPS) was performed using an Omicron Nanotechnology ESCAProbeP spectrometer fitted with monochromated Al K Alpha X-ray source working at 1486.6 eV.

Raman spectra were measured on ProRaman-L spectrometer (Laser power 35 mW) Raman spectrometer with 785 nm excitation wavelengths. Spectra were measured 30 times, each of them with 3 s accumulation time.

UV-Vis absorbance spectra of the samples were measured using a HR2000 (Ocean Optics) spectrometer in 400-800 nm wavelengths range using the AvaLight-DHS light source (Avantes).

3.   RESULTS AND DISCUSSION

Successful growth of CTF-1 has been verified using XPS, Raman and UV-Vis methods. **Figure 2 (parts A, B, C)** shows the XPS spectra of pristine surface, surface grafted with -Ph-CN and final samples with immobilized CTF-1 layer. The corresponded table (part D) shows the change in the concentration of surface elements depending on the step of surface modification. It is obvious that a gradual increase of concentrations of carbon, oxygen, and nitrogen confirms the shielding of initial sample surface and formation of a CTF-1 layer. We assume that the reaction proceeds according to the following principle:

Surface atom element concentration (at %)	Sample		
	Pristine Au	Au / Ph-CN	Au / CTF-1
Au (4f)	52,0	22,6	14.7
C (1s)	33,1	63,5	57.3
O (1s)	14,9	11,7	24.7
N (1s)	-	2,2	3.3
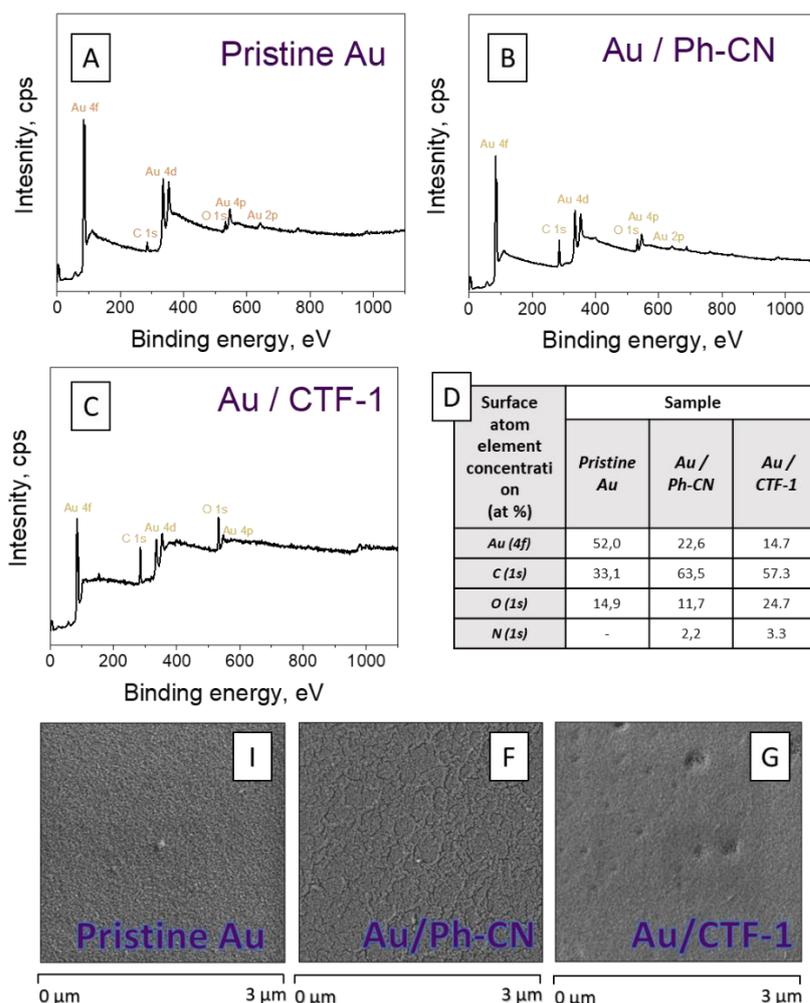
Figure 2 XPS spectra of the surface (A) - pure gold, (B) - gold surface grafted with ADT-CN, (C) gold surface decorated with CTF-1 film. D - Table shows the percentage of elements on the surface. SEM images of the gold surface before (A) and after (B) decoration of the CTF-1 film.

The surface morphology of the samples, before and after decoration with CTF-1 was investigated by SEM. The results are presented in **Figure 2 (parts I, F, G)** and show that the pristine surface has a slightly rough morphology. This morphology is conserved after the –Ph-CN grafting. After the growth of the CTF-1 film, visible changes in the surface morphology were observed (**Figure 2G**), indicating that the COF layer is dominantly formed in the surface valleys.

Figure 3 shows the results of Raman spectroscopy (and the corresponding referencing of the spectral positions of the Raman bands). As is evident, the pristine sample surface does not have any spectral features. Grafting of the sample with ADT-CN leads to the appearance of several bands, corresponded to chemical

fragments of benzene rings and cyano chemical moieties. Further growth of CTF-1 leads to the appearance of several additional Raman bands, the spectral positions of which completely coincide with those in the Raman spectra of CTF-1 powder, also shown in **Figure 3B**.
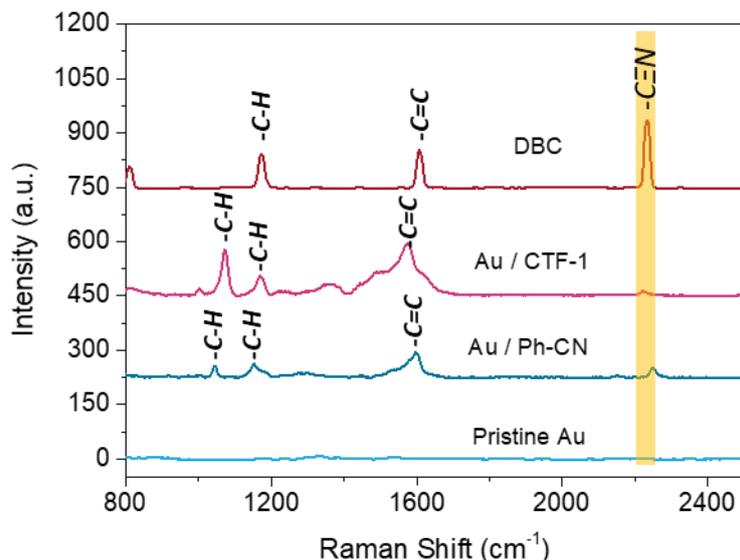
Figure 3 Raman spectra of the surface of primordial gold; a gold surface grafted with ADT-CN and a gold surface decorated with a CTF-1 film

In the next step, sample with CTF-1 were tested for sensitivity to CO_2 in water. As seen from **Figure 4A**, absorption spectrum before and after CO_2 purging for 30 minutes did not change the light transmission spectrum. The absorption spectra after COF decoration show a slight broadening of the absorption peak due to CO_2 presence. **Figure 4B**. So, it is also evident that the sensors decorated with COF shows sensitivity to CO_2. After blowing with air, the absorption peak returns to its original position, confirming the ability of sensor reutilization.
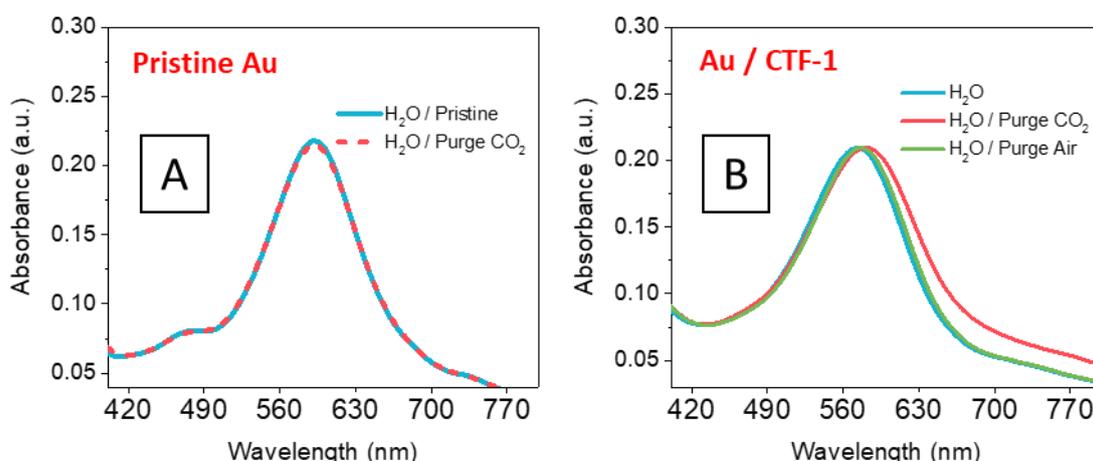
Figure 4 Reaction of an undecorated (A) and decorated COFs (B) sensor to the presence of CO_2 in water

4.   CONCLUSION

In this work, a new method for surface-assisted COF growth is proposed and verified. The COF layer were formed under the ambient condition, without utilization of high temperature or temperature. The COF layer

were grown on the sensor surface, increasing the affinity of device to CO_2. In particular, proposed method allows to identify CO_2 presence in water.

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