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Study of Catalytic Activity of the New Nanohybrid Material Based on Gold Nanoparticles and 1,4-bis(Terpyridine-4'-yl)Benzene

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The paper describes the synthesis of composite material consisting of 1,4-bis(terpyridine-4'-yl)benzene microcrystals and gold nanoparticles with an average size of ~15 nm adsorbed on their surfaces. The nanohybrid material is obtained by the deposition of pre-synthesized nanoparticles on the surface of the organic compound. Mass content of gold in the obtained material is determined by the thermogravimetrical analysis. Catalytic reduction of para-nitrophenol is spectrophotometrically studied.

Keywords: Terpyridine, Gold Nanoparticle, Thermogravimetry, Catalysis.

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1. INTRODUCTION

Owing to unique chemical, optical, and electronic properties differing from properties of metals both in the macrostate and at the atomic level, nanostructures based on gold particles find application in different fields of contemporary chemistry; technology; and the science of materials for creating optical [1-4], nanoelectronic [5-7], and photonic [8, 9] devices, as well as chemical and biological sensors [10-12] and catalysts [12, 13]. Composites based on the nanoparticles of noble metals and conducting organic carriers have recently attracted increased attention due to the wide potential for their use in the creation of storage devices [14]. In this work the creation of a hybrid nanomaterial on the basis of gold nanoparticles adsorbed on the surface of 1,4-bis(terpyridine-4'-yl)benzene crystals is described.

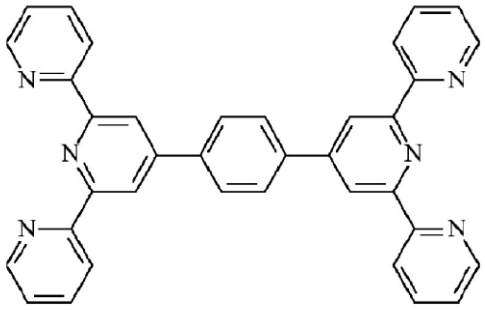

Fig. 1 – Molecular formula of 1,4-bis(terpyridine-4'-yl)benzene

It is known that the interaction of nanoparticles with polydentate organic nitrogen containing ligands most often results in rapid aggregation associated with of interaction of nitrogen atoms of the organic compound with the adjacent nanoparticles [15, 16]. However, for the investigated terpyridine derivative, when the aqueous/acetonitrile suspension of 1,4-bis(terpyridine-4'-yl)benzene is added to a solution of gold particles, the adsorption of the latter occurs on the crystal surface of ligand with the formation of an extraordinary nanohybrid material characterized by the TEM data (see Fig. 2). This phenomenon is described in our work [17].

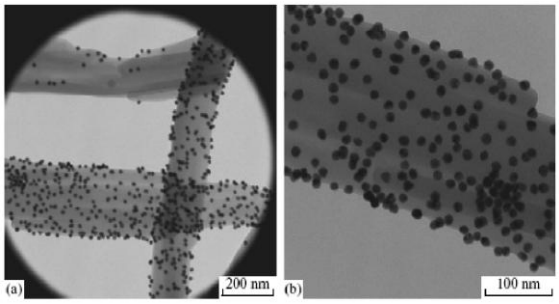

Fig. 2 – The TEM image of crystals of 1,4-bis(terpyridine-4'-yl)benzene with adsorbed gold nanoparticles

2. RESULTS AND DISCUSSION

2.1 Synthesis of Nanoparticles

The stabilized gold nanoparticles with the average particle size 15 nm were prepared according to the Turkevich method [18] through the reduction of the $HAuCl_4$ aqueous solution in the presence of sodium citrate (see Fig. 3).

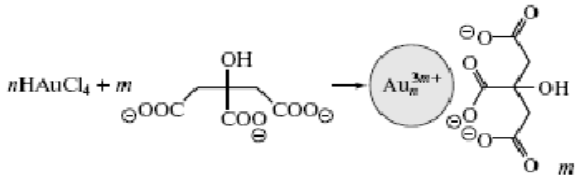

Fig. 3 – The creation of the initial gold nanoparticles

2.2 Obtaining Nanohybrid Material and its Study Using Thermogravimetry

To synthesize the desired complex, solution of 1,4-bis(terpyridine-4'-yl)benzene was added to a solution of gold particles. Obtained suspension was centrifuged and solid precipitate then was formed. To determine the amount of gold nanoparticles in the dry material thermogravimetry was used. Mass portion of gold was found to be 20% (see Fig. 4).

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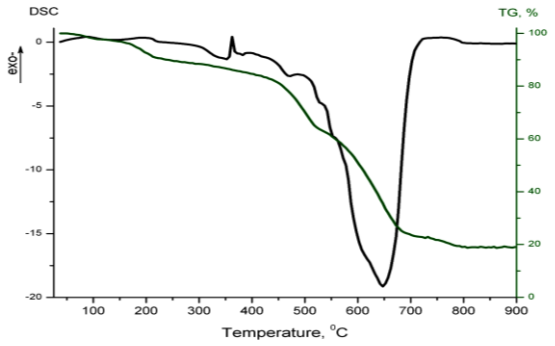

Fig. 4 – The date of the differential scanning thermogravimetry for 1,4-bis(terpyridine-4'-yl)benzene/gold nanoparticle composite. Black line is heat adsorption, green line is loss of mass

2.3 Catalytic Activities of 1,4-Bis(terpyridine-4'-yl)benzene/Gold Nanoparticle Composite in the NaBH4 Reduction of 4-Nitrophenol

Catalytic activity of 1,4-bis(terpyridine-4'-yl)benzene/gold nanoparticle composite was examined by choosing a well-known catalysis reaction involving reduction of 4-nitrophenol (4NP) to 4-aminophenol (4AP) by $NaBH_4$. In the absence of catalysts, the mixtures of 4NP and $NaBH_4$, show an absorption band at $\lambda_{max} = 400$ nm, corresponding to the 4NP ions in alkaline conditions. This peak remains unaltered with the time, indicating that the reduction did not take place in the absence of a catalyst [19]. However, the addition of a small amount of gold-contained powder of composite to above reaction mixture caused bleaching of the yellow color of the reaction mixture. Time-dependent adsorption spectra of this reaction mixture show the disappearance of the peak at 400 nm that accompanied by a gradual development of a new peak at 300 nm corresponding to the formation of 4AP. It was found that addition of 0.25 mg of composite to 3 mL of the mentioned above solution prove reduction of 4NP to be completed at 1 hour. It gave concentration of gold was equal to 0,016 mg/mL.

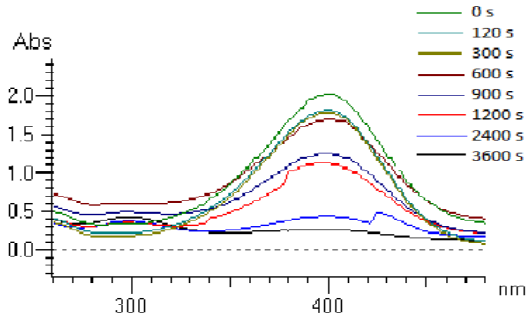

Fig. 5 – UV-vis adsorption spectra of the reduction of 4NP by $NaBH_4$ in the presence of UV-vis adsorption spectra of the reduction of 4NP by NaBH4 in the presence of 1,4-bis(terpyridine-4'-yl)benzene/gold nanoparticle composites with concentration of gold 0,016 mg/mL

3. EXPERIMENTAL SECTION

3.1 Synthesis of Gold Nanoparticles

Before carrying out the synthesis, all glassware was carefully washed with the mixture of HNO_3 and HCl (1 : 3) and then with distilled and deionized water.

The solution of $H[AuCl_4] * 3H_2O$ (75 mg) in distilled water (250 mL) was placed in a round-bottomed flask with a volume of 350 mL equipped with a reverse refrigerator, and the solution was brought to boiling. A 1% solution of sodium citrate (26.25 mL) was added rapidly, and boiling lasted for an hour. In the process of boiling, the solution changed its color from pale yellow to dark cherry. The solution was cooled with stirring to room temperature. The solution was stored in a refrigerator at a temperature of ~4 °C; under these conditions, nanoparticles remain without appreciable aggregation for several months.

3.2 Synthesis of 1,4-Bis(terpyridine-4'-yl)benzene/Gold Nanoparticle Composite

We synthesized 1,4-bis(terpyridine-4'-yl)benzene using the technique from [20]. Then to the solution 50 mL of gold nanoparticles, obtained as described above, 50 mL of 1,4-bis(terpyridine-4'-yl)benzene solution in 2% aqueous acetonitrile (0.001 M) was added. Obtained suspention was centrifuged at 3000 rpm for 10 minutes. Formed powder was taken by decantation and dried under low pressure.

3.3 NaBH4 reduction of 4NP Catalyzed by 1,4-Bis(terpyridine-4'-yl)benzene/Gold Nanoparticle Composite

Aqueous solution of $NaBH_4$ (0.1 mL, $3 * 10^{-1}$ M) and aqueous 4NP solution (0.1 mL, $3 * 10^{-3}$ M) was mixed with 2.8 mL of water in the quartz cell (1 cm path length), leading a color change from light yellow to yellowgreen. Then, gold catalysts (0.25 mg, 20%) were added to the mixture and quickly placed in the cell holder of the spectrophotometer. The progress of the conversion of 4NP to 4AP was then monitored via the UV-vis spectroscopy by recording the time-dependent adsorption spectra of the reaction mixture with a time interval of 2, 5 and 10 min in a scanning range of 200 – 700 nm at ambient temperature.

3.4 Characterisation

Electronic spectra were recorded on a Hitachi U-2900 instrument. Microphotographs of samples were taken by a LEO 912 AB OMEGA transmission electron microscope (Carl Zeiss, Germany) with an operating accelerating voltage of 100 kV. The samples were prepared by applying a solution (1 – 2 μL) to copper mesh coated with formvar (d = 3.05 mm), which was then air dried. For thermogravimetry differential scanning calorimeter DSC 204 F1 Phoenix was used.

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