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INFLUENCE OF EXPERIMENTAL CONDITIONS ON DEPOSITION OF SILVER NANOPARTICLES ONTO SURFACE OF GRAPHENE OXIDE

WPLYW WARUNKÓW EKSPERYMENTALNYCH NA PROCES OSADZANIA NANOCZĄSTEK SREBRA NA POWIERZCHNI TLENKU GRAFENU

Present work describes the influence of silver nanoparticles precursor form as well as the impact of graphene oxide initial concentration on deposition of the silver nanoparticles onto graphene oxide. Borane dimethylamine complex (DMAB) was used as the reducing agent. It was observed that application of silver ammonia complexes as the silver nanoparticles precursor as well as alkaline solution effect in higher quantity of deposited AgNPs in comparison to deposition process with the use of silver(I) nitrate in acidic solution.

Praca przedstawia wyniki badań nad wpływem wybranych parametrów na proces syntezy i osadzania nanocząstek srebra na powierzchni tlenku grafenu. W badaniach uwzględniono wpływ następujących czynników: stężenie początkowe tlenku grafenu, stężenie początkowe prekursora oraz jego rodzaju. Jako reduktor jonów Ag(I) zastosowano dimetyloamino boran (DMAB). Stwierdzono, iż zastosowanie kompleksu amoniakalnego srebra jako prekursora, jak również zastosowanie środowiska alkalicznego skutkuje wyższą efektywnością procesu osadzania AgNPs na powierzchni tlenku grafenu w porównaniu do procesu prowadzonego z zastosowaniem azotanu(V) srebra(I) w środowisku kwaśnym.

1. Introduction

Preparation of hybrid materials of high photocatalytic [1], biologic [2] and electrocatalytic activity is one of the most important challenge for modern materials engineering. It is expected that this type of materials will exhibit high durability, thermodynamic stability and often high catalytic activity. Therefore, a lot of attention has been paid to synthesis of composite materials using different method among of them electrochemical [3-5] and chemical ones [6, 7]. It is known, that the graphene is one of the most promising material due to its high electrical [8] and thermal conductivity [8] as well as chemical resistance [9]. For the first time graphene was described by Hanns'a Petera Boehm'a et al. [10]. They have observed one dimensioned structure of carbon, which was later named as graphene. The next significant date for graphene was 2004 when A. Geim and K. Novoselov have described novel method of synthesis and separation of single layer structured carbon [11]. For this discovery they were awarded with Noble Price in 2010.

Due to the fact that graphene is chemically stable its modification is quite difficult. Graphene oxide was used for investigations described in the work because of its chemical

stability. Moreover massive production of graphene oxide is less expensive in comparison to graphene. Graphene oxide consists of sp^3 and sp^2 hybridized functional groups, what makes possible further chemical modification of its surface.

The selection of proper synthesis parameters enables size control of synthesized silver nanoparticles [12, 13]. Moreover modification of synthesis conditions allows on permanent deposition of AgNP's on graphene oxide. The last phenomenon is one of main challenge for modern chemical synthesis. Investigations describing synthesis of such kind of materials creates opportunities for producing Ag size controlled NP's – GO based hybrid materials of interesting, unique properties, including catalytic ones [14-16].

2. Experimental

The samples for XPS analysis were prepared by sequential drop-casting on Si wafer and evaporation of the solvent in vacuum drier (70°C). High resolution XPS spectra were recorded on a PHI 5000 VersaProbe II (ULVAC-PHI, Chigasaki, Japan) system using a microfocused (100 μm , 25 W) Al K α X-ray beam with a photoelectron take-off angle of 45°. A dual-beam charge neutralizer was used to compensate the charging

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effect. The operating pressure in the analytical chamber was less than 2×10^{-9} mbar. High resolution spectra were collected with analyzer pass energy of 11.75 eV. All XPS peaks were referenced to the neutral (C-C) carbon C1s peak at 284.8 eV. Spectrum background was subtracted using the Shirley method.

Zeta potential of the obtained composite material was determined using Zetasizer Nano ZS (Malvern). HR-TEM analysis were performed using (HR – TEM) – FEI TECNAI TF 20 X-TWIN. Moreover, UV-Vis spectra were registered using Shimadzu model U-2501 PC.

Analytic purity chemical agents were used in all experiments. Graphene oxide (GO), colloidal suspension with concentration 5 g/L purchased from Graphene Supermarket. As precursor of silver nanoparticles silver nitrate (AgNO_3 , Avantor Materials) was used. Borane dimethylamine complex 97% (DMAB, Fluka) was used as the reducing agent. The silver ammonia complex was synthesized as follow: required amount of silver nitrate was dissolved in water. Then appropriate amount of ammonium hydroxide was added to form silver ammonia complex. The 50% excess of ammonium hydroxide was used in reference to stoichiometry of this reaction.

3. Results

The synthesis of composite material consisting of graphene oxide and silver nanoparticles, was performed using cyclic reactor. For this purpose required amount of graphene oxide suspension was mixed with DMAB which was sonicated for 10 min. Then the solution was mixed with silver nanoparticles precursor in 1 to 1 volumetric proportion. Obtained solutions were analyzed spectrometrically with the use of XPS, DLS, and UV-Vis methods.

3.1. UV-Vis analysis of obtained materials

Fig. 1 presents UV-Vis spectra of solutions containing different initial concentration of GO B) and different mass ratio of Ag with GO solutions A).

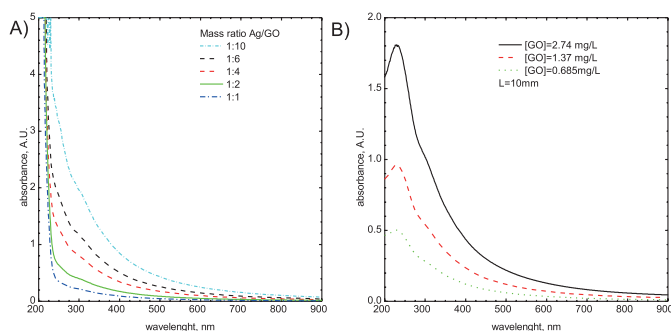


Fig. 1. A) UV-Vis spectra of solutions containing silver nitrate and graphene oxide B) UV-Vis spectra of graphene oxide

In Fig. 1B at the wavelength 233 nm a single peak can be observed. Visible absorption peak can be related to $\pi-\pi^*$ bonding, while observed at c.a. 290 nm inflection may be related to $n-\pi^*$ interactions [17, 18].

Fig. 2 shows UV-Vis spectra of the solutions containing

GO and AgNPs at different mass ratios. The increase of absorption intensity at 400 nm, which is related to plasmon resonans effect is observed [12, 19]. Plasmon resonance effect confirms course of reduction reaction of silver ions to the metallic silver. Changes in GO/Ag mass ratio results in displacement of peak maximum. There is a general agreement that the shift of absorption maximum can be related to changes in size and/or shape of synthesized particles [20].

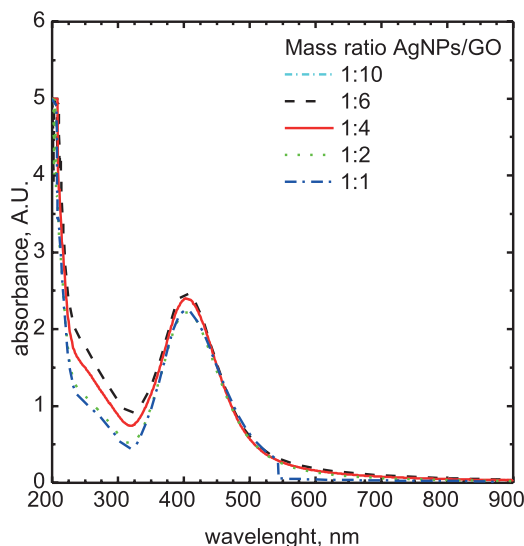


Fig. 2. UV-Vis spectra of colloid containing AgNPs/GO particles in acidic media

Fig. 3 shows spectra of silver nanoparticles deposited on graphene oxide (AgNPs@GO). There are visible absorption peaks at $\lambda = 400$ nm. The changes of absorbance intensity as well as a maximum absorption band shift can be observed (see. Fig. 3 B).

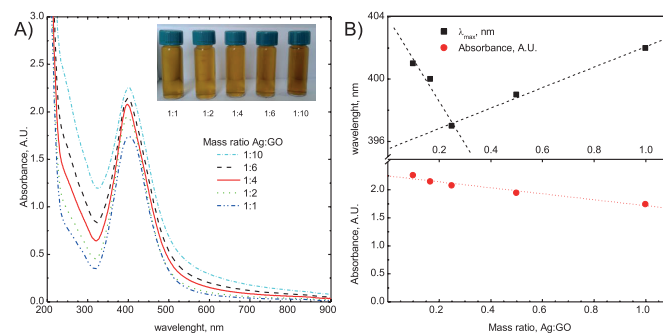


Fig. 3. UV-Vis spectra of obtained material in alkaline media A and changes in absorbance level as well as in shift of maximum absorption band B

Based on obtained results it can be concluded that GO plays an important role as stabilizing agent. It was observed that increase of GO initial concentration resulted in decrease of particles diameter.

Moreover, in Fig. 3 B (black points) two linear regions can be observed. The first one from 0.1 to 0.25 and the second one from 0.25 to 1 of Ag:GO mass ratio. Such an effect is unexpected. It should be pointed out, that silver ammonia complex was obtained by addition of ammonia hydroxide in 50

% excess. Then stock solution was dissolved using deionised water to obtain required concentration. The free ammonia ions can react with the functional groups present at the surface of GO through their reduction or salt formation [21]. In such case, obtained curve may represent the effect of neutralization of functional groups at the surface of GO. Preliminary, elimination of functional groups, facilitates deposition of AgNPs by elimination of strong negative charge from the surface of GO. It is known that GO as well as AgNPs exhibit strong negative charge. Moreover, the deposition is also possible due to the presence of cationic functional groups which are also eliminated by further addition of free ammonia. In case of lack of available active sites at the surface of GO, further particles growth is preferential. Therefore, decrease of absorbance level and the shift of maximum absorption are observed.

3.2. The analysis of surface charge of GO

The zeta potential of obtained material was determined by using Malvern ZetaSizer Nano ZS. Obtained results are presented in TABLE 1. As it is visible, the zeta potential of obtained materials in weakly acidic media is lower in comparison to those obtained in alkaline media. The differences between a zeta potential of pure GO and obtained composite material are negligible in alkaline solution, however in case of weakly acidic media observed differences are significant.

TABLE 1
Zeta potential of obtained material

| Mass Ratio Ag:GO | Zeta potential [mV] | |
|---------------------|---------------------|----------------|
| | Acidic media | Alkaline media |
| GO | -38.3±0.6 | -39.1±3.3 |
| 1:1 | -36.8±11.8 | -41.2±16.1 |
| 1:2 | -43.0±13.4 | -38.8±11.3 |
| 1:4 | -40.8±15.3 | -47.4±13.9 |
| 1:6 | -45.9±14.1 | -38.3±12.8 |
| 1:10 | -50.5±15.0 | -40.4±12.2 |

As it is visible GO amount strongly influences surface charge especially in acidic media. This effect is probably related to reduction reaction of functional groups on GO's surface. At Ag/GO ratio equal to 1:10 amount of uncovered functional groups with metallic silver is relatively high, which may result in increase of zeta potential. On the other hand surface charge is not related to amount of analyzed material. In such case the increase of zeta potential may be associated with formation of not adsorbed silver nanoparticles which are exhibiting a significant negative charge.

3.3. HR-TEM analysis of obtained material

Fig. 4 A presents HR-TEM image of obtained silver nanoparticles. It can be seen, that the particles size is below 20 nm. It is also visible that obtained nanoparticles exhibit spherical shape. As it can be seen, also 5 nm in diameter

AgNPs were formed. Such a particles size distribution was also confirmed by registered UV-Vis spectra, where a significant broadening of absorption spectra was observed. To investigate crystal structure, the FFT (Fast Fourier Transform) of HR-TEM analysis was performed. Obtained result is shown in Fig. 4 B.

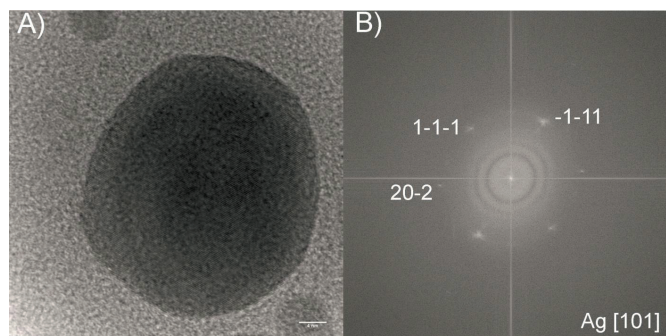


Fig. 4. HR-TEM analysis of obtained material A and B FFT analysis of obtained image

In the center of the picture, two rings were observed. Those rings are commonly called Thon rings, and are probably related to contamination of the sample effect. Moreover, a bright points are observed. Those points are related to crystal silver phase.

3.4. AgNPs adsorption test

The fraction of AgNPs deposited on GO surface was determined based on adsorption test. A simple test was performed to separate graphene oxide with deposited silver nanoparticles from not bonded nanoparticles. The test consists of 3 steps. The first one based on UV-Vis analysis of freshly prepared suspension, then the solution is filtered using 50 nm syringe filter and again analysis of the obtained filtrate was performed. As it was shown above, the particles size is below 20 nm. From this point of view, the AgNPs not bonded to GO should pass through syringe filter. Registered spectra are shown in Fig. 5 A and B.

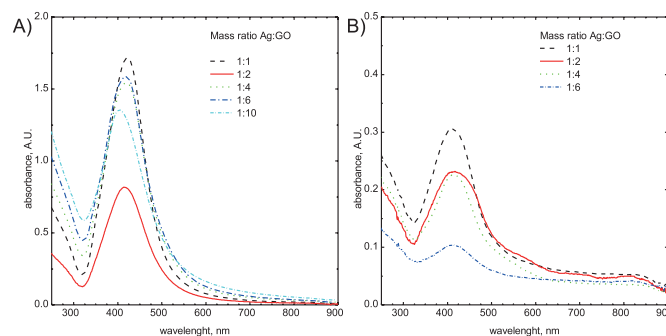


Fig. 5 UV-Vis spectra of the solution after filtration of the composite synthesised A) in weakly acidic media B) in alkaline media

As it can be seen in Fig. 5 A) the filtrate still contains a large amount of silver nanoparticles. The amount of silver nanoparticles decreases with increase of Ag/GO mass ratio. This clearly suggests that in weakly acidic media, deposition of AgNPs at the surface of GO is negligible. A contrary situation was observed in alkaline media. In this case a large majority

Atomic concentration [% at.] of the fitted components

| Sample | C=C | C-C | C-O | C=O | O-C=O | O | Ag | C/O ratio |
|----------|-----|------|------|-----|-------|------|-----|-----------|
| GO | 5.6 | 27.2 | 28.2 | 3.5 | 3.4 | 32.1 | - | 2.11 |
| AgNPs@GO | 4.8 | 28.2 | 27.0 | 3.7 | 2.9 | 32.1 | 1.3 | 2.08 |

of AgNPs is deposited on GO surface. In this case, also an influence of Ag:GO mass ratio was observed.

Results of UV-Vis analysis confirmed the conclusions based on zeta potential analysis. In acidic media the zeta potential measured was relatively higher in comparison to material synthesized in alkaline media. It is due to fact that silver nanoparticles exhibit high negative surface charge. Deposition of strongly charged silver nanoparticles is difficult due to GO negative charge.

3.5. XPS analysis of obtained material

The spectra registered at C1s region for graphene oxide and graphene oxide/Ag nanoparticles are very similar and each one can be fitted by five components (FWHM=1.2 eV): C=C (283.9 eV), C-C (284.8 eV), C-O (286.6 eV), C=O (288.0 eV) and O-C=O (288.8 eV) which are consistent with previous reports [22-24]. The spectra collected at Ag3d region for Ag nanoparticles containing sample exhibits one doublet structure where Ag3d_{5/2} peak (FWHM=1.1 eV) is centered at binding energy of 368.1 eV, which indicate Ag⁰ state [25, 26]. Atomic concentrations of fitted compounds are presented in Table 2 for both samples.

As it can be seen, the C/O ration after AgNPs deposition slightly decreased. It suggest, that the reduction of GO accrue.

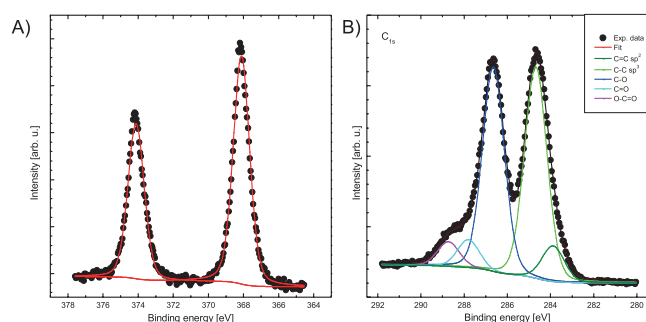


Fig. 6. A) High resolution Ag3d core-level spectra of silver nanoparticles deposited in graphene oxide and B) high resolution C1s core-level spectra of graphene oxide. The obtained data was fitted with five components as described in the legend

4. Conclusions

The influence of silver nanoparticles precursor as well as the influence of graphene oxide initial concentration were described in present work. As the reducing agent the borane dimethylamine complex (DMAB) was used. It was observed that application of silver ammonia complexes as the silver nanoparticles precursor as well as alkaline media effect in

higher level of AgNPs deposition in comparison to application of silver(I) nitrate in acidic media as the precursor.

Moreover, a simple catalytic test of obtained material was performed. The catalytic test procedure was described in previous papers [6, 27]. However obtained AgNPs@GO material does not exhibit catalytic activity in the process of glucose electrooxidation in opposite to silver wire.

Acknowledgments

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