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ARTICLE

Platinum-Containing nanocomposites based on Humic substances from brown coal

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Abstract: *In the presentreport we look intosynthesized silver and gold-containing nanocomposites based on humic substances. The composition and properties of humic substances isolated from brown coal in Mongolian deposits have beenestablished. The methodology of obtaining platinum-containing nanobiocomposites using a matrix of humic substances is described. Our investigation shows thattheir composition and structure are characterized by a complex of modern physicochemical methods, such as X-ray, energy dispersive spectral microanalysis, infrared spectroscopy (IR), ultraviolet spectroscopy (UV), X-ray diffraction analysis, Scanning electron microscopy (SEM).*

Keywords: *brown coal; humic substances; nanoparticles; platinum;*

INTRODUCTION

The search for new functional materials is one of the defining characteristics of modern science and technology. Metal nanoparticles (MNPs), in particular, platinum nanoparticles (PtNs) can possess a wide range of properties that can be used for many practical applications. Platinum is one of the rarest and most expensive metals. It has a high corrosion resistancequality and numerous catalytic applications including in automotive catalytic converters and petrochemical cracking catalysts. Platinum nanoparticles are usually used in the form of colloid or suspension in a fluid. They are the subject of extensive research due to their antioxidant properties.

Previously, to begin withwe studied the characteristics of water-soluble silver and gold containing nanocomposites with a variable amount of metal component based on reducing and stabilizing matrix of humic substances isolated from various deposits in Mongolia [1-4]. Their matrices are activated byincreasingthe activity of all studied humic substances in alkaline medium hydrolysis.

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The humic substances of therapeutic mud have the greatest reducing and stabilizing ability from among other investigated objects [5-27]. For gold nanoparticles, the least-oxidized HS isolated from coals have the greatest reducing ability [11]. Humic substances and silver- and gold-containing nanocomposites exhibit high antioxidant activity, comparable to well-known antioxidants [26].

Humic substances from coal and sediments can be defined as surface active substances based on literature and our previousstudies. Many industrially produced humic materials hadlittle or no impact of surface tension, whereas humic substances isolated from natural environments (soil, coal water, sediments) exerted a large impact of surface tension. Surfactants playa major role in the formation of metal-containing nanocomposite.

Due to its high redox potential, humic substances can function as a reducing agent for noble metal ions, including platinum. Chemical methods for synthesizing nanoparticles using platinum hydrochloric acid as precursors and polymeric biomatrices as stabilizers are the most common and are acceptable in the development of promising bio-nanomaterials. Due to potential technological interests of PtNs, the synthesis and study of nanoparticles have been the object of research carried out in the last few years byour team.In particular, studies intonanostructured materials show a strong dependence of their properties on size and shape. For example, the size effect on the catalytical efficiency is known,whilethe perspective effect on catalysis by the shapes of metal nanoparticles is yet to be determinedand so is under investigation [28-31].

MATERIALS AND METHODS

Isolation of humic substances

Long-term stable platinium-containing nanocomposites have been synthesized based on humic substances extracted from brown coal of Baga Nuur deposit inMongolia. Humic substances isolated from brown coal using alkaline extraction procedure have beenreported by Dolmaa et al.The isolation was carried out as follows: brown coal (10 g) was dried in air and dissolved in HCl (100 mL, 10%) solution at room temperature for one hour, and in water bath heated for 2 hours. The mixtureafter coolingwas filtered and washed with distilled water. Residues were extracted with NaOH (0.2 N) at 60°C overnight. Supernatant were recovered by centrifugation and filtration pH was adjusted to 1 using HCl (0.6 N). Produced humic substances were separated from supernatant and washed with distilled water until Cl- was removed, and then they were driedat 80°C.

Synthesis Method

The Pt-containing nanocomposites were synthesized by the reaction of Pt ions with humic substances in the aqueous alkaline medium [3, 5, 8, 10,11]. Humic substances of coal (15 g each sample) were dissolved in an aqueous solution of sodium hydroxide and mixed with platinum precursor solutions of platinum chloride ($H_2P_tC_{16}$), the reaction was carried out bystirring the solution for 120-180 minutes at a temperature of 90°Celcius.

The IR absorption spectra were recorded as KBr pellets on a Bruker Vertex 70 spectrophotometer.The optical absorption spectra of aqueous solutions of nanocomposites and initial humic substances were recorded on a PerkinElmer Lambda 35 spectrophotometer in a quartz cuvette (path length, 1 cm).

The X-ray diffraction patterns were recordedonaBrukerD8Advancediffractometer (CuKαradiation, Goebel mirror). The unit cell parameters and CSR for each sample were averaged for three independent measurements and calculated using the DIFFRACplus EVA 13. Software package.

SEM. Scanning electron microscopy was performed on a Hitachi TM 3000 scanning electron microscope with an SDDXFlash 430-4 detector.

HS-coal, (wt %): C, 53.6; O, 37.1; O / C, 0.69; H, 3.9; Si, 4.9; Al, 2.71; S, 0.4; Fe, 0.9; IR: 3432 (OH); 2924 (C = C); 2855 (C-C); 1801, 1717, 1700 (C = O); 1623 (HOH), 1455, 1436, 1418, 1418, 1388, 1339 (Ar); 1211 (C-O), 1032 (C-O carbohydrates); 911 (β-glycosidic bonds of pyranose rings).

RESULTS AND DISCUSSION

Humic substances from studied Mongolian resources are black crystalline powders with ash content (20-22%). The main mineral elements in all studied humic substances are Si, Al, Fe and the amount of Na increasedto 8.7% (initially 0.2%) caused by formation of sodium humates when the samples were dissolved in alkaline. The degree of oxidation (O/C) varies in the ranges 0.69-0.92. IR spectroscopy of platinum containing nanocomposites revealed the following: HS-coal/Pt: IR (v, cm-1): 3428 (OH); 2923 (C = C); 2856 (C-C); 1574 (OH), 1445, 1380, (aromatic ring); 1031 (C-O carbohydrates); 911 (β-glycosidic bonds of pyranose rings).

The final product yield was high (95-99%), the amount of platinum in nanocomposite varies by 2.3-5.5% depending on the amount of precursor and the stabilizing capacity of the HS source (Table 1). Variation ofthe quantitative content of nanoscale metal in the composition of nanocomposites was carried out by changing the ratio of precursor of platinum/HS. Nanocomposites based on all studied samples are capable of stabilizing 1.2 to 5.5% of platinum in a nanoscale state.

Table 1. Ash elements in platinum containing nanocomposites

Samples	yield, %	Pt, %	Na, %	Si, %	AI, %	S, %	Fe, %	N, %	C, %	O, %	O/C
HS-coal	-	-	-	4.9	2.71	0.4	0.9	-	53.6	37.1	0.69
HS-coal^1	95.6	2.3	8.2	5.6	2.8	0.3	1.0	2.4	42.6	34.3	0.81
HS-coal^2	99.5	3.8	8.7	4.3	2.3	0.3	0.6	2.6	42.1	35.4	0.84
HS-coal^3	95.9	5.5	8.3	4.2	2.2	-	0.4	3.5	39.4	36.3	0.92

Presumably, the recovery of platinum from $H_2P_tCl_6$ occurs due to oxidizable carbonyl groups with different aliphatic, aromatic and phenolic hydroxyl groups in a significant amount (2.7-4.1%) in the composition of HS.This assumption is confirmed by the degree of oxidation (O/C) of HS fromcoal andthe synthesis of nanocomposites increases by 30% depending on the source of HS, which is caused by simultaneous hydrolysis and interactive oxidation-reduction of HS with a precursor of platinum.

Figure 1 shows the ratio of oxidation state (O/C) of platinum containing nanocomposites. Comparison of data in the diagram shows that HS and their nanocomposites have a unique molecular composition in the range of 0.69 to 0.92. This indicates the presence of aliphatic carbonyl- and carboxyl-containing components, which are linearly related to the observed oxygen distribution among HS compounds.

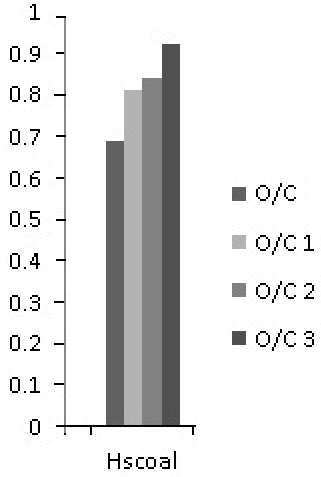

Figure 1. The ratio of oxidation degree (O/C) of initial HS and platinum containing nanocomposites: HS extracted from coal (1- 2.3; 2-3.8; 3- 5.5%Pt).

A comparison of data in the diagrams of oxidation degree for silver and gold nanocomposites shows that HS from various sources and their nanocomposites have a similar dependence [8].

The composition and structure of new nanocomposites have been studied using modern physico-chemical methods, including spectral (UV/vis, IR, X-ray phase) analysis.

X-ray diffraction analyses confirm the presence of zero-valence platinum nanoparticles in Pt-HS nanocomposites. The diffraction patterns of the nanocomposites show a halo of an amorphous phase of humic substances in the range of angles 15-30°, and also three intense reflections at 39.8°, 46.2° and 67.4°, referring to the faces of a face-centered cubic platinum lattice.

The average size of the coherent scattering region of platinum nanoparticles of coal humic substances are 6.0 nm based onXRDanalysisthatusesScherrerequation.

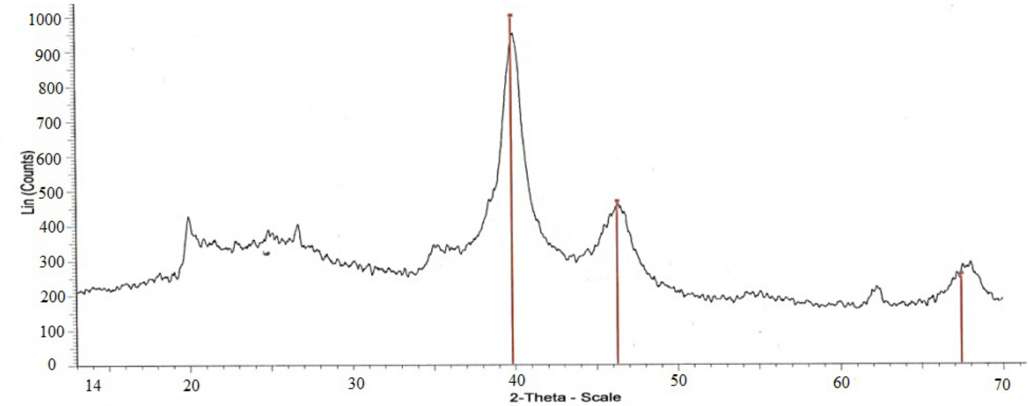

Figure 2. Diffractogram of a platinum nanocomposite based on HS extracted from coal (containing 5.5% platinum).

Previous study confirmed that HS is characterized by a high intensity of light absorption, which is due to the presence of double carbon-carbon and carbon-oxygen bonds, whichcorrelates well with the degree of aromatization of the HS.Light adsorption of all samples in the UV-Vis region, a decrease in the absorption intensity with an increase inthe wave length was observed. Plasmon absorption of platinum nanoparticles should be manifested in the region of 220 nm, where HS have a strong absorption (Fig. 3).

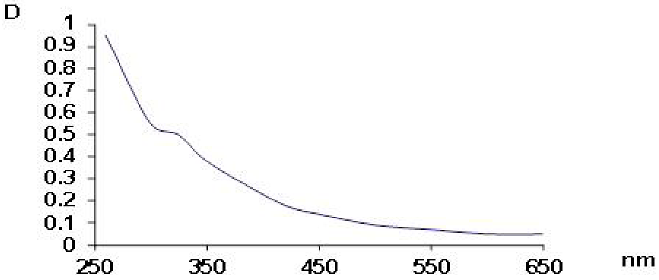

Figure 3. Electronic spectrum of Pt containing nanocomposite based on HS isolated from coal

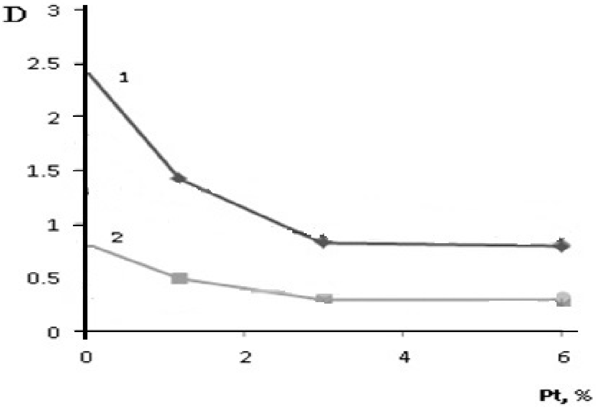

Figure 4. Color input (absorption at 465 and 650 nm) of initial HS from various sources withplatinum nanocomposites, (1-HS-coal/465, 2-HS-coal/650)

It is known that plasmon resonance of nanoscale platinum is observed in the 230 nm region [27]. Since the source HS itself also has high absorption in this region (Fig. 4), it is not possible to use electron spectroscopy data for direct characterization of platinum nanoparticles.

Table 2. The color factor E465/E650 of platinum nanocomposites based on HS from coal

Sample	E_{465}/E_{650}			
	Initial HS	HS/ Pt (2.3 % Pt)	HS/ Pt (3.8 % Pt)	HS/ Pt (5.5% Pt)
HS-coal	2.99	2.90	2.85	2.85

Signals were observed inIR spectra of nanocomposites in the range of 1800-1600 cm-1but theydiffer from the spectra of initial HS samples, which indicates a change in theirchemical structure. Thus, in the IR spectra of nanocomposites, the absence of peak in the 1715-1713 and 1704 cm-1 indicates there are aldehyde groups, which is presented in IR spectra of initial HS. This is indicative ofa reduction in the number of aldehyde groups in platinum-containing nanocomposites as a result of their expenditure on metal reduction. The disappearance of absorption intensity at 1700 cm-1, cofactor with a significant increase in absorption at 1385-1379 cm-1 observed in IR spectra of nanocomposites, which were an indication of the oxidative transition of aldehyde groups to carbonyl due to their consumption of metal reduction.

Consequently, the reduction of platinum from the precursor to zero-valent state occurs due to phenolic and alcoholic hydroxyl groups capable of oxidation, which are a significant part of humic substances, as well as carbonyl groups.The phenolic, carboxyl and amino groups present in HS obviously act as stabilizing agents.

A study of the morphology of HS/Pt showed their common unidirectional difference from the morphology of initial HS to the decrease in particle size and greater looseness of the precipitate, as demonstrated by the examples of nanocomposites of platinum based on coal HS (Figure 5).

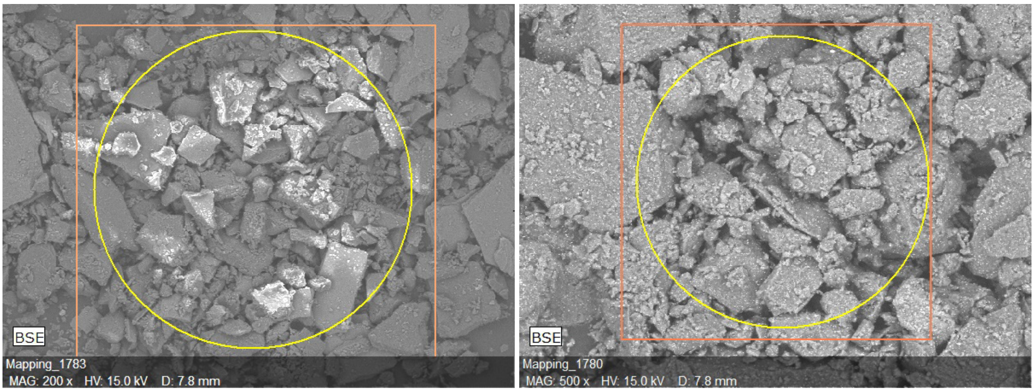

Figure 5. Morphology of initial HS sample (magnified 200) and platinum nanocomposite based on HS coal (magnification 500).

Thus, the use of humic substances of various origins as a matrix makes it possible to obtain long-term stable nanocomposites containing nanoparticles of zero-valent platinum, characterized by the same type of loosened morphology of powder samples with a lighter color as compared to the initial HS.

CONCLUSIONS

Due to its high redox potential, humic substances can function as a reducing agent for noble metal ions, including platinum. Chemical methods for synthesizing nanoparticles using platinum hydrochloric acid as precursors and polymeric biomatrices as stabilizers are the most common and acceptable practice in the development of promising bionanomaterials.

The new methodological approach developed by our team, based on the specific adsorption of biogenic polymer to the surface of nano-sized metal aggregating from aqueous solution of inorganic nuclei, which provides self-organization of the resulting hybrid inorganic-organic nanostructures with fine regulation of their dimensionality, can be used to simulate the formation of organomineral nanocomposites in nature and can beused for the analysis of the origin of dispersed ore formations in geology.

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