ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2013, Vol. 39, No. 7, pp. 487–492. © Pleiades Publishing, Ltd., 2013.
Original Russian Text © I.L. Laure, S.V. Tkachev, E.Yu. Buslaeva, E.V. Fatushina, S.P. Gubin, 2013, published in Koordinatsionnaya Khimiya, 2013, Vol. 39, No. 7, pp. 387–392.

The Coordination Chemistry of Graphene Oxide: Interactions with Metal Ions in Water

I. L. Laure, S. V. Tkachev, E. Yu. Buslaeva*, E. V. Fatushina, and S. P. Gubin
Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,
Leninskii pr. 31, Moscow, 119991 Russia
**e-mail: buslaeva@igic.ras.ru*

Received December 24, 2012

Abstract—Interactions of graphene oxide with Ag^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Bi^{3+} ions were studied. The minimum (threshold) ion concentrations required for the interaction with graphene oxide to occur were determined in a series of experiments. A possible model of the interaction between the metal ions and the oxygen-containing groups of graphene oxide was proposed.

DOI: 10.1134/S1070328413070038

INTRODUCTION

In the last few years, graphene has been actively studied by the scientific community. This unique material is attractive by its mechanical, electrical, thermal, and optical properties. To get the greatest possible benefit from the use of graphene, its large-scale production should be provided.

A method that allows the production of graphene and graphene-based materials in appreciable amounts involves a multistep transformation of graphite into graphene oxide (GO) followed by its reduction [1]. Graphene oxide is a polyfunctional compound: it bears various oxygen-containing groups and is a conjugated π-system consisting of many fused aromatic rings.

The presence of oxygen-containing surface functions in the plane and on the edges of graphene oxide allows its dispersion in water and organic solvents, thus ensuring wide scope for the design of GO-based materials.

It has been demonstrated that modification of this precursor with metal ions affords high-strength macroscopic objects [2]. Graphene oxide is a 2D nanoentity belonging to a new class of dispersible polyaromatic systems suitable for conducting a variety of chemical syntheses. Apart from its unique properties, GO is an accessible product and hence can find wide use in diverse areas [3].

Heavy metal ions in waters of various origins present a challenge for they are very toxic and nonbiodegradable and tend to accumulate in living organisms or a food chain. The copper(II) ion, a toxic heavy metal, is one of the most frequently encountered metals of great concern. Many agricultural chemicals and fertilizers contain copper and pollute soils when in use [4]. These ions should be removed from waste water prior to its discharge into the environment. A number of technologies are available for removal of heavy metal ions from waste water. They include the use of ion-exchange membranes, reverse osmosis, adsorption, etc. Adsorption is regarded as one of the most promising and widely employed methods because of its low costs and efficiency [5]. Some materials such as activated charcoal, ashes, peat, zeolites, biomaterials, alum, manganese oxide, peanut shells, and resins are known to adsorb heavy metal ions from aqueous solutions. Graphene oxide is an oxygen-rich material, is produced by oxidation of graphite with strong oxidants, and has an extended layered structure with hydrophilic polar (–OH, –COOH, and epoxy) groups. The large surface area [6] and the presence of many functional groups make GO promising as a sorbent of metal ions.

EXPERIMENTAL

China natural graphite (99.9% C) ground in a ball mill to a grain size of 200–300 μm served as a starting material for the preparation of GO. Reagent-grade metal salts ($Bi(NO_3)_3 \cdot 5H_2O$, $Fe(NO_3)_3 \cdot 9H_2O$, $FeCl_2 \cdot 4H_2O$, $CuCl_2 \cdot 2H_2O$, and $AgNO_3$) were used.

The preparation of the target product can be divided in three steps.

(a) Preparation of graphite oxide (GrO) by modified Hummers' method, with conversion to gram of natural graphite. The product was isolated and dried at <50–60°C for 6 h (for details, see [7]).

(b) Preparation of graphene oxide (GO). The product obtained was dispersed with ultrasound. A weighed

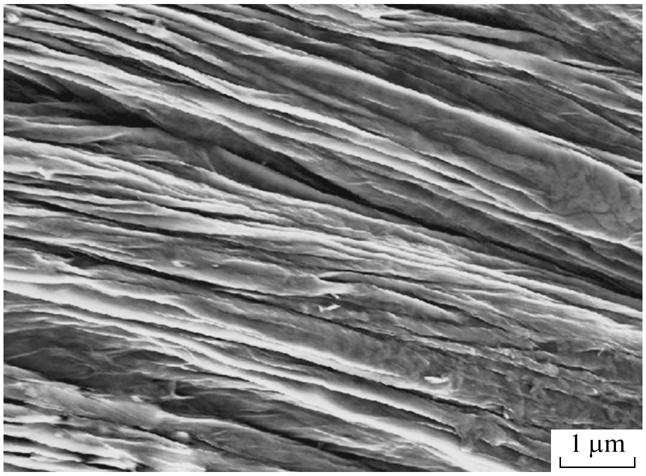


Fig. 1. Microstructure of GO.

sample of GrO (0.4–0.5 g) was placed in a 250-mL cylindrical beaker and distilled water (150 mL) was added. Then GrO was exposed to powerful ultrasound (20.4 kHz, specific power 0.1–1 W/cm^3) for 15 min. The resulting dispersion of graphene oxide was centrifuged (6000 rpm, 10 min) and the final product was isolated and dried at 70°C for 6 h.

(c) Interactions of GO with metal ions. A 100-mL beaker was charged with a steady-state dispersion of GO ($c = 1$, 2, or 3 mg/mL) in water (50 mL). Then a certain volume of a solution of a metal salt was added dropwise. The resulting dispersion was exposed to ultrasound for 5 min using standard parameters. The exposure yielded a black flaky precipitate from which the transparent supernatant was decanted. The solid precipitate was washed with water five times greater in volume. The precipitate was transferred to a Petri dish and left in air at room temperature for 12 h.

Comparison of the minimum concentrations of the metal ions for modification of GO ($c_{GO} = 1$ mg/mL, $V_{GO} = 50$ mL)

Metal ion	Starting metal salt	Minimum metal ion concentration (mol/mL) required for sedimentation
Bi^{3+}	$Bi(NO_3)_3 \cdot 5H_2O$	2.8×10^{-5}
Fe^{3+}	$Fe(NO_3)_3 \cdot 9H_2O$	4.7×10^{-5}
Fe^{2+}	$FeCl_2 \cdot 4H_2O$	2.3×10^{-4}
Cu^{2+}	$CuCl_2 \cdot 2H_2O$	2.8×10^{-4}
Ag^{+}	$AgNO_3$	1.8×10^{-3}

RESULTS AND DISCUSSION

The principal result of the present work is rapid sedimentation of dispersed graphene oxide in the presence of metal ions.

The starting material for the preparation of GO is graphite whose properties and characteristics are described in detail in many monographs and reference books [8, 9].

Preparation of graphite oxide (GrO) and graphene oxide (GO) and their characterization. Graphite oxide is extensively characterized in [7]. For better lamination of GrO, we used ultrasound to obtain GO flakes consisting of one to several layers. The exposure to ultrasound resulted in steady-state dispersions of GO in different solvents such as water, isopropyl alcohol, chloroform, DMF, and THF. It is known that the dispersibility of GO and the steady state of its dispersions depend on the oxidation state of the starting GrO and the solvent [10–12].

The microstructure of GO was examined using scanning electron microscopy (SEM) (Fig. 1). We found that GO has a layered structure. The presence of oxygen-containing groups (C=O, C–O, OH, C–OH, and C(O)C) in GO was confirmed by IR and X-ray photoelectron spectroscopy (XPS) (given below). IR (ν, cm^{-1}): 3214 ν(–OH and H_2O), 1721 ν(C=O), 1621 ν(H_2O), 1562 ν(C=C), 1348 ν(C–OH), 1031 ν(C–O), 984 ν(C(O)C).

Atomic force microscopy (AFM) studies revealed that graphene oxide flakes have lateral dimensions from 0.1 to 4 μm and that the minimum thickness is 1.5 nm (~2–3 oxidized graphene layers) (Fig. 2). The topographical images show distinct folds of separate flakes and “stacks” of several flakes; the dark valley in the central part is an irremovable artifact of the com-

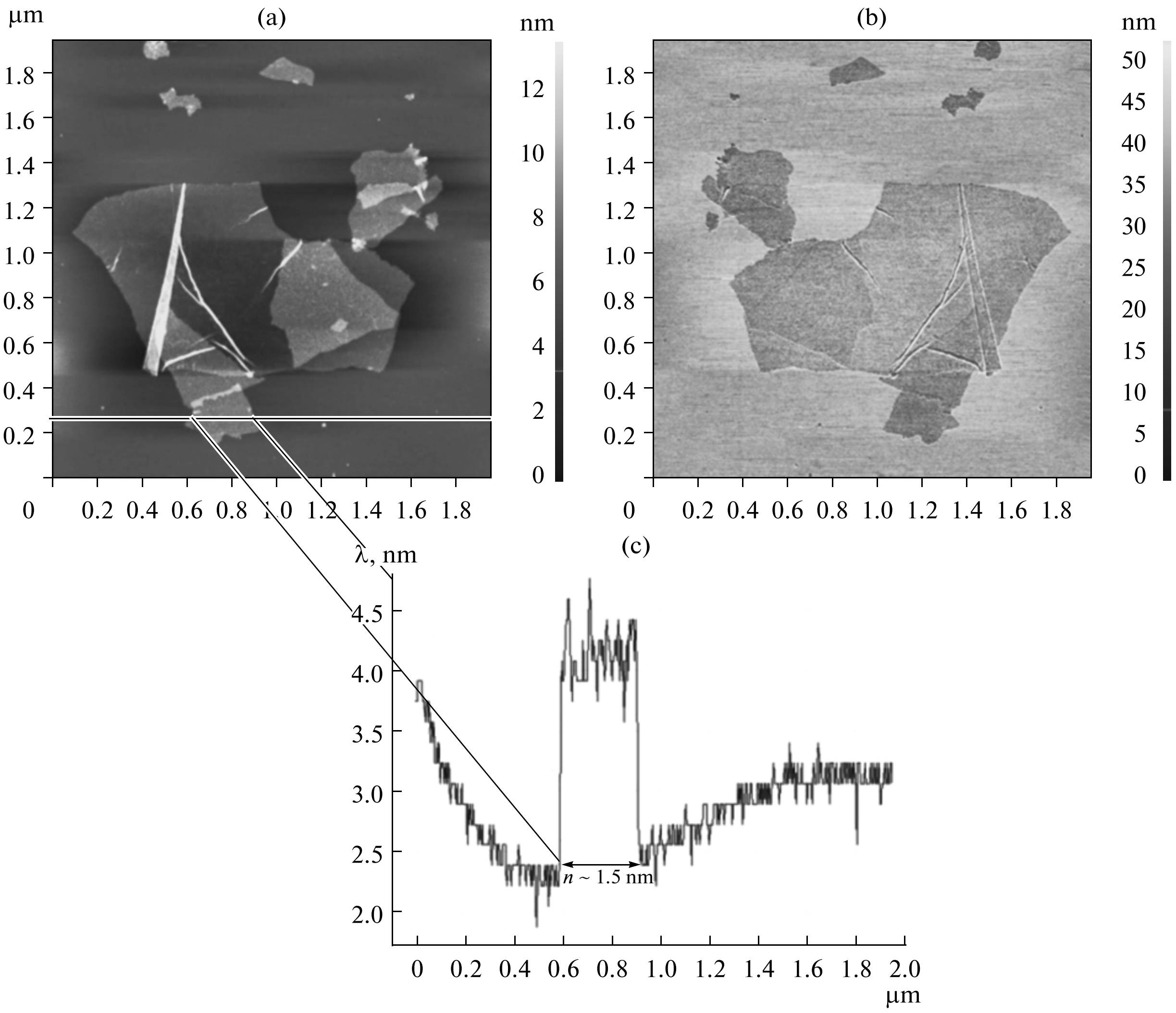


Fig. 2. AFM images of GO flakes from aqueous dispersions: (a) topographical mode, (b) phase mode, and (c) cross-section of a GO flake.

puter processing. In reality, the sheet is absolutely flat (see the phase image).

Interactions of graphene oxide with metal ions and characterization of the samples obtained. We determined the minimum (threshold) concentrations of each metal ion (Ag^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Bi^{3+}) that are required to initiate sedimentation upon the interaction with GO dispersions of different concentrations ($c = 1$, 2, and 3 mg/mL).

We found that the metal ion concentration required for complete sedimentation of a GO dispersion is inversely related to the ion charge. For a dispersion with $V_{GO} = 50$ mL and $c_{GO} = 1$ mg/mL, these concentrations are 5×10^{-5}, 3×10^{-4}, and 1.8×10^{-3} mol/mL for the metals in the oxidation states +3 and +2 and for Ag(I), respectively (table).

Also we discovered a relationship between different GO concentrations and the minimum concentration of a metal ion that initiates sedimentation. For instance, for Cu^{2+} at $c_{GO} = 1$ mg/mL, the required concentration of the metal ion is 2.8×10^{-4} mol/mL. When c_{GO} is twice as high, the metal concentration should be doubled. This relationship was verified for all the ions involved and $c_{GO} = 1$, 2, and 3 mg/mL. Some experiments were carried out for a lower GO concentration (e.g., 0.5 mg/mL). In all cases, the results obtained are similar, showing a distinct dependence with an increase in the GO concentration.

It should be noted that the coordination of metal ions to GO results in prompt sedimentation. After the sedimentation and filtration, the filtrate was analyzed for the presence of metal ions. Atomic emission spectroscopy (AES) studies revealed no metal ions in the

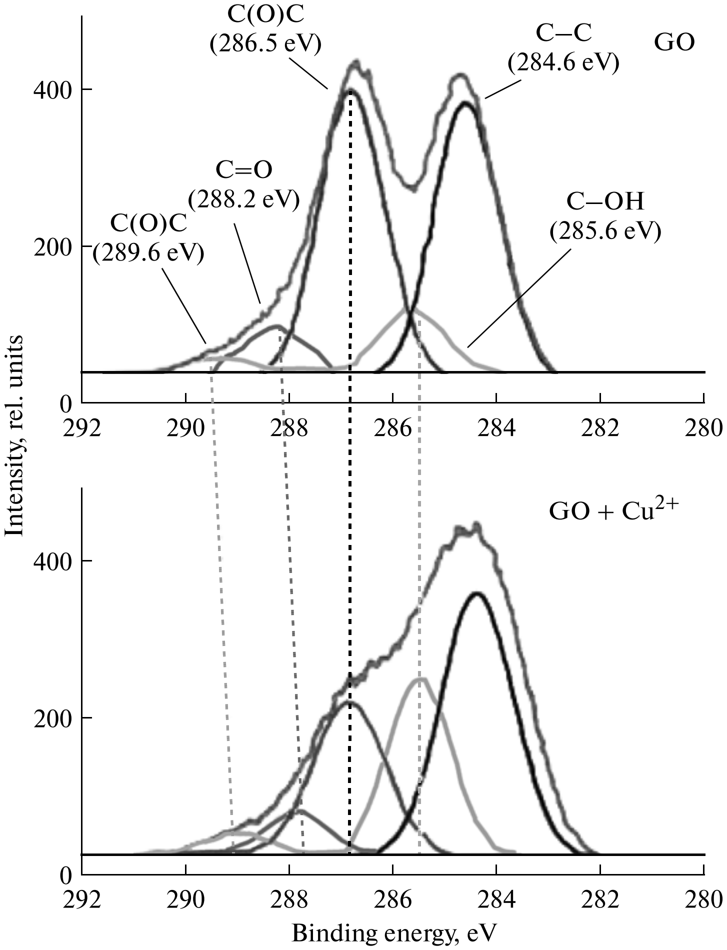


Fig. 3. X-ray photoelectron spectra (C1*s*) of GO and GO + Cu^{2+}.

aqueous phase, which suggests their complete coordination to GO.

The samples GO + Cu^{2+}, GO + Fe^{2+}, and GO + Fe^{3+} were also examined by XPS. The X-ray photoelectron spectra (C1*s*) of the initial GO and the modified compound are shown in Fig. 3. The spectrum of GO shows two distinct peaks with binding energies of 284.6 and 286.5 eV, which correspond to the C–C and C(O)C groups [13]. For accurate description of the spectrum, three other states with binding energies of 285.6, 288.2, and 289.6 eV should be added (C–OH, C=O, and C(O)O, respectively [13]).

Taking into account that the peak at 286.5 eV corresponds to the C(O)C group and its relative concentration, one can state that more than half of all the carbon atoms are bound to oxygen and that the greater energy contribution (about 70%) is made by epoxy groups. The oxygen concentration determined from the element sensitivity factors is 28.2% in GO, which is in some agreement with the data from C,H,N-analysis.

The XPS spectrum of the GO modified with metal ions noticeably differs in the intensity of additional states from the spectrum of the initial GO sample. The differences include a reduced (nearly by two) intensity of the peak due to C(O)C, a higher peak due to the C–OH group, the shifts of the centers of the peaks, and slight (compared to the aforementioned peaks) changes in the intensities of the peaks due to the C=O (287.8 eV) and C(O)O groups (289.0 eV). Similar results were obtained for the GO samples modified with Fe^{2+} and Fe^{3+} ions.

It can be concluded from the above XPS data that the epoxy groups undergo opening upon the coordination to metal ions, which results in a decreased number of epoxy groups and an increased number of hydroxide groups. The shifts and partial changes of the peaks due to the C=O and C(O)O groups are characteristic of coordination of carboxyl groups to metal ions. One can believe that the edges of GO molecules bear bridging groups and the interior metal ions interlink separate layers.

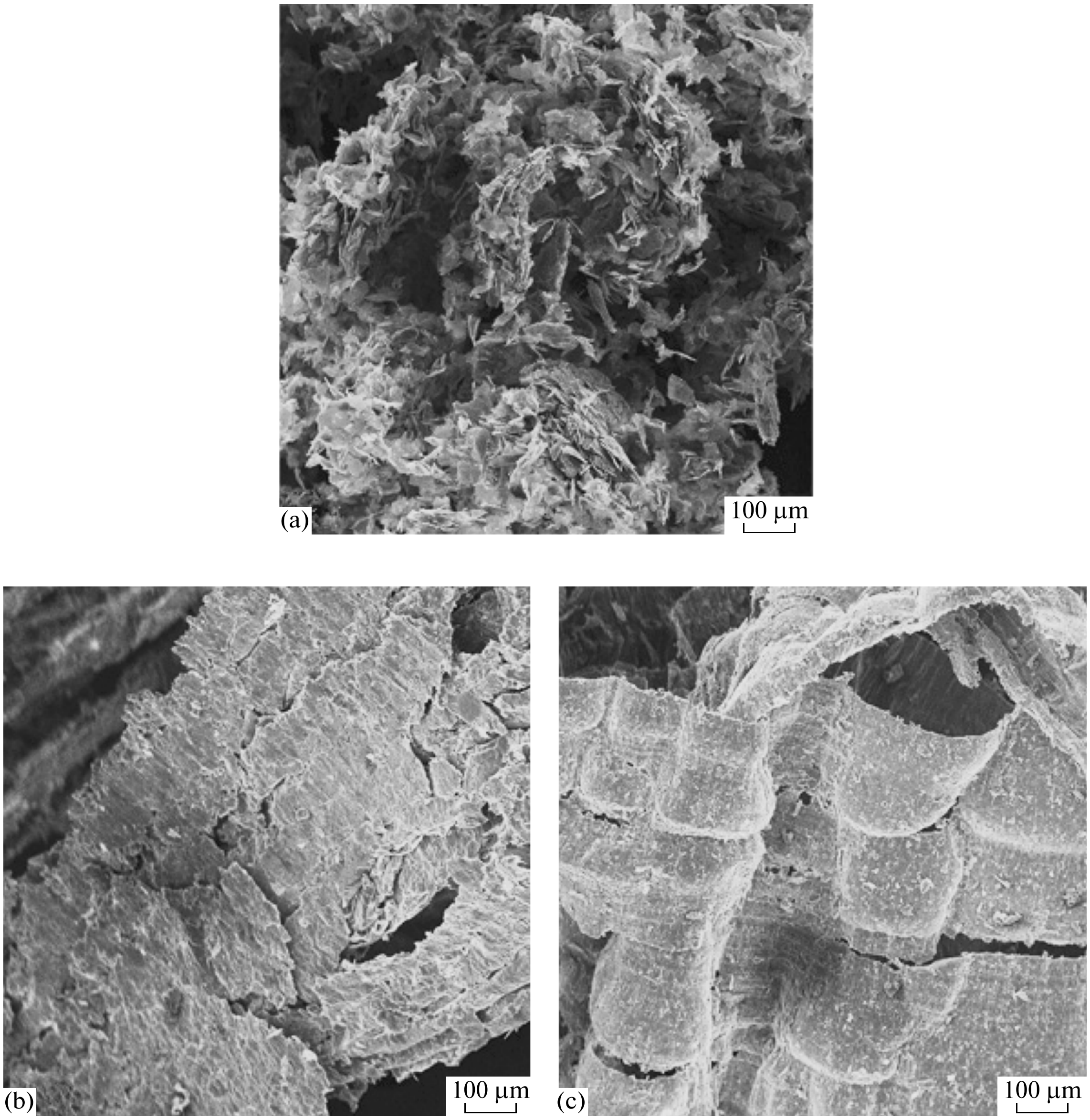


Fig. 4. SEM images of (a) the initial GO sample, (b) GO + Cu^{2+}, and (c) GO + Fe^{3+}.

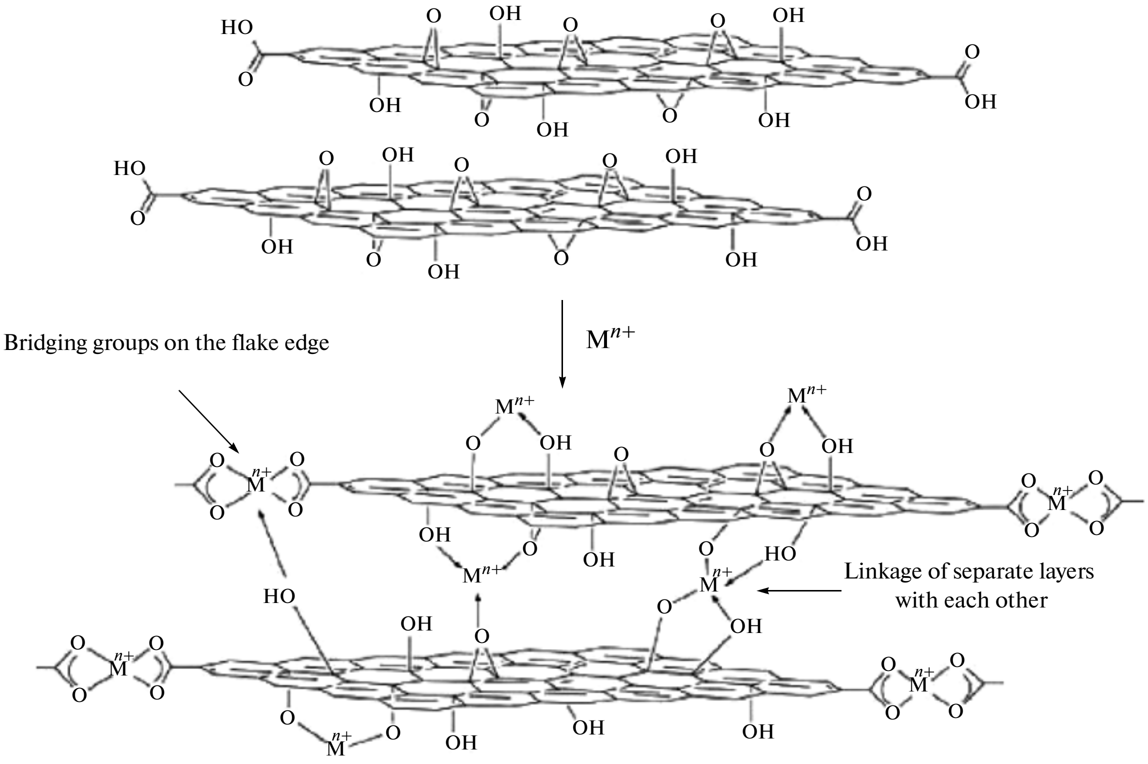
Such a structure of the precipitate is confirmed by the IR spectra showing a weaker C(O)C peak (984 cm^{-1}), a virtually the same C=O peak (1721 cm^{-1}), and a substantially higher C–OH peak (1348 cm^{-1}).

The GO samples modified with the Cu^{2+} and Fe^{3+} ions were examined by SEM. The SEM images (1000 × 1000 μm) of the initial and modified GO samples are shown in Fig. 4. For clarity, the photomicrographs are displayed in the same scale (100 μm). It can be seen that the initial GO has a layered structure but flakes are usually arranged randomly. However, coordination to metal ions causes individual GO flakes to unite into 3D frameworks.

The formation of similar 3D structures has been noted in [14, 15]. Presumably, the interactions of metal ions with GO occur in two ways (Fig. 5): through bridging groups on the flake edges and through epoxy and hydroxyl groups on separate layers.

Interlayer linkage through the metal atoms accounts for further formation of 3D frameworks from GO flakes.

To sum up, we found that GO interacts with Ag^+, Cu^{2+}, Fe^{2+}, Fe^{3+}, and Bi^{3+} ions and determined the minimum (threshold) ion concentrations required for



Bridging groups on the flake edge

M^{n+}

Linkage of separate layers with each other

Fig. 5. Model of the interactions of graphene oxide with metal ions.

sedimentation of GO from its dispersion in water. The modified GO samples were studied by a number of physicochemical methods. We proposed a possible model of coordination of the metal ions to oxygen-containing groups of GO. Based on the results obtained, one can believe that GO can be used as an efficient sorbent of metal ions from aqueous solutions.

ACKNOWLEDGMENTS

This work was supported by the Russian Foundation for Basic Research, project nos. 11-03-93962-RSA and 12-03-00533, and Department of Chemistry and Materials Science of RAS (grant no. OKh 2.7).

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Translated by D. Tolkachev