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Immobilization of In_2O_3 nanoparticles on the surface of reduced graphene oxide

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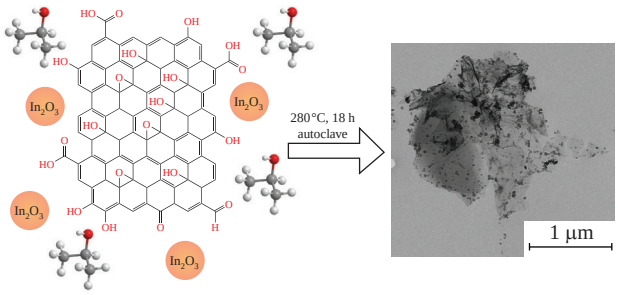
This communication describes a new method for immobilizing indium oxide nanoparticles (~20 nm) on the surface of reduced graphene oxide. Dispersion of graphene oxide with added In_2O_3 nanoparticles was treated in supercritical isopropanol, both a reducing agent of graphene oxide and a reaction medium. The resulting nanocomposite was characterized by different methods of physical and chemical analysis.



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A new class of materials based on graphene and its derivatives attracts considerable research interest due to the new properties obtained by combining these materials with different nanoparticles.[1–3] Among the most studied compounds are semiconductor materials with nanoparticles of metals or their oxides, which can be uniformly distributed on the surface of a graphene sheet.[4–6] In_2O_3 is an important n-type semiconductor with a bandgap of 3.6 eV.[7] Due to its strong interaction with gas molecules NH_3 and NO_2, it is possible to create new optoelectronic devices and gas sensors based on In_2O_3.[8,9] Also, In_2O_3 nanoparticles can act as a new efficient catalyst for the oxygen evolution reaction.[10] Further, materials based on indium oxide and reduced graphene oxide can be used for CO_2 reduction[11] or electrocatalytic nitrogen fixation.[12] Developing new synthesis methods for obtaining indium oxide on graphene or graphene oxide is a good challenge.

Supercritical fluids as alternative reaction media are interesting for their availability and environmental friendliness.[13–15] They have intermediate properties between gases and liquids, low viscosity, high mass transfer coefficients and the ability to dissolve depending on pressure.[16] In our works, we investigated the effect of supercritical isopropanol (SCI) on magnetite and noble metal nanoparticles deposited on the surface of graphene oxide.[17,18] This communication describes a new method for depositing In_2O_3 nanoparticles on reduced graphene oxide using supercritical technology. Despite the rather harsh synthesis conditions, it is shown that indium oxide nanoparticles (In_2O_3 NPs) can be retained on the graphene surface.

As shown earlier, the treatment of magnetite nanoparticles deposited on the surface of graphene oxide in supercritical isopropanol leads to the disappearance of oxygen-containing functional groups, which can act as ligands for oxide nanoparticles.[17] Magnetite nanoparticles were not removed from the graphene oxide surface after reduction; however, they migrated over the surface of the sheet, which led to agglomeration and, as a consequence, an increase in the nanoparticle diameter from 10 to 40 nm. In some cases, it is convenient to obtain metal oxide nanoparticles without an intermediate stage of their deposition on the graphene oxide surface. Therefore, in this work, we used previously prepared In_2O_3 nanoparticles, which, simultaneously with graphene oxide, were dispersed in isopropyl alcohol under the action of ultrasound.† The resulting mixture was placed in a supercritical fluid state. Isopropyl alcohol under supercritical conditions can convert to acetone, thus forming two hydrogen atoms that can hydrogenate double bonds in organic compounds,

† *Synthesis of In_2O_3 nanoparticles*. A solution of indium(III) acetate (0.25 mmol) in a mixture of ethanol (10 ml) and ethylenediamine (3 ml) was sonicated for 30 min. The resulting dispersion was placed in a steel autoclave and heated in an oven at 240 °C for 18 h. After cooling the autoclave to room temperature, the liquid was decanted, and the formed precipitate was washed with deionized water and ethanol (3 times, 30 ml of each solvent) by centrifugation (6000 rpm, 5 min). The substance was dried in the air. The resulting white precipitate was calcined in an oven at 500 °C for 4 h. As a result, a powder of In_2O_3 NPs was obtained.

Synthesis of graphene oxide. Graphene oxide was obtained by the modified Hammers' method.[28] Graphite powder (1 g, Sigma Aldrich, fraction 200 μm) was placed in concentrated sulfuric acid (40 ml). Then, keeping the mixture in an ice bath, $KMnO_4$ (5 g) was slowly added in small portions. The mixture was stirred for 2 h. Then, distilled water (120 ml) was carefully added dropwise to the resulting mixture and stirred at a temperature not exceeding 35 °C. After another 2 h, water (200 ml) was added, and hydrogen peroxide (10 ml, 30%) was added dropwise with vigorous stirring, while the color of the suspension changed to yellow-brown. The obtained graphene oxide was washed with 1 M HCl solution and a large amount of water by centrifugation (6000 rpm, 10 min) and dried at 50 °C.

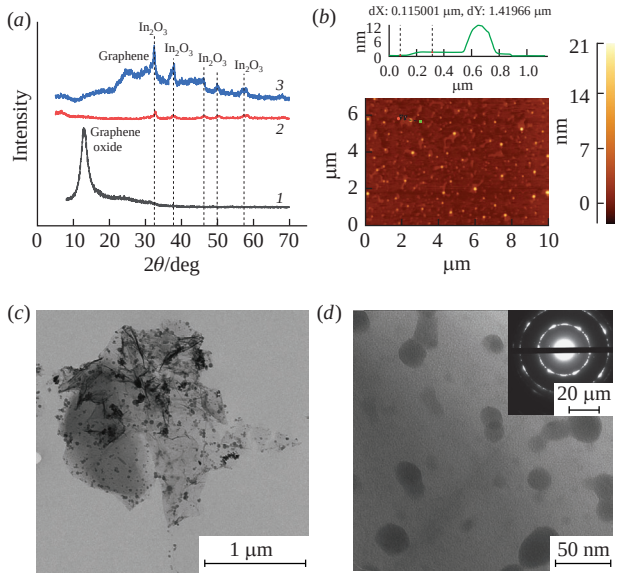

Figure 1 (*a*) XRD patterns of (*1*) graphene oxide, (*2*) In_2O_3 NPs and (*3*) reduced graphene oxide with In_2O_3 NPs. (*b*) AFM and (*c*),(*d*) TEM images at (*c*) lower and (*d*) higher magnifications and (*d*, inset) the SAED pattern for reduced graphene oxide sheets with In_2O_3 NPs.

participate in the hydrogenolysis of single bonds of carbon with heteroatoms (C–N, C–O, C–P, C–S) and reduce various substances.[19] Graphene oxide contains many functional groups[20] that interact with H atoms, resulting in the formation of reduced graphene oxide. The term 'reduced graphene oxide' is used instead of the term 'graphene' to emphasize the chemical nature of the reduction of graphene oxide to graphene as opposed to physical preparation methods such as chemical vapor deposition.[21,22] A more detailed process of reduction of oxygen-containing functional groups located on the surface of graphene oxide after treatment with a supercritical fluid was studied in earlier works.[23,24] Indium oxide is not reduced to a zerovalent metal in supercritical isopropanol; therefore, this technique can be applied to similar metal oxides,[19] for which it is essential to preserve their phase composition.

Indium(III) oxide nanoparticles were obtained by high-temperature synthesis from indium acetate.[25] The size distribution of nanoparticles was determined by dynamic light scattering. The average diameter was 12 ± 2 nm.‡ X-ray diffraction (XRD) analysis data [Figure 1(*a*)] showed the presence of a single In_2O_3 phase (JCPDS card no. 06-0416, cubic, face-centered crystal structure, space group $Ia\bar{3}$, a = 10.118 Å). The average particle size of about 18 nm was calculated using the Debye–Scherrer formula. Graphene oxide has a single peak at 2θ = 11.3°. After treatment of graphene oxide and nanoparticles with SCI, a composite was obtained. Then it can be shown that the graphene oxide phase completely disappears, but a broadened peak appears at 2θ = 26.5°, corresponding to the graphene phase. The peaks corresponding to the In_2O_3 phase (JCPDS card no. 06-0416) are retained in the sample, and the calculated nanoparticle diameter was found to be approximately 28 nm.

According to transmission electron microscopy data [Figures 1(*c*),(*d*)], In_2O_3 NPs have a shape close to spherical. All nanoparticles are immobilized on the surface of reduced graphene oxide with a layered structure. According to the histogram of the size distribution, the average size of In_2O_3 NPs was 20 nm; however, the size distribution was rather wide. According to the atomic force microscopy data [Figure 1(*b*)] of a sample deposited on a silicon substrate, In_2O_3 NPs are collected on reduced graphene oxide plates 100–800 nm in size and about 1.5 nm thick. According to the surface profile data, the size of In_2O_3 NPs is approximately 23 nm.

Despite the absence of oxygen-containing groups that could be ligands, In_2O_3 NPs are located only on the surface of reduced graphene oxide. This phenomenon is associated with the defectiveness of graphene obtained by chemical reduction. Nanoparticles interact with defects in the carbon structure, and the folding of the two-dimensional structure can lead to the appearance of new defects.[26,27] In this case, reduced graphene oxide acts both as a chemically inert substrate and as a macroligand for In_2O_3 nanoparticles. The proposed method is preparative and can later be used to deposit metal oxide nanoparticles on the surface of reduced graphene oxide to study their photocatalytic activity.

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Preparation of In_2O_3 nanoparticles on the surface of reduced graphene oxide. A mixture of the obtained In_2O_3 NPs (10 mg) and graphene oxide powder (100 mg) was dispersed in isopropanol (5.8 ml) using ultrasonic treatment. The dispersion was placed in a quartz container and kept in a steel autoclave at ~300 °C for 18 h. After cooling the autoclave to room temperature, the supernatant was decanted. The dry residue was washed three times with isopropanol and acetone and dried at room temperature to constant weight.

‡ The size of the resulting nanoparticles dispersed in isopropanol was determined by dynamic light scattering on a Zetasizer Nano ZS instrument. X-ray phase analysis was carried out on a Bruker D8 ADVANCE diffractometer operating in reflection mode using CuKα radiation (λ = 1.54056 Å). Diffraction data were recorded for 2θ angles up to 80°. Interpretation of diffraction patterns was carried out using the database of the International Center for Diffraction Data. The morphology of the samples was analyzed on a JEOL JEM-1011 transmission electron microscope (TEM) and by atomic force microscopy (AFM) on a NANOSCOPE III scanning probe microscope.

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