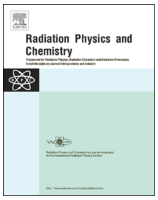
Radiation Physics and Chemistry 123 (2016) 68–72

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem



One-step synthesis of graphene-Pt nanocomposites by gamma-ray irradiation

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HIGHLIGHTS

- Graphene-Pt nanocomposites were synthesized by gamma-ray irradiation.
- Reduction of Pt(IV) complex ions and oxidation of graphene occurred simultaneously.
- Smaller Pt nanoparticles were formed in the presence of IPA than SDS.
- Mechanism for formation of graphene-Pt nanocomposites was proposed.

ARTICLE INFO

Article history:
Received 30 December 2015
Received in revised form
11 February 2016
Accepted 11 February 2016
Available online 12 February 2016

Keywords:
Graphene
Pt nanoparticles
Nanocomposite
Gamma-ray
Surface modification

ABSTRACT

We developed a one-step gamma-ray irradiation method to synthesize nanocomposites composed of graphene and Pt nanoparticles from aqueous solution containing graphene and Pt(IV) complex ions in the presence of 2-propanol (IPA) or sodium dodecyl sulfate (SDS). It was confirmed that gamma-ray irradiation provided carbonyl groups on graphene and Pt nanoparticles formed from the radiolytic reduction of Pt(IV) complex ions were deposited onto the carbonyl modified graphene. In the presence of IPA, small Pt nanoparticles were deposited on graphene, but large Pt nanoparticles were deposited in the presence of SDS: the size of Pt nanoparticles formed was larger in the presence of SDS than IPA. Based on the results, formation and deposition mechanisms of Pt nanoparticles were proposed.

1. Introduction

Graphene has outstanding characteristics for electro-conductivity, thermal-conductivity, mechanical strength and large specific surface area, because of its two dimensional structure composed of sp^2-bonded carbon atoms (Novoselov et al., 2004,2005; Morozov et al., 2008; Balandin et al., 2008; Lee et al., 2008). Taking into account these unique characteristics, graphene is considered as an ideal support material for metal nanoparticles (Zhu et al., 2010; HongKun and Chao, 2011). On the other hand, Pt nanoparticles and their nanocomposites have been widely used as catalysts in various reactions because of their excellent catalytic activity (Chen and Hindle, 2010). It is possible that nanocomposites synthesized by combining graphene with Pt nanoparticles have high catalytic activity and selectivity due to their excellent properties of graphene and Pt nanoparticles. However, it is a great challenge to deposit uniform metallic nanoparticles directly onto graphene because of its low surface energy and chemical inertness (Zhao et al., 2015). Therefore, chemical modification of graphene is essential to combine with Pt nanoparticles effectively: if modified graphene could provide adsorption sites, Pt nanoparticles would be deposited onto graphene by any interactions.

In this study, we have performed chemical modification of graphene and synthesis of Pt nanoparticles simultaneously in one-pot by using gamma-ray irradiation in aqueous solution. Gamma-ray irradiation has been used to synthesize various nanoparticles and nanocomposites (Marignier et al., 1985; Belloni et al., 1998; Wu et al., 1997; Doudna et al., 2002; Seino et al., 2004; Rao et al., 2013). Zhao et al. reported that Ni-graphene nanocomposites can be synthesized by simultaneous reduction of Ni^{2+} ions and graphene oxide by gamma-ray irradiation (Zhao et al., 2014). Hareesh et al. reported the radiolytic synthesis of Ag-graphene nanocomposites from Ag^{+} ions and graphene oxide (Hareesh et al. 2016). Rojas et al. reported the radiolytic synthesis of Ru-graphene oxide nanocomposites from Ru^{3+} ions and graphene oxide (Rojas et al., 2016). In most cases in the radiolytic synthesis, graphene

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http://dx.doi.org/10.1016/j.radphyschem.2016.02.019

oxide is often used as a starting material and the number of the reports for using graphene as a starting material is still limited.

A gamma-ray irradiation method is considered as a simpler, purer and less harmful approach than a conventional chemical reduction method, because strong reducing agents such as $NaBH_4$ are not needed (Li et al., 2014). Gamma-ray decomposes water molecules to hydrated electrons (e_{aq}^-), hydrogen radicals (•H) and hydroxyl radicals (•OH). Hydrated electrons and hydrogen radicals are strong reductive species, which are capable of reducing metal ions to metal atoms (Marignier et al., 1985; Remita et al., 2005). On the other hand, hydroxyl radicals are oxidative radicals so that oxidation reactions can be proceeded. It is considered that these radical species as well as hydrated electrons react with graphene and Pt complex ions in aqueous solutions. Therefore, in this study, we tried to prepare Pt-graphene nanocomposites by the radiolysis of aqueous solutions containing graphene, Pt complex ions and organic additives, where sodium dodecyl sulfate (SDS) or 2-propanol (IPA) were used as organic additives. We investigated the surface structure change of graphene before and after gamma-ray irradiation in the absence and presence of organic additives. The characteristics of the formed Pt nanoparticles and role of organic additives were also investigated.

2. Experimental

2.1. Materials

Graphene powder (6 – 8 nm thick × 5 μm wide) was purchased from Strem Chemicals, United States. Hydrogen hexachloroplatinate (IV) hexahydrate ($H_2PtCl_6 \cdot 6H_2O$, Pt(IV)), SDS and IPA were purchased from Wako Pure Chemical Industries, Japan. Ar was purchased from Osaka Sanso, Japan. Milli-Q water was used for all experiments.

2.2. Experimental procedure

Two kinds of 20 mL aqueous solutions were prepared in given concentration (5 mg graphene and 0.5 mM Pt(IV)) with 8 mM SDS or 10 mM IPA. These aqueous solutions were prepared in polyethylene containers and purged with argon gas for 15 min. After dispersion by an ultrasonic cleaning bath, they were irradiated at room temperature with gamma-ray from ^{60}Co radioactive source at a dose rate of 15 kGy h^{-1} for 40 min at Kyoto University Research Reactor Institute. After irradiation, the products were separated by centrifugation, washed with water several times and dried by freeze-drying. Hereafter, these two kinds of products will be referred to as Pt/graphene-SDS and Pt/graphene-IPA, respectively.

2.3. Characterization

UV–vis spectra of the sample solutions were measured by using a spectrophotometer, Shimadzu UV-2450. Before the measurement, the sample solutions were 10 times diluted by water. Morphologies of the prepared samples were characterized by a transmission electron microscope (TEM), JEOL JEM-2000FX with the accelerating voltage of 200 kV. Infrared spectra of the prepared samples were collected by a Fourier-transform infrared spectrophotometer (FT-IR), JASCO FT/IR – 6100 using a KBr pellet technique. Resolution of the spectra acquisition was 4 cm^{-1} resolution. Raman spectra were obtained by a Raman spectrophotometer, JASCO NRS-3300. The wavelength of the excitation laser was 532 nm.

3. Results and discussion

Fig. 1 shows the UV–vis spectra for sample solutions with (a) SDS and (b) IPA before and after gamma-ray irradiation. The absorption peaks of Pt(IV) complex ions, $[PtCl_6]^{2-}$, at around 260 nm disappeared both with SDS and IPA after gamma-ray irradiation, indicating that Pt(IV) complex ions were reduced completely by gamma-ray irradiation.

Fig. 2 shows the typical TEM images and electron diffraction patterns of Pt/graphene-SDS (Fig. 2a and b) and Pt/graphene-IPA (Fig. 2d and e). It can be seen that the Pt nanoparticles formed from the radiolytic reduction of Pt(IV) complex ions were homogeneously supported on graphene both with SDS and IPA. Fig. 2c and f show the size distribution of Pt nanoparticles of Pt/graphene-SDS and Pt/graphene-IPA, respectively. The average size of Pt nanoparticles was 29 ± 7.8 nm for Pt/graphene-SDS and 15 ± 4.0 nm for Pt/graphene-IPA. These results indicated that smaller Pt nanoparticles with narrower size distribution were formed in the presence of IPA. In addition, it seemed that the number of Pt nanoparticles of Pt/graphene-IPA was larger than that of Pt/graphene-SDS.

Fig. 3 shows the FT-IR spectra of (a) raw graphene, (b) Pt/graphene-SDS, and (c) Pt/graphene-IPA. FT-IR spectrum of raw graphene shows the presence of only skeletal vibration absorption peak at 1570 cm^{-1} (Sahoo et al., 2014). On the other hand, both Pt/graphene-SDS and Pt/graphene-IPA show the presence of carbonyl group (C=O) at around 1700 cm^{-1} in addition to the skeletal vibration absorption peak of graphene, indicating that C=O groups were formed on graphene by gamma-ray irradiation. As a comparison, graphene in water (without organic additive) was irradiated with gamma-ray under the same conditions. The FT-IR spectrum of this sample is shown in Fig. 3d. The result indicates the presence of C=O at around 1700 cm^{-1}, suggesting that C=O

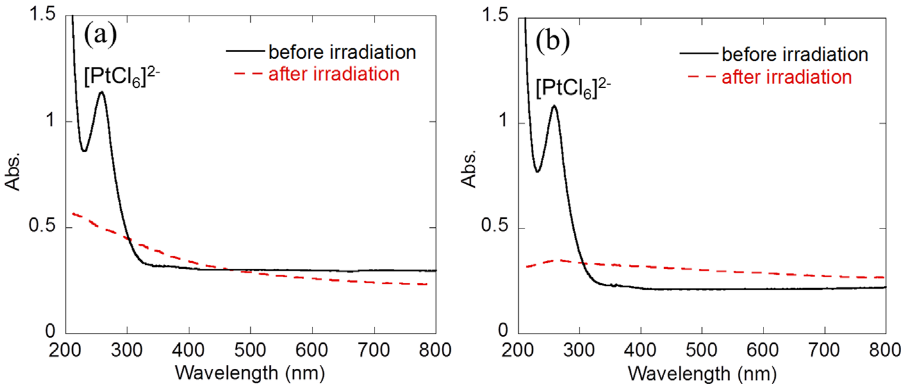

Fig. 1. UV–vis spectra for sample solutions containing 5 mg graphene and 0.5 mM Pt(IV) with (a) SDS and (b) IPA before and after gamma-ray irradiation.