

Preparation, characterization and thermal stability of reduced graphene oxide/ silicate nanocomposite

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Reduced graphene oxide-silicate (RGO/SiO₂) nanocomposites were prepared by a sol-gel method by mixing 10 wt% and 20 wt% of RGO with tetraethyl orthosilicate (TEOS). RGO sheets were prepared by chemical exfoliation of purified natural graphite powder. The phase formation and the structural transformations of the samples are verified by X-ray diffraction analysis. Thermal behavior was studied using differential thermal analysis (DTA) in air atmosphere. FTIR spectrophotometry was used to determine the short range order of the obtained nanocomposites. Scanning electron microscopy (SEM) with EDS was also used to determine the structure and morphology of the samples in addition to elemental analysis of constituents. The analysis showed that the carbon phases start firing after heating at 400°C to completely disappear between 550 to 600°C. Cristobalite phase appeared at 800°C in the sample containing 20 wt % RGO, while the amorphous silica structure was dominant in the sample containing 10 wt% RGO at the same temperature.

Keywords: *Reduced Graphene Oxide, TEOS, Nanocomposite, Thermal stability, Sol-gel.*

INTRODUCTION

Since Andre Geim & Kostya Novoselov isolated graphene in 2004 and received the Nobel Prize in 2010, an explosion in the investigation of graphene and composites based on graphene in terms of synthesis, characterization, properties, as well as specifically potential applications were reported. Graphene has wonderful physicochemical properties such as high values of its Yong's modulus, fracture strength, thermal conductivity, specific surface area, and electrical conductivity [1, 2]. These features have made graphene and graphene derivatives ideal for diverse applications. Reduced Graphene Oxide (RGO) is known as chemically modified graphene, functionalized graphene, chemically converted graphene, or simply graphene [3]. RGO is like the pristine graphene but has some oxygen functional groups remained after the incomplete reduction of the graphene oxide sheets during its production by chemical methods [4, 5]. During the last half decade, RGO has been studied in the context of many applications, such as polymer composites, energy-related materials, sensors, field-effect transistors and biomedical applications, due to its

excellent electrical, mechanical, and thermal properties. One of the methods considered as an effective route to synthesize RGO sheets due to its simplicity, reliability, ability for large-scale production and exceptionally low price is the isolation of graphene sheets from graphite by chemical treatments which are suitable for large-scale production [6].

In the past few years, significant efforts have been directed toward the preparation of nanocomposites based on graphene such as graphene/Bi₂O₃ [7], graphene/SnO₂ [8], graphene/gold [9], graphene/silver [10], graphene/Mn₃O₄ [11], Ag₃VO₄/TiO₂/graphene [12], TiO₂/graphene [13, 14], ZnO/graphene [15, 16] and graphene/cobalt [17]. The unique properties of these materials have been demonstrated for a variety of catalysts, super capacitors and fuel cell batteries. One of the future challenges is to preserve the excellent physical properties of graphene in the process of synthesizing nanocomposites [18].

Silica is a very appropriate compound due to its high chemical and thermal stability. It has been known since ancient times. Silica is most commonly found in nature as quartz, as well as in various living organisms [19]. It is one of the most complex and most abundant families of materials, existing as several minerals and produced synthetically. Notable examples include fused

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quartz, crystal, fumed silica, silica gel, and aerogels. Applications range from structural materials for microelectronics to components used in the food industry. The graphene fabricated on silica depicts interesting properties due to the local atomic configuration, and the binding sites of graphene with SiO₂. It can find applications in the development of super capacitor devices, devices for drug delivery, heavy metal removal, biosensors and electrochemical sensors [20-22]. Moreover, by the sol-gel method it is easier to prepare a homogenous composite with random distribution of RGO sheets in the volume of the materials. There are a few works which presented the methods for synthesis of RGO/SiO₂ composite by using graphite oxide and TEOS as precursors with or without surfactant [23-25]. In this study, we prepared a nanocomposite from silica with reduced graphene oxide, which may find possible applications in the development of super capacitor devices, devices for drug delivery, biosensors and electrochemical sensors [26].

EXPERIMENTAL

Preparation of reduced graphene oxide (RGO)

RGO was successfully prepared by chemical exfoliation of purified natural graphite powder (99.9 %, Alfa Aesar Co.) typically as mentioned in our previous study [28] with complete characterization to confirm that we obtained RGO as mentioned in the literature. Briefly, we can summarize it in three steps.

1- Firstly, graphite was oxidized by a strong acid to obtain graphite oxide using the Hummers and Offeman method [29].

2- Graphite oxide was ultrasonicated for 2 h to exfoliate the compact sheets to produce a dispersion solution of the graphene oxide nanosheets.

3- Finally, the dispersion solution of graphene oxide was reduced using the strong reducing agent sodium borohydride (98%, Alfa Aesar) to obtain the reduced graphene oxide nanosheets.

Preparation of reduced graphene oxide / silicate (RGO/SiO₂)

The RGO/SiO₂ nanocomposite was prepared by the sol-gel technique using tetraethyl orthosilicate (TEOS) (98%, Aldrich Co.) and freshly prepared RGO as precursors. In order to avoid the aggregation process in RGO sheets and to solve the problems related to the exfoliation and distribution of the sheets inside the composites we selected definite amounts of RGO (10 wt% and 20 wt%) not less than the detectable amounts inside the

silica matrix. Mixture of the target amounts of RGO dispersed in deionized water using ultrasonication was added to the solution of TEOS and ethanol under stirring at 110°C for 1 h in order to obtain a gel following the scheme shown in Figure (1).

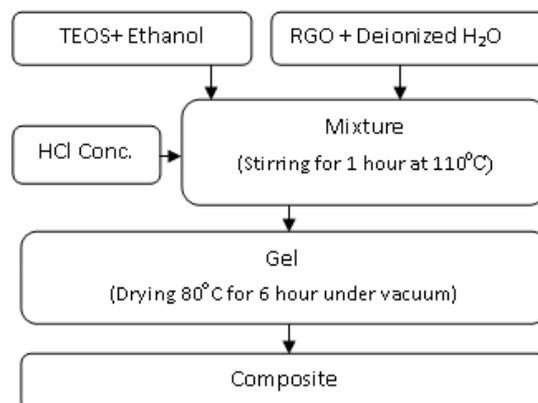


Fig. 1. Scheme of preparation of RGO/SiO₂ composite by the sol-gel method.

Samples characterization

The phase formation and structural transformation were detected by X-ray phase analysis (Bruker D8 Advance, Cu K α radiation). The micro-nano structure and the morphology of the crystalline products were studied by scanning electron microscopy (SEM) (Jeol-357) with energy-dispersive X-ray spectroscopy (EDS) for elemental analysis of the constituents. Differential thermal analysis (DTA) in air atmosphere was carried out on STA PT1600 TG-DTA/DSC Simultaneous Thermal Analysis, (LINSEIS Messgeräte GmbH, Germany). The main short range orders of the nanocomposites were determined on a Channel FTIR spectrophotometer VARIAN series 600, with a wide wavelength range (4000-400 cm⁻¹) and spectral resolution not worse than 0.07 cm⁻¹ at room temperature using a standard KBr pellet technique.

RESULTS AND DISCUSSION

XRD analysis of the samples containing 10 wt% and 20 wt% of RGO showed that the crystal phases appeared at different temperatures. In the beginning of heating up to 200°C it was found that the composites contain amorphous silica and RGO sheets. Lignite was identified at 400°C (Ref. Code 00-005-0625). All carbon phases disappeared between 550°C and 600°C. The samples which contain 10 wt% RGO at 800°C became completely amorphous, the so called silica gel glass, while cristobalite crystal phase appeared in the samples which contain 20 wt% RGO at the same temperature, as shown in Figure (2). This means

that with increasing the amount of RGO the formation of cristobalite was accelerated.

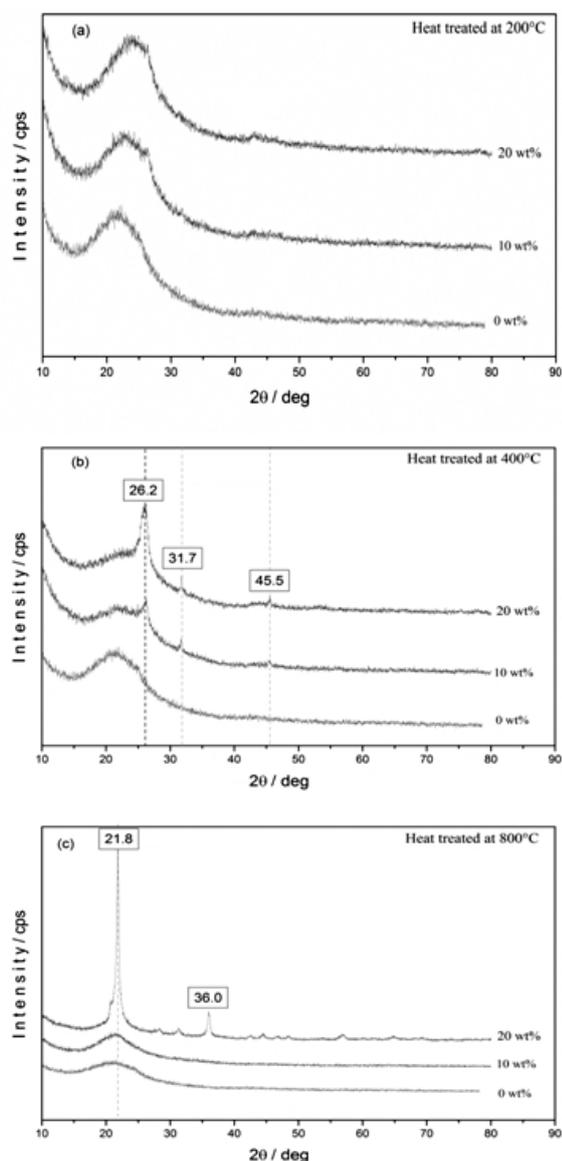


Fig. 2. X-ray diffraction pattern of the samples containing 0 wt%, 10 wt% and 20 wt% of RGO treated at a) 200°C, b) 400°C, and c) 800°C.

According to the results of the DTA/TG analysis the samples showed significant weight loss with an onset temperature above 100°C, which was attributed to the elimination of the water, followed by removal of the weak oxygen-containing functional groups as CO, CO₂ and H₂O vapors. As shown in Figure (3a), the mass loss for the samples containing 20 wt% RGO is higher than that for the other samples, especially above 400°C.

Figure (3b) presents the differential thermal analysis results for the target samples. It was found that the strong exothermic effect observed near to 600°C for samples which contain 20 wt% RGO is due to firing of the carbon content.

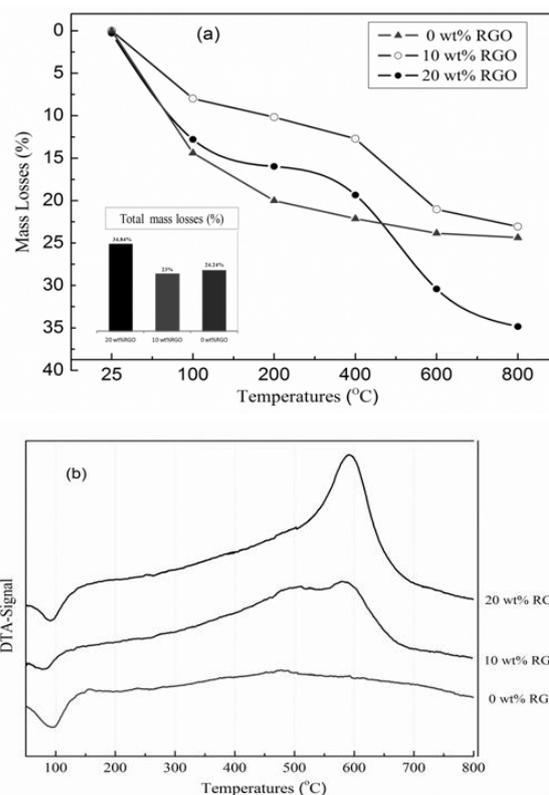


Fig. 3. Thermal analysis for the samples containing 0 wt%, 10 wt% and 20 wt% of RGO (a) Mass loss (b) DTA signal.

Table 1. Elemental analysis in weight percent at different positions inside the samples containing RGO (10 wt% & 20 wt%).

Samples		C %	O %	Si %	Total
10 wt% RGO	A1	37.48	51.5	11.02	100
	A2	29.91	54.81	15.28	100
	A3	71.16	24.54	4.31	100
20 wt% RGO	B1	20.13	39.29	40.57	100
	B2	77.5	21.15	1.34	100
	B3	76.73	21	2.27	100

The IR spectra of samples treated at 200, 400 and 800°C are presented in Figure (4a, b, c). It was established that between room temperature and 400°C transformation of silica gel to silica gel glass takes place because the band at 950 cm⁻¹ decreased to a small shoulder. This can be connected with replacement of the Si-OH group with Si-O-Si bridge bond [30]. The bands corresponding to vibration of the water molecules around (3450, 1635 cm⁻¹) were drastically reduced on increasing the temperature. The dominant band at 1090 cm⁻¹ (800°C) was connected with the stretching vibration of Si-O-Si bonds between SiO₄ tetrahedra [30]. The band with small intensity at 660 cm⁻¹ in the spectra of the samples containing 20% RGO can be attributed to the formation of cristobalite [27]. These results are in good agreement with the XRD analysis data.

From the SEM images (Figure (5)) it is seen that randomly distributed aggregates of stack small sheets are imbedded in the amorphous matrix. The EDS analyses of the samples are presented in Table (1). According to these results we can confirm that the samples display random distribution of RGO which is presented as carbon (C).

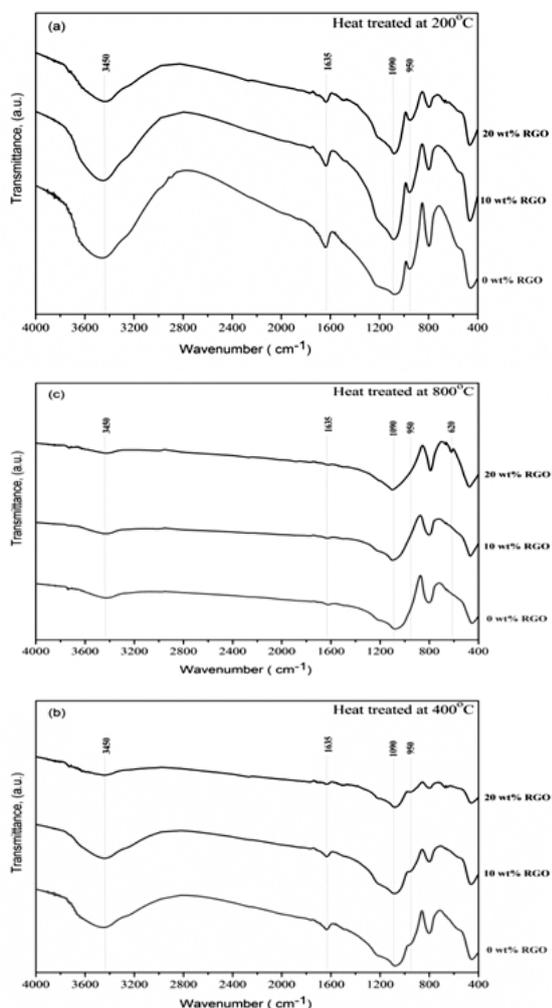


Fig. 4. IR-Spectra pattern of the samples containing 0 wt%, 10 wt% and 20 wt% of RGO treated at a) 200°C, b) 400°C, and c) 800°C.

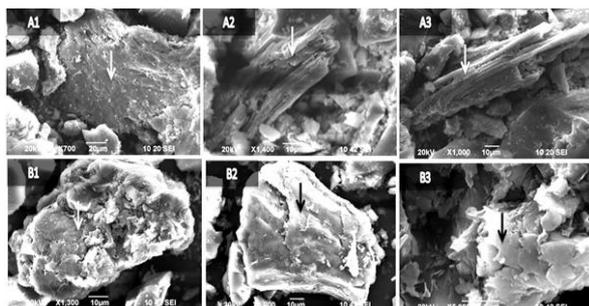


Fig. 5. SEM images of samples heated at 200°C containing (A) RGO 10 wt% (B) RGO 20 wt% at different positions. The arrows inside the SEM pictures point to the exact positions of performed elemental analysis.

CONCLUSIONS

In this study, it was established that by direct mixing of RGO and TEOS by the sol-gel technique, it is possible to obtain composite materials. Inside the matrix RGO interacts with the silica glass to form lignite which is detected at 400°C. Under continuous heating all of carbon contents burned and the carbon phases completely disappeared at about 600°C. Cristobalite phase was detected at 800°C in the composite containing 20 wt% RGO, while amorphous silica structure was dominant at the same temperature for the composite containing 10 wt% RGO. This means that the increase in the amount of RGO inside the silica matrix enhances the crystallization of silica at low temperature. We believe that this information will be useful for further understanding of the complex nature of this composite, and it will be taken into account for possible applications according to its unique properties.

REFERENCES

1. K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, Y. Zhang, S. V. Dubonos, I. V. Grigorieva, A. A. Firsov, *Science*, **306**, 666 (2004).
2. A. K. Geim, *Science*, **324**, 1530 (2009).
3. B. F. Machado, P. Serp, *Catal. Sci. Technol.*, **2**, 54 (2012).
4. S. Pei and H.-M. Cheng, *Carbon*, **50**, 3210 (2012).
5. S. Park, J. An, J.R. Potts, A. Velamakanni, S. Murali, R.S. Ruoff, *Carbon*, **49**, 3019 (2011).
6. S. C. Tjong, *Polymer Composites with Carbonaceous Nanofillers*, Wiley-VCH Verlag GmbH & Co. KGaA, 2012, p.1.
7. K. R. Nemade, S. A. Waghuley, *Solid State Sci.*, **22**, 27 (2013).
8. F. Li, J. Song, H. Yang, S. Gan, Q. Zhang, D. Han, A. Ivaska, and N. Li, *Nanotechnol.*, **20**, 455602 (2009).
9. A. R. Biris, S. Pruneanu, F. Pogacean, M. D. Lazar, G. Borodi, S. Ardelean, E. Dervishi, F. Watanab, A. S. Biris, *Int. J. Nanomed.*, **8**, 1429 (2013).
10. S. V. Kumar, N. M. Huang, H. N. Lim, M. Zainy, I. Harrison, C. H. Chia, *Sens. Actuators B*, **181**, 885 (2013).
11. Y. Wu, S. Liu, H. Wang, X. Wang, X. Zhang, G. Jin, *Electrochimica. Acta.*, **90**, 210 (2013).
12. J. Wang, P. Wang, Y. Cao, J. Chen, W. Li, Y. Shao, Y. Zheng, D. Li, *Appl. Catal. B*, **136-137**, 94 (2013).
13. Y. Zhang, C. Pan, *J. Mater. Sci.*, **46**, 2622 (2011).
14. J. Guo, S. Zhu, Z. Chen, Y. Li, Z. Yu, Q. Liu, J. Li, C. Feng, D. Zhang, *Ultrason. Sonochem.*, **18**, 1082 (2011).
15. X. Chen, Y. He, Q. Zhang, L. Li, D. Hu and T. Yin, *J. Mater. Sci.*, **45**, 953 (2010).
16. T. Xu, L. Zhang, H. Cheng and Y. Zhu, *Appl. Catal. B*, **101**, 382 (2011).
17. Z. Ji, X. Shen, Y. Song and G. Zhu, *Mater. Sci.*

- Eng. B, **176**, 711 (2011).
18. X. Wang, S. Chen, In: Nanotechnology and Nanomaterials "Physics and Applications of Graphene - Experiments", Dr. Sergey Mikhailov (Ed.), InTech, 2011.
19. R.K. Iler, The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry of Silica, Wiley: New York, USA, 1979.
20. M. Vallet-Regí, F. Balas, D. Arcos, *Angew. Chem. Int. Ed.*, **46**, 7548 (2007).
21. J.Q. Dalagan, E.P. Enriquez, L.J. Li, *J. Mater. Sci.* **48**, 3415 (2013).
22. T. E. Alam, MSME Dissertation, University of South Florida, Florida, USA, 2012.
23. X. Zhou, T. Shi, *Appl. Surf. Sci.*, **259**, 566 (2012).
24. L. Guardia, F. Suárez-García, J.I. Paredes, P. Solís-Fernández, R. Rozada, M.J. Fernández-Merino, A. Martínez-Alonso, J.M.D. Tascón, *Microporous Mesoporous Mater.*, **160**, 18 (2012).
25. S. B. Yang, X. L. Feng, L. Wang, K. Tang, J. Maier, K. Müllen, *Angew. Chem. Int. Ed.*, **49**, 4795 (2010).
26. C. Hu, T. Lu, F. Chen, R. Zhang, *J. Chin. Adv. Mater. Soc.*, **1**, 21 (2013).
27. A. Shalaby, V. Yaneva, A. Staneva, L. Aleksandrov, R. Iordanova, Y. Dimitriev, *Nanosci. Nanotechnol. (Sofia, Bulg.)*, **14**, 120 (2014).
28. W.S. Hummers, R.E. Offeman, *J. Am. Chem. Soc.*, **80**, 1339 (1958).
29. Y. Yahagi, T. Yagi, H. Yamawaki and K. Aoki, *Solid State Commun.*, **89**, 945 (1994).
30. I.I.Plusnina, in: Infrared Spectra of Minerals (Russ.), MGU Publishers: Moscow, Russia, 1977.

ПРИГОТВЯНЕ, ОХАРАКТЕРИЗИРАНЕ И ТЕРМИЧНА СТАБИЛНОСТ НА РЕДУЦИРАН ГРАФЕНОВ ОКСИД/СИЛИКАТ НАНО-КОМПОЗИТИ

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(Резюме)

Приготвени са нано-композити от редуциран графенов оксид-силикат (RGO/SiO₂) по зол-гел метода чрез смесване на 10 % и 20 % тегл. от RGO с тетраетил-ортосиликат (TEOS). Листове от RGO са приготвени чрез химическо разстилане на пречистен естествен графитен прах. Фазообразуването и структурната трансформация на пробите са потвърдени чрез рентгено-структурен анализ. Термичните отношения са изследвани чрез диференциален термичен анализ (DTA) в атмосфера от въздух. Използвана е инфрачервена спектrophотометрия (FTIR) за определянето на кратък обхват нано-композити. Използвана е и сканираща електронна микроскопия (SEM) с EDS за определянето на структурата и морфологията на пробите в допълнение на елементния анализ. Анализът показва, че въглеродната фаза започва да гори след нагряване при 400°C до пълно изчезване между 550 и 600°C. Кристобалитна фаза се появява при 800°C в пробите, съдържащи 20 % тегл. RGO, докато аморфен силициев диоксид доминира в пробите, съдържащи 10 % тегл. RGO при същата температура.