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Synthesis of reduced graphene oxide/zinc sulfide nano composites with sonochemical route

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Zinc sulphides/reduced graphene oxide nanocomposites were prepared through a sonochemical route. As grown zinc sulfide nanoparticles were added with different ratios in ethanolic solution of reduced graphene oxide. The mixture were ultrasonicated for 2h and then kept for aging. The obtained samples were characterized by optical transmission, FTIR, luminescence, structural and morphological characterizations. On addition of ZnS nanoparticles the shift in luminiscence peak is observed towards higher wavelength. A small peak is obtained at 440nm to 450nm which might be due to electron tapping in band gap region. Sharp luminescenct peak in UV region is observed for higher addition of ZnS.

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1. Introduction

Semiconductor nanoparticles are emerging as an important area of interest because of their unique optical and electronic properties at nanoscale due to quantum confinement effect [1,2]. The bandgap and other size dependent properties these nanoparticles can be tuned hence be tailored for many optoelectronic applications. Among other II–VI metal sulfide semiconductors, Zinc sulfide (ZnS) has proven his candidature for its applications in the field of optoelectronic devices such as, light emitting diodes and flat panel displays [3-5]. It has direct energy bandgap (3.7 eV), suitable to be used as host matrix for variety of dopants shown broad band luminescence from the near ultraviolet to near infrared region [6]. Recently nanocomposites of Carbon based compounds with metal and metal oxides are also been reported, in which filling of carbon nanotubes with metals and metal oxides [7-8] was done.

With the advent of grapheme and reduced graphene, researchers are involved in modifying the properties of graphene for [9]. Graphene, a single layer of carbon atoms is booming in material science these days because of its unique electronic, thermal and mechanical properties [10–13]. Stankovich et al., 2006[14] reported Graphene-based nanocomposites. According to their results, incorporation of the reduced graphene oxide enhanced the electrical conductivity of the composite which opened a broad new class of Graphene-based composite materials. Graphene oxide based nanocomposites has also attracted attention due to low cost for large-scale production [15-16]. In recent years, Graphene-based nanocomposites have been widely reported and explored for various applications [17]. An attempt is made to synthesize and study the optical properties of ZnS–reduced graphene composite.

2. Experimental

2.1. Materials used

Reduced Graphene oxide, ethanol, distilled water, Zinc chloride and thiourea were supplied from Ranbaxy. All the chemicals were of analytical grade and used by weighing on analytical balance without further purification.

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2.2. Instruments used
Electrical stirrer, water bath, ultrasonicator, autoclave reactor

2.3. Synthesis
The whole process is divided into two parts; namely Synthesis ZnS nanoparticles using sol gel route, and inclusion of these particles in ethanolic reduced grapheme using hydrothermal route.

For ZnS nanoparticles synthesis 0.1M of Zinc chloride dissolved in100ml of distilled water, magnetically stirred for one hour at 60^0C and added 0.5M of thiourea in it after 15 min of reaction. The solution were placed in ultrasonicator for another half an hour. The remaining solution were divided into 5ml,10ml and 25ml.

0.4g Reduced Graphene oxide is dissolved in 40ml of ethanol, continuously stirred for one hour and then placed the mixture in ultrasonicator for other half an hour. For inclusion of ZnS nanoparticles, nanoparticles were added in various ratios (rGOZnS1: 5ml, rGOZnS2: 10ml and rGOZnS3: 25ml) in 10ml of reduced graphene oxide. The mixture were placed in autoclave reactor and the setup was kept in hot air oven for 3 hour at 150^0C.

2.4. Characterization
The samples were characterized by structural, morphological, optical, PL and FTIR studies. X- Ray Diffraction (XRD) patterns were obtained by 300/600 mini flex at Jiwaji University, Gwalior. The absorption spectra were obtained by Perkin Elmer lambda 25, Luminescence spectra were obtained by Perkin Elmer LS-55 and FTIR spectra were obtained by Perkin Elmer alpha at PC ray center, ITM University, Gwalior.

3. Results and discussion

3.1. Structural studies
Fig. 1 shows the X-ray diffraction (XRD) patterns of the rGo and rGo/ZnS nanocomposites. Pure rGO has only two peaks small peak at $2\Theta=11.7^o$ and sharp peak at $2\Theta=26.6^o$. All the diffraction peaks of ZnS nanoparticles has zinc blende structure, the peaks are shown at 2Θ values is 26.6^o = (111) plane, 33.5^o =(200) plane and 55.43^o = (311). All in good agreement with standard card (JCPDS Card No. 05-0566). Peak positions of the ZnS sample indicate the formation of the Zinc blende structure with three most preferred orientations (111), (200) and (311).

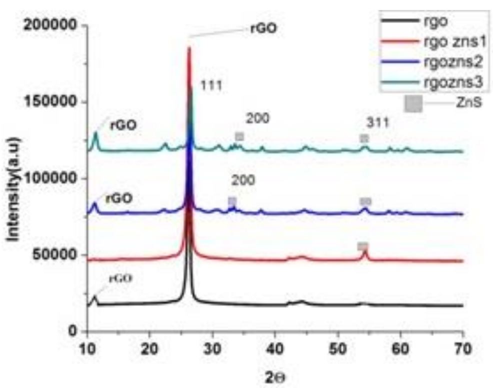


Fig. 1. X ray difractograms of rGO and rGO/ZnS nanosomposites.

3.2. Crystallite size and microstrain
The crystallite size (D) and microstrain(ε) of the obtained nano composites can be calculated from the peak broadening in the XRD patterns using Williamson-Hall analysis. As illustrated from eq.(2), the total line broadening considers two physical factors; the first one is responsible about the crystallite size (D), while the second one reflects the strain (ε) effects: β

$$\beta = \beta D + \beta\varepsilon \tag{1}$$

The Williamson-Hall equation can be written as in the following:

$$\boldsymbol{\Gamma cos\theta} = \mathbf{0.94}\boldsymbol{\lambda D} + \mathbf{4}\boldsymbol{\varepsilon sin\theta} \tag{2}$$

The size broadening (β_D) is proportional to cosθand the strain broadening (βε) is proportional to tanθ. In order to calculate the crystallite size and microstrain of the ZnS nanoparticles, a relationship between $\boldsymbol{\Gamma cos\theta}$ and sinθ is drawn for prepared sample and is shown in Fig.2. The average crystallite size 16 nm, 15 nm, 21 nm and 34nm, while its macrostrain value is about -0.00315, -0.00513 and -0.00758 and exhibit negative slope confirms the presence of compressive strain. The size of the nanocomposite particles calculated by debye Scherer equation and shown in Table 1.

$$D = {}^{0.9\lambda}\!/_{\beta \mathrm{Cos}\theta} \qquad [3]$$

Table 1. Size calculated using Debye Scherer equation, William halls points for calculating slope and intercept and also estimated the size from FESEM images by using histogram.

Sample	FWHM	Size	Intercept	slope	FESEM size
rGO	0.0087	16.6			1.4
rGOZnS1	0.0129	15.4	0.01658	-0.0032	2.6
rGOZnS2	0.0104	21.9	0.01604	-0.0051	3.21
rGOZnS3	0.0087	34.19	0.01793	-0.0076	0.35

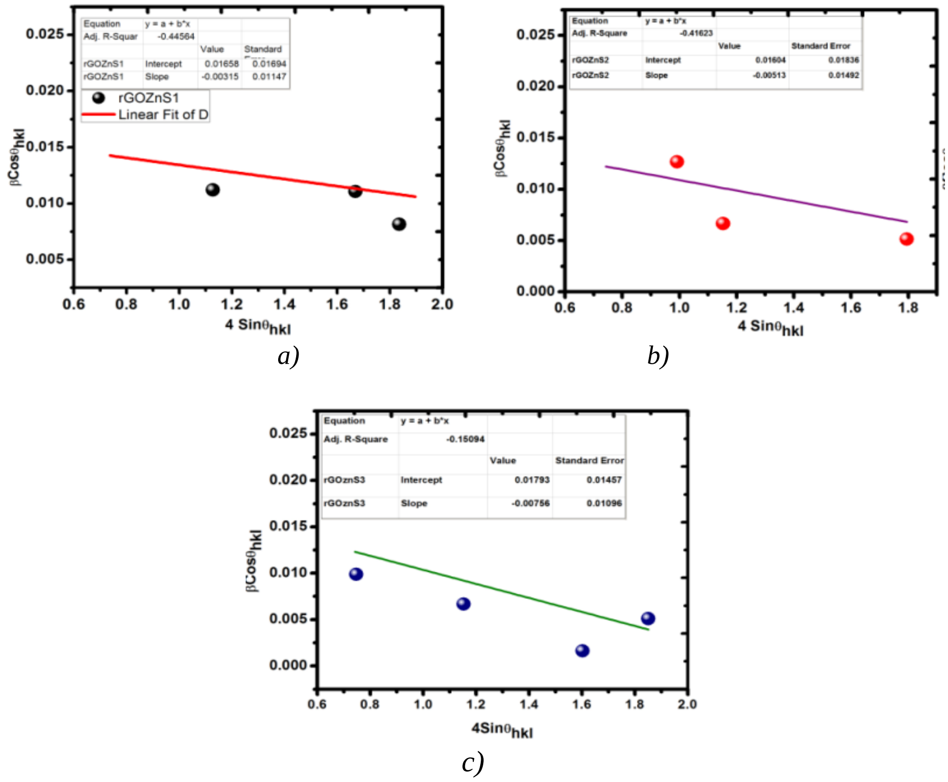


Fig. 2. Williamson-Hall plotsof ed rGO (a) rGO (b) rGOZnS1 (c) rGOZnS2 (d) rGOZnS3.

3.3. FESEM studies (morphological studies)

In morphological studies, FESEM Micrographs of pure reduced Graphene oxide and their composites with ZnS are shown in Fig 3. pure reduced graphene oxide has banana leaf type structure as shown in Fig.3 (a). On increasing the ZnS particles in rGO the particles size decreases and the hexagonal structures were found. Some particles alongated from their edges and as the result they break into small particles. No of particles are increased throughout the entire sample. The sample have high concentration of ZnS nanoparticles have small sized particles and no particles greater than other low range rGO. This FESEM results also supports the XRD results. Zinc blende type structures found in XRD and FESEM. EDX graph shows well formed rGO, no impurity were found in rGO. Fig.4 show the FESEM EDX index of pure reduced Graphene oxide and their composites. Presence of Zinc and Sulphur is verified and the results are compiled in Table 2. The Histograms for estimation of size distribution using FESEM has been prepared and shown in Fig.5 for rGOZnS nanocomposites. Uniformity improves on increasing concentration of ZnS in rGO.

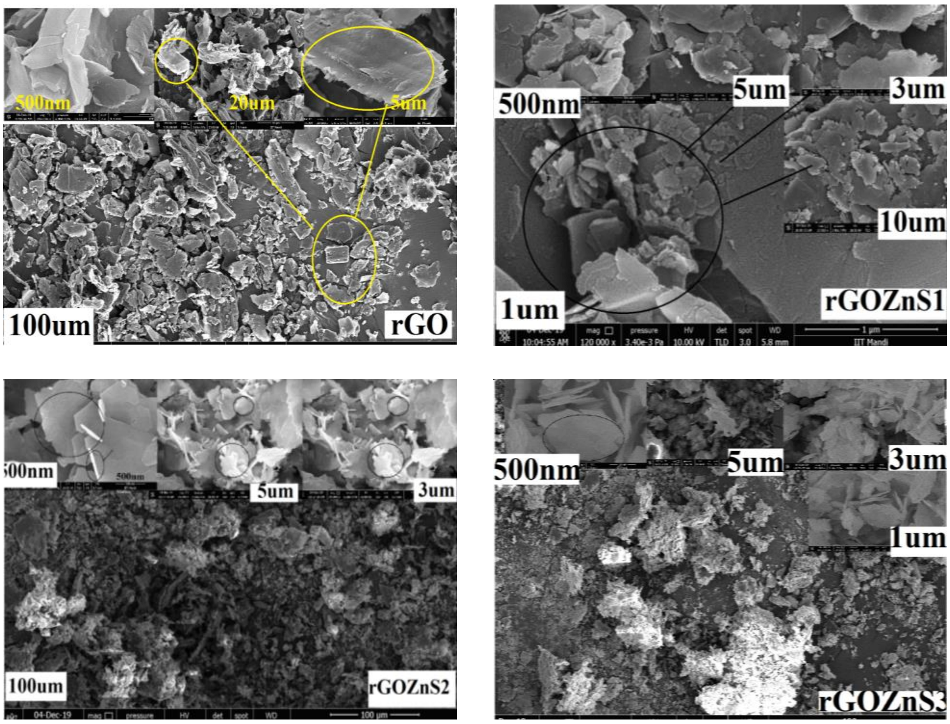


Fig.3 FESEM Micrographs of pure reduced Graphene oxide (a) rGO (b) rGOZnS1 (c) rGOZnS2 (d) rGOZnS3.

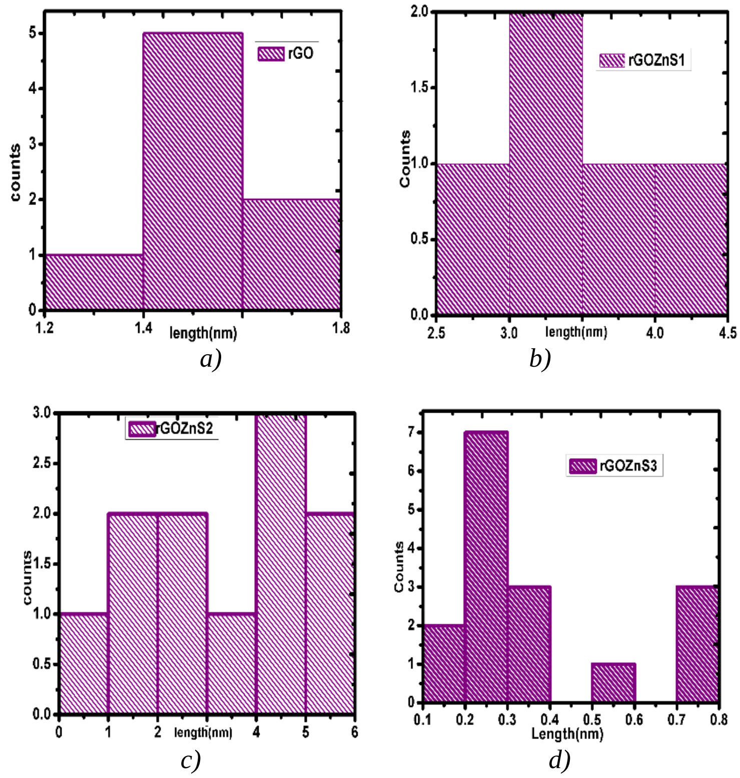


Fig.4 FESEM EDX index of pure reduced Graphene oxide (a) rGO (b) rGOZnS1 (c) rGOZnS2 (d) rGOZnS3.

Table2.EDX index of pure reduced Graphene oxide and ZnS doped rGO (a) rGO (b) rGOZnS1 (c) rGOZnS2 (d) rGOZnS3.

Element	Weight %	Atomic %	Net Int.	Weight %	Atomic %	Net Int.	Weight %	Atomic %	Net Int.	Weight %	Atomic %	Net Int.
code	rGO			rGOZnS1			rGOZnS2			rGOZnS3		
C K	87.52	90.33	178.28	85.95	89.26	336.33	73.57	80.88	107.95	46.32	62.80	32.34
O K	12.48	9.67	8.60	13.65	10.64	19.28	21.75	17.95	18.92	30.52	31.06	31.47
S K	-	-	-	0.11	0.04	4.94	1.08	0.45	24.36	1.42	0.72	20.17
ZnK	-	-	-	0.29	0.06	3.79	3.59	0.73	25.57	21.75	5.42	135.9

3.4. FTIR studies

FTIR studies of pure reduced graphene and composite of rGO/ZnS of various ratios. Are shown in Fig.6. A reduced graphene oxide shows a IR spectra in which it contain broad peak at 3386cm^{-1}, 3467cm^{-1}, 3419cm^{-1} and 3484cm^{-1} which shows O-H bonding. 1582cm^{-1}, 1409 cm^{-1} show strong asymmetric stretching of carboxylic acid (-COOH) and 1611cm^{-1} shows the stretching vibrations of C=O. The peaks 914cm^{-1}, 915cm^{-1}shows the absorption of sulphur. 715cm^{-1}, 756cm^{-1}, 432cm^{-1}, peaks gives Zn stretching vibrations.

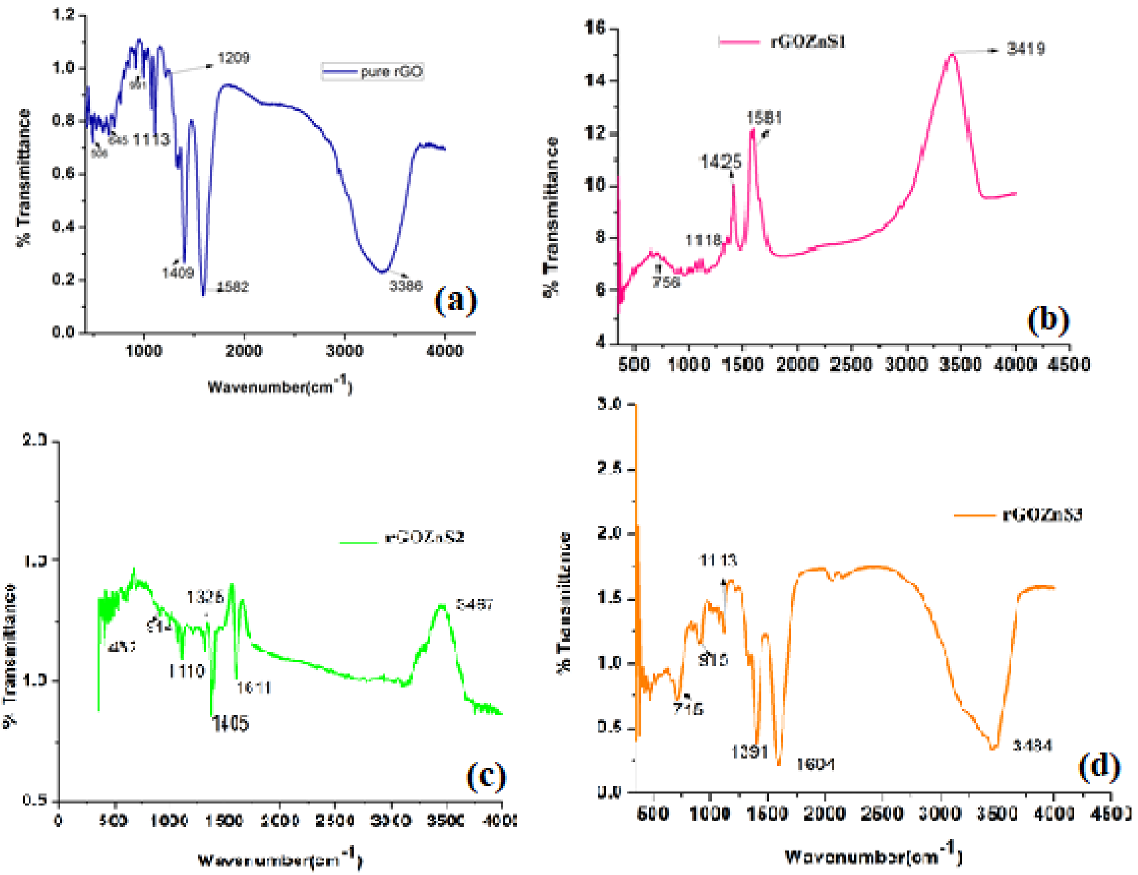
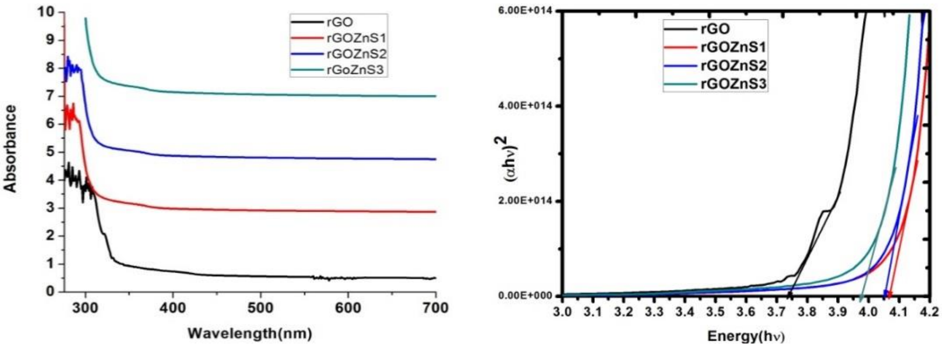


Fig.6. FTIR of pure reduced graphene and composite of rGO/ZnS of various ratios.
(a) Pure rGO (b) rGO ZnS1(c) rGO ZnS2.(d) rGOZnS3

3.5. Absorption studies

Absorption spectra of pure rGO and nanocomposites with ZnS of various ratios are shown in Fig. 7 (a). The absorption of rGO is lower than other doped ZnS nanoparticles in rGO. The absorption of composites exhibits blue shift. The tauc plot between energy and $(\alpha h\nu)^2$ were drawn to calculate band gap shown in fig 7(b). The pure rGO has 3.7eV band gap and on incorporation of ZnS the band gap increases, however for high concentration the band gap start decreasing. Slight shift towards higher wavelength is observed on increasing zinc sulphide.



a) b)

Fig7(a). Absorption spectrum and (b)Tauc plot between energy and $(\alpha h\nu)^2$of of pure reduced graphene and composite of rGO / ZnS of various ratios

3.6. Photoluminescence (PL)

Photoluminiscence spectra of pure rGO and nanocomposites with ZnS of various ratios are shown in Fig.8.The pure reduced graphene has broad luminiscence peak from 250 nm to 400 nm and small peak is obtained at below 600 nm and again braod peak at higher wavelength. On addition of ZnS nanoparticles in reduced graphene oxide the luminiscence peak shifted at higher wavelength and also small peak is obtained at 440 nm to 450nm. It is due to the electron trapping in band gap region.

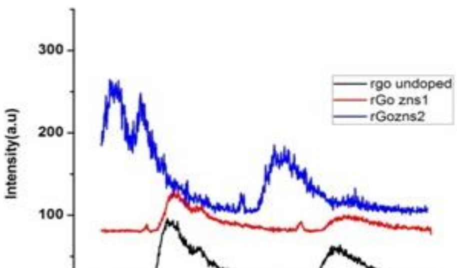


Fig.8. Photoluminiscence of pure rGO and nanocomposites with ZnS of various ratios .

4. Conclusions

rGO/ZnS (reduced Graphene oxide/zinc silfide) nanocomposites were synthesized by hydrothermal method. rGO has sheet like structure shown by FESEM micrographs. Regular Hexagonal pattern obtained on sheet these hexagonal are of ZnS particles. The crystalinity and intensity of rGO/ZnS composites peaks increase as the amount of ZnS nanoparticles increases into rGO. These composites exhibit increase in band gap due to quantum confinement. The luminescence property also increased in sample with higher concentration of ZnS in rGo. These nanocomposites are used as a photocatalyst in visible region. FESEM images revealed that the ZnS particles were attached onto the rGO sheet with the particle diameter of about 4.5 nm -15nm. The graphene sheets play an important role to assist ZnS nanoparticles growth and dispersion on its surface and also help to prevent the aggregation of the Graphene sheet. Reduced Graphene oxide/ZnS nanocomposites exhibit fluorescence property compared with pure ZnS and rGo. It also enhances the photocatalytic activity by efficient light harvesting, improved interfacial charge transfer, and suppressing charge recombination.

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References

[1] N. Kumar, T. K. Pathak, L. P. Purohit, H. C. Swart, Y. C. Goswami, Nano-Structures & Nano-Objects **16**, 1 (2018).
[2] R. Bisauriya, D. Verma, Y. C. Goswami, Journal of Materials Science: Materials in Electronics **29**(3), 1868 (2018).
[3] C. Y. Yeh, Z. W. Lu, S. Froyen, A. Zunger, Phys Rev B **46**, 10086 (1992).
[4] Nitin Kumar, L. P. Purohit, Y. C. Goswami, AIP Conference Proceedings **1675**, 020030 (2015).
[5] G. Z. Shen, P. C. Chen, Y. Bando, D. Golberg, C. Zhou, Chem Mater **20**(20), 6779 (2008).
[6] Kumar Nitin, L. P. Goswami, E. Physica E, Low-dimensional Systems and Nanostructures **83**, 333 (2017).
[7] S. Anandan, A. Manivel, M. Ashok Kumar, Fuel Cells **12**, 956 (2012).
[8] S. Bae, H. Kim et al., Nat Nano **5**, 574 (2010).
[9] S. Bai, X. SHen, RSC Advances **2**, 64 (2012).
[10] S/ Bai, X/ Shen, G/ Zhu, Z/ Xu, Y. Liu, Carbon **49**, 4563 (2011).
[11] A. Balandin, S. Ghosh, W. Bao, I. Calizo et al., Nano Letters **8**, 902 (2008).
[12] X/ Li, W. Cai, J. An et al., Science **324**, 1312.
[13] X. Li, W. Cai, L. Colombo, R. S. Ruoff, Nano Letters **9**, 4268 (2009).
[14] S. Stankovich, D. A. Dikin, G. H. Donnett, K. M. Kohlhaas, E. J. Zimney et al., Nature **442**, 282.
[15] Y. Kopelevich, P. Esquniazi, Advanced Materials **19**, 4559 (2007).
[16] L. Kou, C. Gao, Nanoscale **3**, 519 (2011).
[17] X. Zheng, J. Liu, L. Chen, J. Gao, Y. Tao, Recent Innovations in Chemical Engineering **6**(3), (2013).