Liquid Exfoliation Process Optimization of Graphene-Like Molybdenum Disulfide with Orthogonal Experiment Method

Tianyun Zhang¹, Haiqing Wang², Xiaoping Zheng¹ and Kui Chen³,*

¹School of Electronic and Information Engineering, Lanzhou City University, Lanzhou, China
²Gansu Radio & TV University, Lanzhou, China
³School of Bailie Mechanical Engineering, Lanzhou City University, Lanzhou, China

*Corresponding author e-mail: 874390294@qq.com

Abstract. The values of process parameters have direct effect on the concentration and thickness of graphene-like molybdenum disulfide (MoS₂) in dispersions during liquid exfoliation. For the purpose of optimization liquid exfoliation process of MoS₂ and obtaining dispersions with concentration of MoS₂ as high as possible, orthogonal experiment of 3 factors at 4 levels was determined by taking absorbance of absorption peak (located at 620 nm nearby) of graphene-like MoS₂ in UV-Vis spectra as criteria for decision-making of quality. The results were further analyzed with range analysis method. The results indicate that, within given test range, the process parameters affecting absorbance, i.e. concentration of graphene-like MoS₂, from high to low are 1,4-butanediol (BDO) content in BDO/water mixture, ultrasonic power and ultrasonic time, and the optimal process parameters of liquid exfoliation are BDO content being 80 vol%, ultrasonic power being 600 W and ultrasonic time being 40 h, which is further verified by additional test.

1. Introduction

Graphene-like molybdenum disulfide (MoS₂), as a new two-dimensional (2D) crystal material following the study of 2D layered nanomaterials such as graphene, is composed by monolayer or few-layer MoS₂ with strong covalent bonding in each layer and weak van der Waals forces between the layers. Each layer typically has a thickness of 6.5 Å [1]. Being similar to montmorillonite [2-4], graphene [5], attapulgite [6], etc., graphene-like MoS₂ deriving from quantum size effect associated with ultrathin structure can improve the crystallization behavior of polyester in the form of heterogeneous nucleation, and then optimize their properties. Furthermore, graphene-like MoS₂ can also improve gas and liquid barrier properties of polyester matrix for the existing of nanosheets.

According to the report of mixed-solvent being an efficient strategy for the liquid exfoliation of inorganic graphene analogue [7], a two-step reaction of esterification and polycondensation in melt state by replacing pure alcohol with graphene-like MoS₂ dispersion, prepared with liquid exfoliation by choosing alcohol and deionized water as mixed-solvent, can not only realize polyester modification, but also avoid the shortcomings of preparing nanomaterials with liquid exfoliation, i.e. the difficulty of removing solvent and the reaggregation of nanosheets in the process of slow solvent evaporation.

The key factor deciding the concentration of graphene-like MoS₂ in dispersions is the selection of liquid exfoliation process parameters. While liquid exfoliation, as the most common technique in recent years to prepare 2D nanomaterials [8], is a multivariable, periodic unsteady and nonlinear
process. Therefore, to obtain a dispersions containing graphene-like MoS$_2$ as high as possible, and reach the purpose of improving the content of inorganic nanoparticles in polyester accordingly, a large amount of liquid exfoliation experiments should be carried out. The orthogonal experiment is an effective method to optimize process parameters under fewer tests [9, 10]. In this research, taking absorbance of absorption peak of graphene-like MoS$_2$ in obtained dispersions as criteria for decision-making of quality, orthogonal experiment and range analysis method will be used to study the influences of the liquid exfoliation process parameters on the concentration of graphene-like MoS$_2$ in dispersions, and determine liquid exfoliation process in the scope of experiment through which graphene-like MoS$_2$ dispersion with the maximum concentration can be obtained. All the above provide reference for the preparation of graphene-like MoS$_2$ dispersion.

2. Experiments

2.1. Materials
MoS$_2$ (<2 um) was purchased from Sigma-Aldrich (Shanghai) Trading Co., Ltd., 1,4-butandiol (BDO, AR) was purchased from Xilong Chemical Co., Ltd. (China).

2.2. Preparation of graphene-like MoS$_2$ dispersion
50 mg of MoS$_2$ powder was added to a 100 mL one-neck round-bottomed flask. 50 mL of BDO and deionized water mixture was added as dispersion solvent. And the sealed flask was sonicated for a certain hours at a certain power using a bath sonicator, then the as-obtained “milky” solution was centrifuged at 10000 rpm for 30 min followed with the top two-thirds of the supernatant was collected.

2.3. Characterization
UV-Vis spectra with a spectral range from 500 to 800 nm were reported for graphene-like MoS$_2$ dispersion on a Pgeneral TU-1810 twin-beam spectrophotometer.

2.4. Parameter selection of liquid exfoliation process
As mentioned above, the effect of liquid exfoliation process parameters on the concentration of graphene-like MoS$_2$ in dispersions presents great complexity. For the purpose of analysis the effect of process parameters on the concentration of graphene-like MoS$_2$ quantitatively, BDO volume fraction in BDO/water mixture (A), ultrasonic power (B) and ultrasonic time (C) were regarded as main process parameters of liquid exfoliation here in the case of MoS$_2$ being excess.

2.5. The orthogonal experiment design
Orthogonal test is a method to arrange and analyze multi-factor test scientifically with orthogonal table. As shown in Tab. 1, the effect of process parameters selected on the concentration of graphene-like MoS$_2$ in dispersions obtained by liquid exfoliation was studied through an orthogonal experiment with three factors at four levels. And Tab. 2 was the experiment design L$_{16}$($4^3$) accordingly.

| Level | Factor | A /vol% | B /W | C /h |
|-------|--------|---------|------|------|
| 1     |        | 60      | 240  | 16   |
| 2     |        | 70      | 360  | 24   |
| 3     |        | 80      | 480  | 32   |
| 4     |        | 90      | 600  | 40   |
3. Results and discussion

3.1. Importance analysis of process parameters

The light absorption properties of MoS$_2$ are closely related with their own thickness: bulk MoS$_2$ do not exist absorption peak, while that of nanoscale MoS$_2$ locates at 620 and 670 nm nearby [11]. Absorbance of absorption peak located at 620 nm nearby was chosen as decision standard of graphene-like MoS$_2$ concentration in dispersions obtained. Obviously, the higher the absorbance value at 620 nm, the higher the concentration of graphene-like MoS$_2$ in mixture. And Tab. 2 presents absorbance values of absorption peak of graphene-like MoS$_2$ in dispersions corresponding to orthogonal experiment array.

| Number | Factors  | Absorbance /cm$^{-1}$ |
|--------|----------|------------------------|
|        | A /vol%  | B /W | C /h |                      |
| 1      | 1        | 1   | 1   | 0.2479               |
| 2      | 1        | 2   | 2   | 0.2869               |
| 3      | 1        | 3   | 3   | 0.3521               |
| 4      | 1        | 4   | 4   | 0.7795               |
| 5      | 2        | 1   | 2   | 1.1464               |
| 6      | 2        | 2   | 1   | 0.7503               |
| 7      | 2        | 3   | 4   | 1.0186               |
| 8      | 2        | 4   | 3   | 1.3069               |
| 9      | 3        | 1   | 3   | 1.5536               |
| 10     | 3        | 2   | 4   | 1.3848               |
| 11     | 3        | 3   | 1   | 0.6996               |
| 12     | 3        | 4   | 2   | 1.8761               |
| 13     | 4        | 1   | 4   | 0.4928               |
| 14     | 4        | 2   | 3   | 0.4206               |
| 15     | 4        | 3   | 2   | 0.2397               |
| 16     | 4        | 4   | 1   | 0.3896               |

Table 3. Range analysis.

|         | A /vol%  | B /W | C /h  |
|---------|----------|------|-------|
| $K_1$   | 1.6664   | 3.4407| 2.0874|
| $K_2$   | 4.2222   | 2.8426| 3.5491|
| $K_3$   | 5.5141   | 2.3100| 3.6332|
| $K_4$   | 1.5427   | 4.3521| 3.6757|
| $k_1$   | 0.4166   | 0.8602| 0.5219|
| $k_2$   | 1.0556   | 0.7107| 0.8873|
| $k_3$   | 1.3785   | 0.5775| 0.9083|
| $k_4$   | 0.3857   | 1.0880| 0.9189|
| $R$     | 0.9929   | 0.5105| 0.3971|

The effect of liquid exfoliation process parameters on absorbance can be analyzed by the following two formulas with range analysis method.

$$ k_i = K_i / s \quad i = 1, \ldots, 4 $$  \hspace{1cm} (1)

$$ R = \max\{k_i\} - \min\{k_i\} \quad i = 1, \ldots, 4 $$  \hspace{1cm} (2)
where $K_i$ and $k_i$ are the sum and arithmetic mean of absorbance of a factor at level $i$ respectively, $R$ is range, and $s$ represents the number of occurrences of a factor at each level. Tab. 3 shows the results calculated through range analysis.

The range ($R$) means the importance of a factor on absorbance. The higher the $R$, the more the importance is. Hence, Tab. 3 indicates that parameters affecting absorbance from high to low are volume fraction of BDO (A), ultrasonic power (B) and ultrasonic time (C). Experiments show that MoS$_2$ flakes can hardly be exfoliated from their bulk material with ultrasound when choosing pure BDO or deionized water as single-component solvent, but it can be realized in BDO/water mixture with appropriate volume ratio (Fig. 1), which is agreed with the point that mixed-solvent is an efficient strategy for the liquid exfoliation of inorganic graphene analogue [7]. Hence, the importance degree of BDO volume fraction, located at the first place, is higher than that of other two process parameters.

![Figure 1. Photograph of dispersions with different BDO content.](image1)

Fig. 2 shows directly the difference of effect of each factor on absorbance through $k_i$ variation range according to Tab. 3. Obviously, the greatest effect factor on absorbance is BDO volume fraction, which is consistent with the results of range $R$.

![Figure 2. The effect of factor on absorbance.](image2)

![Figure 3. UV-Vis spectrum of dispersions achieved by additional test.](image3)

3.2. Parameters optimization of process

The higher the $k_i$, the better the level $i$ of a factor is. Hence, $A_3B_4C_4$ is the optimization scheme of factor and level according to Fig. 2. And the optimal parameter values of liquid exfoliation process, through which dispersion with high concentration graphene-like MoS$_2$ can be obtained, are volume fraction of BDO in mixed solvent being 80 vol%, ultrasonic power 600 W and ultrasonic time 40 h.

3.3. Validation of optimized process

Since the optimization scheme of liquid exfoliation has not been implemented, additional test should be carried out. Fig.3 is UV-Vis spectrum of dispersions obtained by additional test. As can be seen, absorbance of absorption peak of graphene-like MoS$_2$ located at 620 nm nearby is 2.1802, higher than that existed (see Tab. 2), which shows, from the standpoint of test, the above optimization scheme is effective.
4. Conclusion
Choosing BDO and deionized water as mixed-solvent, graphene-like MoS$_2$ dispersion was prepared by liquid exfoliation. In order to obtain dispersions containing MoS$_2$ as high as possible, taking absorbance of absorption peak of graphene-like MoS$_2$ located at 620 nm nearby as criteria for decision-making, orthogonal experiment with three factors at four levels was determined on condition that MoS$_2$ is excess. Range analysis shows that liquid exfoliation process parameters (factors) affecting absorbance in descending order are volume fraction of BDO in mixed-solvent, ultrasonic power and ultrasonic time. And the optimal liquid exfoliation process in the scope of experiment is as follow: 50 mg of MoS$_2$ powder was added to a mixed-solvent formed by 40 mL BDO and 10 mL deionized water, then sonicated for 40 hours at 600 power after sealing. The as-obtained “milky” solution was centrifuged at 10000 rpm for 30 min followed with the collection of the top two-thirds of the supernatant. The absorbance characterization of the additional test verifies the effectiveness of the above parameter optimization scheme.

5. Acknowledgments
The paper was financially supported by the National Natural Science Foundation of China (No. 51865025), the Gansu Natural Science Foundation (No. 18JR3RA223, 218, 230), the Scientific Research Project of Bureau of Gansu Education (No. 2019B-176, 2018D-19), Talent Innovation and Entrepreneurship Project of Lanzhou (No. 114).

References
[1] Xue Li, Jinhua Li, Xiaohua Wang, Preparation, applications of two-dimensional graphene-like molybdenum disulfide, Integrated Ferroelectrics, 158 (2014) 26-42.
[2] Yi Jing Phua, Nyok-Sean Lau, Kumar Sudesh, A study on the effects of organoclay content and compatibilizer addition on the properties of biodegradable poly(butylene succinate) nanocomposites under natural weathering, Journal of Composite Materials, 49 (2014) 891-902.
[3] Suprakas Sinha Ray, Visualisation of nanoclay dispersion in polymer matrix by high-resolution electron microscopy combined with electron tomography, Macromolecular Materials and Engineering, 294 (2009) 281-286.
[4] Suprakas Sinha Ray, Mosto Okamoto, Kazuaki Okamoto, Structure and properties of nanocomposites based on poly(butylene succinate-co-adipate) and organically modified montmorillonite, Macromolecular Materials and Engineering, 290 (2005) 759-768.
[5] Chaoying Wan, Biqiong Chen, Reinforcement of biodegradable poly(butylene succinate) with low loadings of graphene oxide, Journal of Applied Polymer Science, 127 (2013) 5094-5099.
[6] Zhiguo Qi, Haimu Ye, Jun Xu, Synthesis and characterizations of attapulgite reinforced branched poly(butylene succinate) nanocomposites, Colloids and Surfaces A: Physicochemical and Engineering Aspects, 436 (2013) 26-33.
[7] Kai-ge Zhou, Nan-nan Mao, Hang-xing Wang, A mixed-solvent strategy for efficient exfoliation of inorganic graphene analogues, Angewandte Chemie International Edition, 50 (2011) 10839-10842.
[8] Xiaming Feng, Xin Wang, Weiyi Xing, Liquid-exfoliated MoS2 by chitosan and enhanced mechanical and thermal properties of chitosan/MoS2 composites, Composites Science and Technology, 93 (2014) 76-82.
[9] Ozcelik Babur, Sonat Ibrahim, Warpage and structural analysis of thin shell plastic in the plastic injection molding, Materials and Design, 30 (2009) 367-375.
[10] J Koszukul, J Jnabialek, Viscosity models in simulation of the filling stage of the injection molding process, Journal of Materials Processing Technology, 157-158 (2004) 183-187.
[11] Ronan J Smith, Paul J King, Mustafa Lotya, Large-scale exfoliation of inorganic layered compounds in aqueous surfactant solutions, Advanced Materials, 23 (2011) 3944-3948.