Synthesis and characterization of in-situ MoS_2-graphene hybrid nanostructured material

Bui Thi Hoa[1,2*], Nguyen Duc Lam[2], Bui Xuan Khuyen[1,2], Bui Son Tung[1,2], Man Hoai Nam[1,2], Nguyen Thi Ngoc Anh[2], Do Chi Linh[2], Duong Thi Huong[3], Pham Thi San[2]

[1]Graduate University of Science and Technology, Vietnam Academy of Science and Technology;
[2]Institute of Materials Science, Vietnam Academy of Science and Technology;
[3]Faculty of Fundamental Science, Military Science Academy.
[*]Corresponding author: hoabt@ims.vast.ac.vn
Received 19 May 2022; Revised 28 July 2022; Accepted 10 August 2022; Published 26 August 2022.
DOI: https://doi.org/10.54939/1859-1043.j.mst.81.2022.122-127

ABSTRACT

Nowadays, it has been challenging to develop novel techniques and synthesis processes for hybrid two-dimensional materials. Hence, this research presents an innovative technique for the fabrication of MoS_2-Graphene (MoS_2-Gr) hybrid nanostructured materials. The graphene was effectively generated in-situ and incorporated into the interlayer spacing of MoS_2, which was synthesized by using a co-precipitation process with diethyl glycol as the solvent, followed by annealing the as-synthesized MoS_2 at 800 ^oC for two hours in an inert atmosphere. The integrated graphene enhanced the width of MoS_2 interlayers, exposing a substantial concentration of active edge sites in the hybrid material, according to SEM, XRD, HR-TEM, and other characterizations. This research might lead to the development of viable hybrid structured materials for various applications. In addition, this study outlines a novel advanced approach for creating hybrid 2D nanostructured materials with superior characteristics.

Keywords: MoS_2; Graphene; MoS_2-Graphene; Hybrid nanostructured materials; In-situ.

1. INTRODUCTION

Graphene and similar inorganic two-dimensional (2D) nanomaterials are a unique class of substances with fascinating characteristics such as excellent electron mobility, exceptionally high thermal conductivity, tremendous flexibility, extraordinary mechanical strength, and high transparency [1-4]. Additionally, graphene is chemically inert and a gapless semimetal, its isostructural counterpart [5, 6]. In contrast, molybdenum disulfide (MoS_2)- a typical inorganic two-dimensional (2D) material is chemically versatile and bandgaps, making them valuable [7, 8]. Although each of these 2D nanomaterials has a lot of power in different applications [9-12], combining these materials has recently generated a new strategy in upcoming applications, not only for the combination of distinct capabilities but also for advanced features that can arise independently from single-component materials [13-16]. Combining other nanomaterials with graphene can improve the properties of graphene and hybrid materials [17, 18]. Specifically, hybrid heterostructures are made of two 2D layered materials, such as MoS_2 and graphene, which have gotten much attention [13, 14, 19]. These similar nanostructured materials with increased specific surface area benefit from chemical interactions between hybridized components on their interface. That leads to making them promising design materials for next-generation nanomaterial architectures.

A great deal of effort has focused on developing methods and synthesis processes for creating hybrid heterostructured materials, such as liquid exfoliation and chemical modification/functionalization strategies [20]. Kong et al. [19] used ammonium thiomolybdate as a precursor, and chemical vapor deposition (CVD) was employed for producing graphene template to develop MoS_2 layers at the temperature of 400 °C. Because there was a lattice

mismatch between graphene and MoS_2, this straightforward process offers a novel approach for creating graphene heterostructures and surface functionalization of graphene. Robinson et al. [21] also achieved direct MoS_2 generation on epitaxial graphene. As a result, direct MoS_2 production on graphene substrates has considerable promise for developing new optical, electrical, and transparent electrodes for a few applications. These are significant steps forward in the development of hybrid 2D materials. However, the research and findings of new procedures and synthesis processes for hybrid 2D materials have been challenging.

Here, in this work, we introduce *in-situ* generating MoS_2-graphene (MoS_2-Gr) hybrid nanostructured material through the co-precipitation method and then heat treatment in inert conditions. The synthesized MoS_2-graphene hybrid nanostructured was evaluated by X-ray diffraction (XRD), thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and transmission electron microscopy (TEM).

2. EXPERIMENTAL SECTION

2.1. Materials

Sodium molybdenum oxide dihydrate ($Na_2MoO_4.2H_2O$; Sigma-Aldrich), Thiourea ($SC(NH_2)_2$; Sigma-Aldrich), diethylene glycol ($(HOCH_2CH_2)_2O$; Sigma-Aldrich), Acetonitrile (CH_3CN; Sigma-Aldrich) and Ethanol (C_2H_6O; Sigma-Aldrich) were purchased without further additional purification. Through experiments, Deionized water (DI) was used.

2.2. Synthesis of MoS_2 and MoS_2-Gr

Firstly, the co-precipitation method was used to synthesize MoS_2. In a round-bottomed flask, a mixture of $Na_2MoO_4.2H_2O$ and $SC(NH_2)_2$ in diethylene glycol solvent with a mol ratio of 1:4 have prepared. Then, a reflux system was used with steady magnetic stirring to heat the mixture to 200 °C for 24 hours. To prevent oxidation during the synthesis process, argon gas was continuously supplied via an argon-filled balloon. Following the completion of the reaction, the product was carefully washed with ethanol and DI water to remove all the remaining precursors and then centrifuged at 4000 rpm for 30 minutes to collect the aggregate. Black aggregate was selected and dried at 80 ^oC for at least 24 hours to produce black powder MoS_2 for the next experiments.

The selected black powder MoS_2 was calcined in a tube furnace at 800 ^oC for 2 hours at an accelerated temperature rate of 5 $^oCmin^{-1}$ under the flow of N_2 to produce the hybrid nanostructured MoS_2-Gr materials. All powders were collected and stored in a vacuum for further characterization.

2.3. Materials characterizations

Field emission scanning electron microscopy (FE-SEM, HITACHI S-4800) was used to study the surface topography of the synthesized materials at a 15 kV accelerating voltage. Thermogravimetric analysis (TGA) was conducted using a TGA analyzer (SDT Q600/DSC Q20, TGA7 PERKIN ELMER, TG-DTA2200SA) with a heating rate of 5 $°Cmin^{-1}$ in an inert atmosphere. X-ray diffraction (XRD; Rigaku D/MAX 2600 V, Cu K (= 0.15418 nm)), high-resolution transmission electron microscopy (HR-TEM, Omega EM) with an accelerating voltage of 200 kV. Scanning transmission electron microscopy (STEM) was used to map the material's elements (STEM).

3. RESULTS AND DISCUSSION

SEM images of MoS_2 and MoS_2-Gr are shown in figure 1(a) and figure (b), respectively. After heat treatment at 800 ^oC in 2 h, the SEM image of MoS2-Gr in figure 1(b) exhibits the enlargement of the size with more excellent crystallinity and improved grain boundary compared with before heat treatment of MoS_2 in figure 1 (a). These features contribute significantly to enhancing the conductivity and electrochemical properties of MoS_2-Gr.

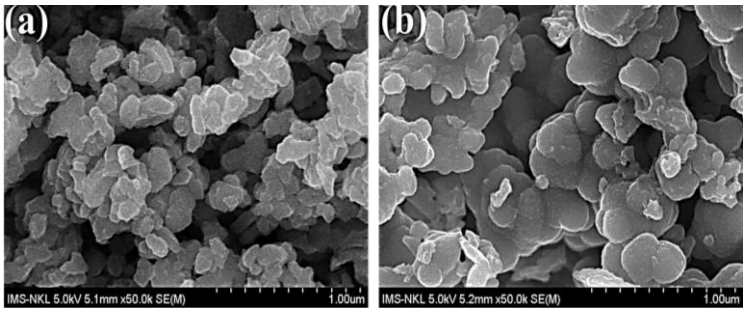

Figure 1. *SEM images of MoS_2 and MoS_2-Gr.*

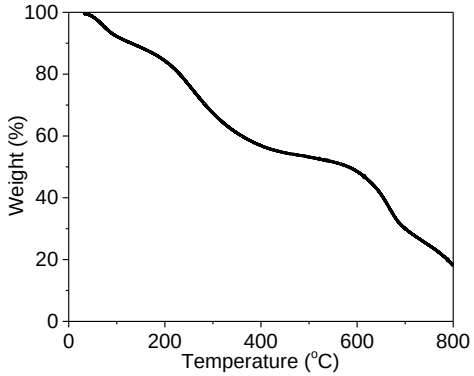

Figure 2. *TGA data of MoS_2 in an inert atmosphere at a heating rate of 5 $^oC.min^{-1}$.*

As shown in figure 2, thermogravimetric analysis (TGA) results were collected using a TGA analyzer in an inert atmosphere with a heating rate of 5 $^oC.min^{-1}$. Due to moisture evaporation, there was a minor weight loss at the start of the heating process, which continued up to 200 ^oC. Then, a relatively rapid shift from 200 ^oC can be noted, which can be attributed to the evaporation of diethylene glycol (DEG) molecules (the boiling point of DEG is 244 ^oC). The weight loss continued up to 600 ^oC due to the start of crystal MoS_2, after which there was a change in the slope. Then another weight-loss trend is observed from 600 ^oC to 800 ^oC, suggesting that the diethylene glycol molecules trapped inside the layers of MoS_2 had begun to carbonize into carbon product (e.g: graphene) (in the MoS_2-Gr sample).

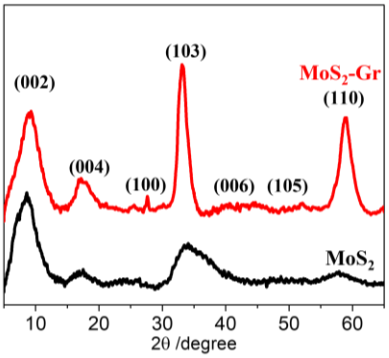

Figure 3. *XRD patterns of MoS_2 and MoS_2-Gr.*

X-ray diffraction (XRD) was used to investigate the crystal structure of the as-synthesized MoS_2 sample and the hybrid MoS_2-Gr sample. Figure 3 displays the XRD patterns of MoS_2 and MoS_2-Gr samples. The XRD peaks are located at 27.8^o, 33.5^o, 39^o, and 58.5^o positions of the MoS_2, and MoS_2-Gr samples, which match well with corresponding indexed diffraction (004), (100), (103), and (110) planes of the reference MoS_2 (JCPDS card no. 37-1492) [22–24]. As the

reference MoS_2 (JCPDS card no.37-1492), the main peak of the MoS_2 reference is at 14.4º with the corresponding (002) plane. However, the major peak of MoS_2 and MoS_2-Gr samples has been shifted to the lower two-theta angle locations, located at 8.6º and 8.9º, respectively. Hence, the shifted (002) diffraction peak in the samples suggested that DEG was trapped in the interlayer spacing of MoS_2, and after calcination, the carbon product (e.g., graphene) caused the interlayer spacing of MoS_2 to expand in MoS_2 and MoS_2-Gr samples, respectively. Furthermore, the (002) diffraction peak of graphene located at 11.14º position is hardly detected in the XRD pattern of the MoS_2-graphene composite, suggesting that the distribution of graphene sheets inside MoS_2 layers nanosheets. Similar results have been reported previously in the literature [25-27].

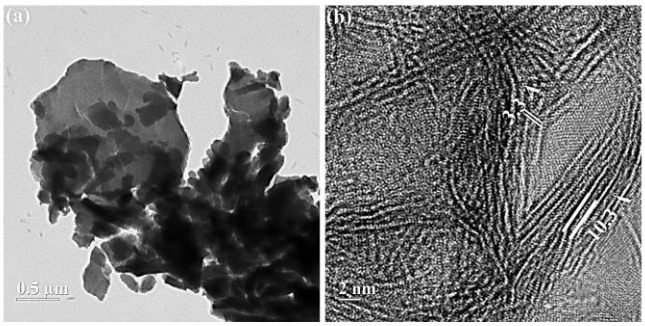

Figure 4. *HR-TEM images of MoS_2-Gr at two different scale bar (a) 0.5 μm, and (b) 2nm, respectively.*

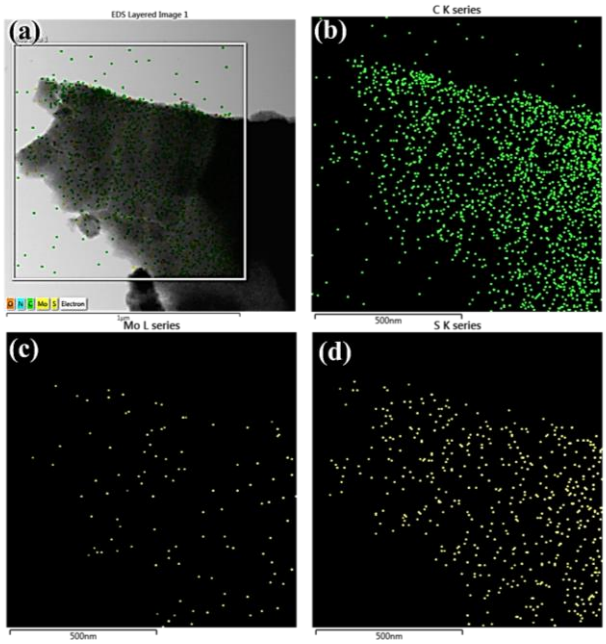

Figure 5. *(a) High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding elemental mapping images of (b)C, (c) Mo, and (d) S of MoS_2-Gr (scale bar= 500 nm).*

Figure 4 (a) shows the HR-TEM image of MoS_2-Gr at a scale bar of 0.5 μm, indicating that synthesized MoS_2-Gr has a nanoplate structure. Furthermore, the d-spacing corresponding to the first XRD peak represents the interlayer distance in the MoS_2-Gr sample. The d-spacing of the MoS_2-Gr is determined to be 10.3 Å from the HR-TEM image displayed in figure 4(b), which may be attributed to the (002) plane located at 8.9º (in figure 3). The finding suggests the formation *in-situ* of graphene inside layer MoS_2, leading to the interlayer's enlarging in MoS_2-Gr.

Furthermore, besides the expanded interlayer of MoS_2, in figure 4 (b), the d-spacing of 3.3Å is observed, corresponding to the typical signal of graphene. This observation supports that graphene was formed and integrated *in-situ* inside the interlayer of MoS_2 in the MoS_2-Gr sample.

Figure 5 (a)-d shows the high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image and the corresponding elemental mapping images of C, Mo, and S of MoS_2-Gr, respectively. Figure 5 (a) indicates the existence of Mo, S, and C in the MoS_2-Gr sample. Moreover, the uniform distribution of each element (C, Mo, S) in the MoS_2-Gr sample is observed clearly in figures 5(b), (c), and (d), respectively. These characterizations logically support the explanations for the successful synthesis of MoS_2 -Gr hybrid nanostructured materials in which *in-situ* formation graphene inside the MoS_2 interlayer in the MoS_2- Gr hybrid sample.

4. CONCLUSION

In conclusion, this work provides an advanced strategy for the synthesis MoS_2-Gr hybrid nanostructure material. The graphene was successfully formed *in-situ* and integrated into the interlayer spacing of MoS_2 synthesized via a co-precipitation reaction using diethylene glycol as the solvent, then annealing the as-synthesized MoS_2 at 800 ^oC for 2 hours in an inert atmosphere. According to SEM, XRD, HR-TEM, and other characterizations, the incorporated graphene increased the width of MoS_2 interlayers, exposing a large concentration of active edge sites in the hybrid material. This finding is believed to provide a promising hybrid material for various applications. Moreover, this research describes a new advanced technique for synthesizing hybrid 2D nanostructured materials with excellent properties.

Acknowledgment: *This research is funded by the Graduate University of Science and Technology under Grant Number GUST.STS.ĐT2020-KHVL10.*

REFERENCES

[1]. Z. Fang, Q. Xing, D. Fernandez, X. Zhang, G. Yu, *"A mini review on two-dimensional nanomaterial assembly"*, Nano Res. 13, pp. 1179–1190, (2020).

[2]. F. Bonaccorso, L. Colombo, G. Yu, M. Stoller, V. Tozzini, A.C. Ferrari, R.S. Ruoff, V. Pellegrini, *"Graphene, related two-dimensional crystals, and hybrid systems for energy conversion and storage"*, Science. 347, p. 1246501, (2015).

[3]. A. K . Geim, K. S. Novoselov, *"The rise of graphene"*, Nat. Mater. 6, pp. 183–191, (2007).

[4]. K. S. Novoselov, A. K. Geim, S. V Morozov, D. Jiang, Y. Zhang, S. V Dubonos, I. V Grigorieva, A.A. Firsov, *"Electric Field Effect in Atomically Thin Carbon Films"*, Science (80-.). 306, pp. 666–669, (2004).

[5]. N.A. Kumar, M.A. Dar, R. Gul, J.-B. Baek, *"Graphene and molybdenum disulfide hybrids: synthesis and applications"*, Mater. Today. 18, pp. 286–298, (2015).

[6]. K.S. Novoselov, *"Graphene: The Magic of Flat Carbon"*, ECS Trans. 19, pp. 3-7, (2009).

[7]. C.-P. Lu, G. Li, J. Mao, L.-M. Wang, E.Y. Andrei, *"Bandgap, Mid-Gap States, and Gating Effects in MoS2"*, Nano Lett. 14, pp. 4628–4633, (2014).

[8]. K.F. Mak, C. Lee, J. Hone, J. Shan, T.F. Heinz, *"Atomically Thin MoS2: A New Direct-Gap Semiconductor"*, Phys. Rev. Lett. 105, 136805, (2010).

[9]. Y. Shi, H. Li, L.-J. Li, *"Recent advances in controlled synthesis of two-dimensional transition metal dichalcogenides via vapor deposition techniques"*, Chem. Soc. Rev. 44, pp. 2744–2756, (2015).

[10]. Y. Chen, K. Yang, B. Jiang, J. Li, M. Zeng, L. Fu, *"Emerging two-dimensional nanomaterials for electrochemical hydrogen evolution"*, J. Mater. Chem. A. 5, pp. 8187–8208, (2017).

[11]. M. Ahmadi, O. Zabihi, S. Jeon, M. Yoonessi, A. Dasari, S. Ramakrishna, M. Naebe, *"2D transition metal dichalcogenide nanomaterials: Advances, opportunities, and challenges in multi-functional polymer nanocomposites"*, J. Mater. Chem. A. 8, pp. 845–883, (2020).

[12]. I. Song, C. Park, M. Hong, J. Baik, H.-J. Shin, H.C. Choi, *"Patternable Large-Scale Molybdenum Disulfide Atomic Layers Grown by Gold-Assisted Chemical Vapor Deposition"*, Angew. Chemie Int. Ed. 53, pp. 1266–1269, (2014).

[13]. J. Zhao, D. Zhang, F. Guo, H. Guo, Y. Liu, Y. Yin, H. Hu, X. Wang, *"Facile one-pot supercritical synthesis of MoS2/pristine graphene nanohybrid as a highly active advanced electrocatalyst for hydrogen evolution reaction"*, Appl. Surf. Sci. 531, 147282, (2020).
[14]. E. Singh, K.S. Kim, G.Y. Yeom, H.S. Nalwa, "*Two-dimensional transition metal dichalcogenide-based counter electrodes for dye-sensitized solar cells"*, RSC Adv. 7, pp. 28234–28290, (2017).
[15]. D.N. Sangeetha, M. Selvakumar, *"Active-defective activated carbon/MoS2 composites for supercapacitor and hydrogen evolution reactions"*, Appl. Surf. Sci. 453, pp. 132–140, (2018).
[16]. X. Zhou, L.-J. Wan, Y.-G. Guo, *"Synthesis of MoS2 nanosheet–graphene nanosheet hybrid materials for stable lithium storage"*, Chem. Commun. 49, pp. 1838–1840, (2013).
[17]. X. Huang, C. Tan, Z. Yin, H. Zhang, *"25th Anniversary Article: Hybrid Nanostructures Based on Two-Dimensional Nanomaterials"*, Adv. Mater. 26, pp. 2185–2204, (2014).
[18]. Y. Li, H. Wang, L. Xie, Y. Liang, G. Hong, H. Dai, *"MoS2 Nanoparticles Grown on Graphene: An Advanced Catalyst for the Hydrogen Evolution Reaction"*, J. Am. Chem. Soc. 133, pp. 7296–7299, (2011).
[19]. Y. Shi, W. Zhou, A.-Y. Lu, W. Fang, Y.-H. Lee, A.L. Hsu, S.M. Kim, K.K. Kim, H.Y. Yang, L.-J. Li, J.-C. Idrobo, J. Kong, *"van der Waals Epitaxy of MoS2 Layers Using Graphene As Growth Templates"*, Nano Lett. 12, pp. 2784–2791, (2012).
[20]. L. David, R. Bhandavat, G. Singh, *"MoS2/Graphene Composite Paper for Sodium-Ion Battery Electrodes"*, ACS Nano. 8, pp. 1759–1770, (2014).
[21]. Y.-C. Lin, N. Lu, N. Perea-Lopez, J. Li, Z. Lin, X. Peng, C.H. Lee, C. Sun, L. Calderin, P.N. Browning, M.S. Bresnehan, M.J. Kim, T.S. Mayer, M. Terrones, J.A. Robinson, *"Direct Synthesis of van der Waals Solids"*, ACS Nano. 8, pp. 3715–3723, (2014).
[22]. D. Lang, T. Shen, Q. Xiang, *"Roles of MoS2 and Graphene as Cocatalysts in the Enhanced Visible-Light Photocatalytic H2 Production Activity of Multiarmed CdS Nanorods"*, ChemCatChem. 7, pp. 943–951, (2015).
[23]. Z. Cheng, Y. Xiao, W. Wu, X. Zhang, Q. Fu, Y. Zhao, L. Qu, *"All-pH-Tolerant In-Plane Heterostructures for Efficient Hydrogen Evolution Reaction"*, ACS Nano. 15, pp. 11417–11427, (2021).
[24]. H. Gao, J. Zang, Y. Wang, S. Zhou, P. Tian, S. Song, X. Tian, W. Li, "*One-step preparation of cobalt-doped NiS@MoS2 core-shell nanorods as bifunctional electrocatalyst for overall water splitting"*, Electrochim. Acta. 377, 138051, (2021).
[25]. Khai, T. Van; Long, L. N.; Phong, M. T.; Kien, P. T.; Thang, L. Van; Lam, T. D. "*Synthesis and Optical Properties of MoS2/Graphene Nanocomposite*". *J.* Electron. Mater. 49 (2), pp. 969–979, (2020).
[26]. Wang, Y.; Zhen, M.; Liu, H.; Wang, C. "*Interlayer-Expanded MoS2/Graphene Composites as Anode Materials for High-Performance Lithium-Ion Batteries*" J. Solid State Electrochem. 22 (10), pp. 3069–3076, (2018).
[27]. Gupta, A.; Chen, G.; Joshi, P.; Tadigadapa, S.; Eklund. "*Raman Scattering from High-Frequency Phonons in Supported n-Graphene Layer Films*". Nano Lett. *6* (12), pp. 2667–2673, (2006).

TÓM TẮT

Nghiên cứu tổng hợp trực tiếp và phân tích vật liệu lai hóa MoS_2-Graphen với cấu trúc nano

Ngày nay, việc phát triển các kỹ thuật, quy trình tổng hợp chế tạo cho các vật liệu lai hóa có cấu trúc nano dạng lớp (hai chiều-2D) đã và đang là một thách thức lớn. Trong bài báo này , nhóm nghiên cứu chúng tôi giới thiệu một quy trình tổng hợp vật liệu lai hóa MoS_2-Graphen (MoS_2-Gr) có cấu trúc nano. Trong đó, graphen được tạo ra trực tiếp tại chỗ và xen vào giữa các lớp của MoS_2 một cách hiệu quả. Vật liệu lai hóa này được tổng hợp bằng cách phương pháp cô lắng với diethylene glycol làm dung môi, sau đó đã được nung ở nhiệt độ 800 ^oC trong hai giờ ở môi trường trơ. Việc graphen tích hợp vào giữa lớp MoS_2 làm nâng cao độ rộng của các lớp MoS_2 cũng như các đặc tính hóa lí trong vật liệu MoS_2-Gr đã được nghiên cứu và chứng minh thông qua các phương pháp phân tích đo đạc vật liệu hiện đại như SEM, XRD, HR-TEM,... Ngoài ra, nghiên cứu này còn đưa ra một cách tiếp cận tiên tiến mới để tạo ra các vật liệu lai hóa có cấu trúc nano 2D với các đặc tính ưu việt.

Từ khoá: MoS_2; Graphen; MoS_2-Graphen; Vật liệu lai hóa ; Phương pháp cô lắng; Trực tiếp.