

## Researches of Topologies and Dynamics of Molecular Agglomeration Network based on Complex Network

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### Abstract

*With appearance of small-world networks and scale-free networks, complex networks have provided natural theories to describe a variety of complex systems in many domains of science. In this paper, from the standpoint of Raman spectrum research aspect in material science, Raman spectrum analysis of graphite and diamond microcrystal retained by gallium phosphide nanoparticles is introduced. We found that molecular configuration of basic fuchsin adsorbed on gallium phosphide nanoparticles through experiments. Based on these, we adopt corresponding method of complex network to research some problems in Raman spectrum analysis and directly use complex network to convert real agglomerations into network model. With the intention of studying the topologies of agglomeration network, synchronizability behavior of agglomeration network are also discussed.*

**Keywords:** Raman spectrum, complex network, agglomeration network, network dynamics, network topologies

### 1. Introduction

Complex network is a network with non-trivial topological features that do not occur in simple networks such as lattices or random graphs [1] but often occur in network modeling real systems. Most social, biological, and technological networks display substantial non-trivial topological features, with patterns of edge between their vertices that are neither purely regular nor purely random. Such features include a heavy tail in the degree distribution, a high clustering coefficient, assortativity or disassortativity among vertices, community structure, and hierarchical structure.

Two well-known and much studied classes of complex networks are scale-free networks [2] and small-world networks [3] whose discovery and definition are canonical case-studies in the field. The two classes of complex networks are characterized by specific structural features: power-law degree distributions for the former and short path lengths and high clustering for the latter [4].

The field continues to develop at a brisk pace, and has brought together researchers from many areas including mathematics, physics, biology, telecommunications, computer science, sociology, epidemiology, material science and others [5-7].

Various large-scale molecular agglomeration networks are becoming important research objects in material science. Study on molecular agglomeration networks has become one of the key focuses in systems material science for demonstrating great potentials to discover basic functions and to reveal essential mechanisms for various material phenomena, by understanding material systems not at individual component level but at a system-wide level.

Although a large number of recent studies on molecular agglomeration networks have created very prolific researches, but there are still many challenging problems in this field.

These problems have attracted comprehensive attention of different field including applied material science, physics and computer scientists. This paper is just the application of complex networks in molecular agglomeration networks.

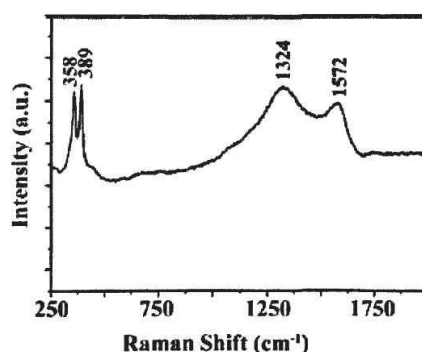
## 2. Raman Spectrum Analysis of Gallium Phosphide Nanoparticles

Comparing to common Gallium Phosphide (GaP) single crystal material, it is enormously different with gallium phosphide nanoparticles in physical and chemical properties, which causes that there are potential application value in fields of Nano optical and electronic devices.

### 2.1. Raman Spectrum of Common Gallium Phosphide Nanoparticles

According to analyzing oscillation spectrum of common gallium phosphide nanoparticles [8], there are P-O bond, P=O bond and O-H bond among surface of common gallium phosphide nanoparticles [9]. In this section, we will use raman spectrum to analyze nano free-state carbon mixed in gallium phosphide nanoparticles for understanding deeply the physical and chemical properties of common gallium phosphide nanoparticles which was synthesized by Benzene-thermal method.

Raman spectrum of common gallium phosphide nanoparticles which was synthesized by Benzene-thermal method is shown in Figure 1.



**Figure 1. Raman Spectrum of Common Gallium Phosphide Nanoparticles**

From Figure 1, we can see that in the scope of 250~2000  $\text{cm}^{-1}$ , there are four strong scattering peaks, peaks in 358  $\text{cm}^{-1}$  and 389  $\text{cm}^{-1}$  belong to TO and LO vibration. Moreover, there are two wide and strong scattering peaks in the scope of 1000~1700  $\text{cm}^{-1}$ , which is individually located in 1324  $\text{cm}^{-1}$  and 1572  $\text{cm}^{-1}$ , chemical substances having nothing to do with common gallium phosphide nanoparticles cause appearing of the two peaks. Hudgens found that vibration peak of P=O was individually located in 1280~1390  $\text{cm}^{-1}$  and 1330~1340  $\text{cm}^{-1}$  [10]. So we can draw a conclusion that there is a great deal of carbon in specimen of common gallium phosphide nanoparticles.

Chemical substances which draw carbon into gallium phosphide nanoparticles should be dimethylbenzene which acts as reaction medium. Gallium phosphide nanoparticles is continuously heated for a long time when the temperature is higher than boiling point of dimethylbenzene, but the two strong scattering peaks are also observed, it reveals that the two scattering peaks do not come from dimethylbenzene. Based on above analysis, substance which best fits the experiment results of raman spectrum is free-state carbon instead of organic combined-state carbon.

There is a sharp peak in 1580  $\text{cm}^{-1}$  in natural monocrystalline graphite [11]. The peak would become wider with increasing of disordering between graphite, peak located in 1360  $\text{cm}^{-1}$  would appear when disordering increased to a certain extent. The scattering peak of graphite fit well to scattering peak located in 1572  $\text{cm}^{-1}$  of gallium phosphide

nanoparticles. It can be inferred that a part of free-state carbon among gallium phosphide nanoparticles exists in the form of graphite.

Diamond is another important existence pattern of free-state carbon. Raman peak of diamond is located  $1332\text{ cm}^{-1}$ , from Figure 1, we can see that there is scattering peak nearby  $1332\text{ cm}^{-1}$  in raman spectrum of gallium phosphide nanoparticles, the wide and strong scattering peak is located in  $1324\text{ cm}^{-1}$ . But feature vibration of diamond would move about  $10\text{ cm}^{-1}$  to low frequency after heating, it would be located in  $1323\text{ cm}^{-1}$ , so it also can be inferred that a part of free-state carbon among gallium phosphide nanoparticles exists in the form of diamond.

## 2.2. Molecular Configuration of Basic Fuchsin Adsorbed on Gallium Phosphide

Basic fuchsin acts as one kind chloride which ionizes in water solution and can be divided into organic kation and  $\text{Cl}^{-1}$ , structure of kation is shown in Figure 2.

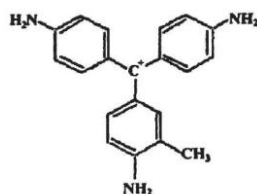
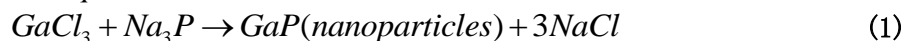


Figure 2. Structure of Kation

Gallium phosphide can be synthesized by  $\text{GaCl}_3$  and  $\text{Na}_3\text{P}$  in dimethylbenzene, the chemical reaction equation as follows:



In order to separate out  $\text{NaCl}$  from  $\text{GaP}$  nanoparticles, we use ionized water of basic fuchsin solution to clean them several times. We place gallium phosphide nanoparticles adsorbed basic fuchsin in desiccator to dry, thus, manufacturing gallium phosphide nanoparticles is specimen whose surface adsorbed basic fuchsin. Raman spectrum of high-concentration and low-concentration basic fuchsin and basic fuchsin adsorbed on gallium phosphide nanoparticles are individually shown in Figure 3 and Figure 4.

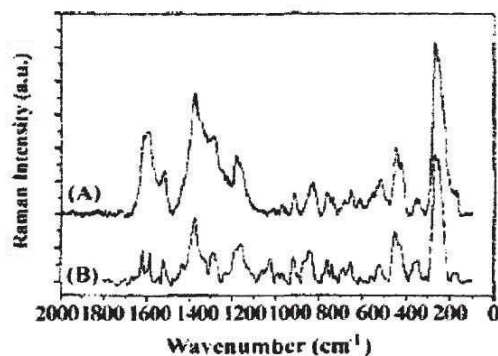
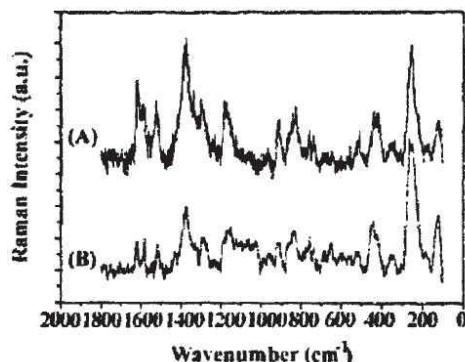


Figure 3. Raman Spectrum of basic Fuchsin in High-Concentration Solution

Comparing spectrum (A) to spectrum (B) in Figure 3, we observe that there is a wide scattering peak area from  $1200\text{ cm}^{-1}$  to  $1320\text{ cm}^{-1}$  in surface spectrum, and a new chemical bond  $\text{P-O-C}^+$  maybe formed.



**Figure 4. Raman Spectrum of basic Fuchsin in low-Concentration Solution**

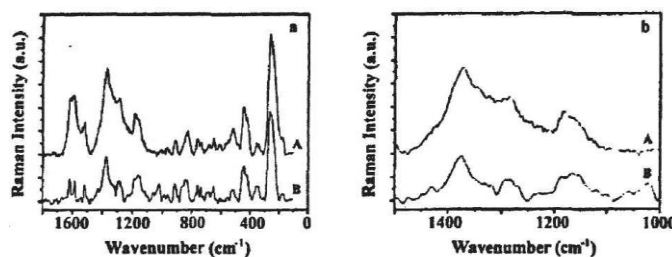
On the contrary, similar phenomenon is not observed in surface spectrum of spectrum (A) in Figure 4, it illustrates that there is not new forming chemical bond in low-concentration solution.

There are two kinds of molecular configuration—end-on and flat—for basic fuchsin adsorbed on gallium phosphide nanoparticles. In consideration of adsorption rate of dye molecules is in proportionate to the concentration of the solution. In high-concentration solution, a large number dye molecules arrive surface of gallium phosphide nanoparticles during unit of time, under these circumstances, its molecular configuration mainly includes end-on and flat, and flat structure is prerequisite of forming new chemical bond P-O-C<sup>+</sup>. In high-concentration solution, its molecular configuration only includes flat.

### 2.3. Raman Spectrum of basic Fuchsin Adsorbed on Surface of Gallium Phosphide

Gallium phosphide nanoparticles adsorbed basic fuchsin is placed in desiccator to dry, thus, surface of gallium phosphide nanoparticles can also be performed raman spectrum.

Raman spectrum of common basic fuchsin and surface of gallium phosphide nanoparticles adsorbed basic fuchsin are shown in Figure 5.



**Figure 5. Raman Spectrum of basic Fuchsin and Surface of Gallium Phosphide Nanoparticles**

From Figure 5 we can see that raman spectrum is different in different location of the same surface of specimen, we thought that it is caused by nanoparticles arrangement.

Surface enhancement raman spectrum can be defined by enhancement factor (EF) as follows [12]:

$$EF = \frac{I_{REL}}{(n_{ad}/n_{crys})} \cdot \frac{1}{f_{sh}} \quad (2)$$

Where,  $n_{ad}$  represent the number of dye molecules adsorbed on gallium phosphide nanoparticles,  $n_{crys}$  represent the number of pure dye crystal molecules, which is defined as follows:

$$n_{crys} = \frac{\rho_{crys} \cdot V_{crys} \cdot N_A}{M} \quad (3)$$

Where,  $\rho_{crys}$  is density,  $V_{crys}$  is scattering range volume,  $M$  is molar mass of dye molecules,  $N_A$  is Avogadro constant.

$n_{ad}$  can be defined as follows:

$$n_{ad} = \rho_{GaP} \cdot V_{GaP} \cdot \alpha \cdot N_A \quad (4)$$

Where,  $\rho_{GaP}$  is cumulative density,  $V_{GaP}$  is scattering range volume of GaP,  $\alpha$  is energy absorbed by unit mass ( $mol \cdot g^{-1}$ ).

$\alpha$  can be expressed as follows:

$$\alpha = \frac{C_{ad} \cdot V_{sat}}{W_{GaP}} \quad (5)$$

Where,  $C_{ad}$  is dye concentration adsorbed on GaP,  $V_{sat}$  is volume of dye (50ml) source solution,  $W_{GaP}$  is mass of GaP nanoparticle (50mg).

In this paper,  $C_{ad}$  can be derivate as follows:

$$C_{ad} = C_0 - C_{stan} \cdot \frac{A_{sus}}{A_{stan}} \quad (6)$$

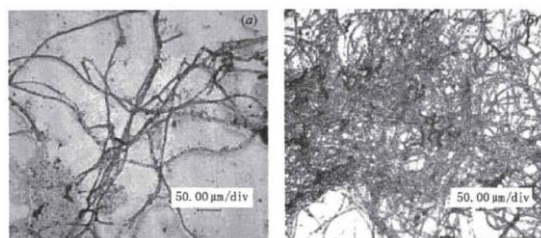
We assume  $V_{crys} \approx V_{GaP}$ , and apply parameter ( $n_{ad}/n_{crys} \approx 0.17$ ) to equation (2), the value of EF is 67, which is in accord with Hayashi's experiment result [13]. According to value of EF, we can conclude that basic fuchsin has absorbed on surface of GaP nanoparticles.

The problem we encountered in raman spectrum research would probably resolve through complex network. Because basic fuchsin absorbed randomly on GaP nanoparticles, so network which consists of nanoparticles has characteristics of randomness, and topological structure of network has fractal character. We can test and verify our surmise through empirical analysis of nanoparticles agglomeration network based on complex network.

### 3. Empirical Analysis of Nanoparticles Molecular Agglomeration Network

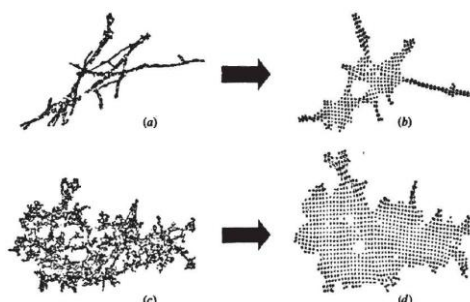
During performing procedure of raman spectrum, an universal and unexplainable problem is encountered, it is that why raman spectrum is different in different location of the same surface of specimen. Because atoms are closely arranged, the arrangement is very difficult to form so obvious difference in absorption. So it is very obvious that the overall environment around test point would become the problem which we have to consider. The problem is the cause why complex network would be drawn into.

We placed individually 200mg GaP in 50ml deionized water high-concentration solution and low-concentration solution for four years, nanoparticles through filter membrane gradually agglomerate and is transformed into agglomerations. We choose the most complete agglomeration in high-concentration solution and low-concentration solution to observe and research, optical microscopic (500 times zoom) picture is shown in Figure 6.



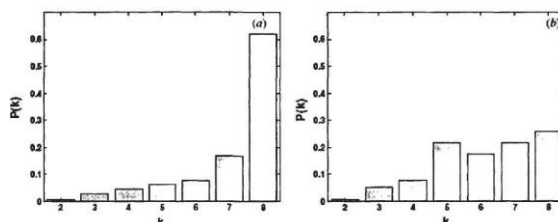
**Figure 6. (a) Optical Microscopic Picture in Low-Concentration Solution (b) Optical Microscopic Picture in High-Concentration Solution**

Then the optical microscopic pictures are cut into slices, the networks of top slice under kamada-kawa energy mode are shown in Figure 7.



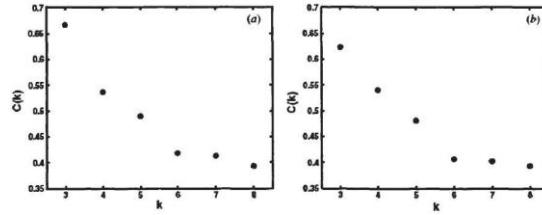
**Figure 7. (a) and (c) Optical Microscopic Picture before Top Slice (b) and (d) Networks under Kamada-Kawa Energy Mode**

It is different from small-world networks and scale-free networks, every node of molecular agglomeration network tends to connect with eight neighbor nodes. Degree distribution of high-concentration solution molecular agglomeration network and low-concentration solution molecular agglomeration network are shown in Figure 8.



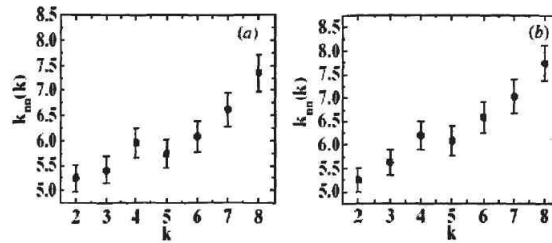
**Figure 8. Degree Distribution of High-Concentration Solution Agglomeration Network and Degree Distribution of low-Concentration Solution Agglomeration Network**

According to empirical analysis, clustering coefficient of high-concentration solution molecular agglomeration network is 0.41, clustering coefficient of high-concentration solution molecular agglomeration network is 0.48. Figure 9 plots the distribution of clustering coefficient vs. degree. Figure 9 reveals that in networks the number of nodes is small but clustering coefficient is high. It shows that agglomeration process is mainly restrictions to space factor. At the same time, average path length of high-concentration solution and low-concentration solution agglomeration network are individually 14 and 16.6 according to empirical analysis. It shows that nanoparticles prefer to agglomerate firmly to form stable structure.



**Figure 9. Distribution of Clustering Coefficient vs. Degree of High-Concentration Solution Agglomeration Network and Distribution of Clustering Coefficient vs. Degree of Low-Concentration Solution Agglomeration Network**

According to nodes with small degree tend to be connected to other nodes with high degree or small degree, networks can be divided into disassortative mixing networks or assortative mixing networks. Degree correlation of high-concentration solution and low-concentration solution agglomeration network are all assortative. The degree correlation is shown in Figure 10.



**Figure 10. Degree Correlation of low-Concentration Solution Agglomeration Network and Degree Correlation of High-Concentration Solution Agglomeration Network**

Based on above empirical analysis, degree distribution, clustering coefficient and average path length of molecular agglomeration network are neither small-world network nor scale-free network.

Synchronization is an important characteristic of network dynamics in complex network. In network every node can be acted as an oscillator, the dynamics equation described N oscillators as follows:

$$\dot{x}^i = F(x^i) + \sigma \sum_{j=1}^N G_{ij} W_{ij} \quad (7)$$

Where  $F(x^i)$  represents independent oscillator, it can be defined as follows:

$$F(x^i) = \sum_{j=1}^{k_i} \overline{F}_{ij} \quad (8)$$

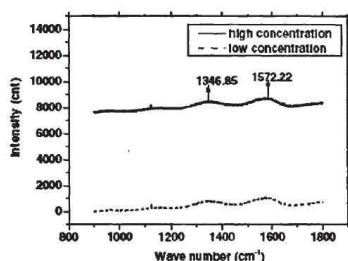
$$F_{ij} = \frac{\partial E_{ij}}{\partial r_{ij}} \quad (9)$$

Where  $E_{ij}$  represents total energy of vibration between node  $i$  and node  $j$ .  $r_{ij}$  represents average bond distances between atoms.

The eigenvalue  $\gamma$  of network' coupled matrix can describe synchronization capability of network. The value of  $\gamma$  is smaller, the synchronization capability is stronger. In this paper, how characteristics of network topologies impact eigenvalue  $\gamma$  is discussed.

Through empirical analysis, in agglomeration network based on pixel 358,  $\gamma_{low} = 1180$ . In agglomeration network based on pixel 896,  $\gamma_{high} = 1032$ . That is to say, the number of oscillators is more, but synchronization is not bad in high-concentration solution. So we can draw the conclusion that high-concentration solution agglomeration network is closer to regular network.

For the purpose of validating our conclusion, two nodes whose number of nanoparticles is similar are chosen, but their network topologies are different. Intensity of Raman spectrum is shown in Figure 11.



**Figure 11. Raman Spectrum of Two Agglomerations**

The two nodes is located center of two agglomerations, it is obvious that pixels of high-concentration solution obtained higher intensity, and pixels of low-concentration solution absorbed less photon, which is in accord with our conclusion.

#### 4. Conclusion

Complex network theory has been applied in material sciences, which drives us to shed some new light on the field. During the researches of agglomeration network topologies, some important topological characteristics are emerged. A given pixel tends to have eight neighbors in two different agglomeration networks, low-concentration agglomerations have larger clustering coefficient, the average path length of these two networks is close to each other, the networks are assortative in the domains, self-similarity exists in the present agglomeration networks, the structure with better synchronizability could have higher intensity enhancement.

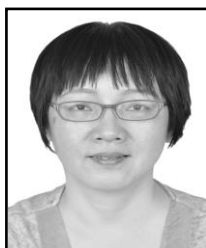
#### References

- [1] Y. Ahn, S. Han and H. Kwak, "Analysis of topological characteristics of huge online social networking services", Proceedings of the 16th international conference on World Wide Web, (2007) May 8-12; Alberta, Canada.
- [2] A. Barabasi and R. Albert, "Emergence of scaling in random networks", Science, vol. 286, no. 5439, (1999).
- [3] S. H. Strogatz and D. J. Watts, "Collective dynamics of 'small-world' networks", Nature, vol. 393, no. 6684, (1998).
- [4] H. E. Stanley, L. Amaral, A. Scala and M. Barthelemy, "Classes of small-world networks", PNAS, vol. 97, 21 (2000).
- [5] A. E. Motter and R. Albert, "Networks in Motion. Physics Today", vol. 4, no. 65, (2012).
- [6] R. Guimera and N. Amaral, "Functional cartography of complex metabolic networks", Nature, vol. 433, no. 7028, (2005).
- [7] A. E. Krause and K. A. Frank, "Compartments revealed in food-web structure. Nature", vol. 426, no. 7024, (2003).
- [8] Z. C. Zhang and D. L. Cui, "Reduction of nitrogen on gallium phosphide nanoparticles", Chin. J. Chem, vol. 23, no. 11, (2005).
- [9] Q. H. Xiong, R. Gupta and K. W. Adu, "Raman spectroscopy and structure of crystalline gallium phosphide nanowires", J. Nanosci. Nanotech, vol. 3, no. 7, (2003).
- [10] J. Hudgens, R. K. Brow and D. R. Tallant, "Raman spectroscopy of the structure of lithium and sodium ultraphosphate glasses", J. Non-Cryst Solids, vol. 31, no. 223, (1998).

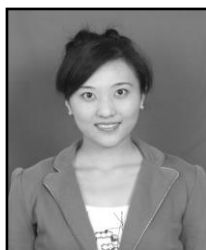


- [11] D. Jiang, E. Burstein and H. Kobayashi, "Resonant Raman Scattering by Crystal-Violet Molecules Absorbed on a Smooth Gold Surface: Evidence for a Charge-Transfer Excitation", *Phys. Rev. Lett.*, vol. 56, no. 23, (1986).
- [12] P. Hilderbrandt, S. Keller, A. Hoffinan, F. Vanhecke and B. Schrader, "Enhancement factor of surface-enhanced Raman scattering on silver and gold surfaces upon near-infrared excitation", Indication of an unusual strong contribution of the chemical effect, *Raman Spectrosc.*, vol. 7, no. 24, (1993).
- [13] S. Hayashi, R. Koh, Y. Ichiyama and K. Yamamoto, "Evidence for surface enhanced Raman scattering on nonmetallic surfaces: Copper phthalocyanine molecules on GaP", *Phys. Rev. Lett.*, vol. 9, no. 60, (1988).

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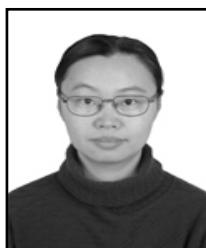
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