

## Applications and Prospects of Graphene in Oilfield

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### Abstract

Graphene was attracted a widespread attention recently years because of its unique atom-thick two-dimensional structure and excellent properties. Graphene materials have been applied in energy storage and conversion, catalysis, electronic, high strength material, chemical and biosensor and biotechnology fields. With the decline of conventional oil and gas resource, unconventional oil and gas resource and complex well increased gradually. The drilling technology encountered new challenge. We reviewed the research and application of Graphene materials in oilfield based on the requirement of drilling technology, and discussed the prospect of Graphene material in oilfield.

**Keywords:** Application Oilfield; Drilling Fluid; Graphene; Nano-Materials

### Introduction

Graphene materials have become a research hotspot in the field of materials because of its unique two-dimensional structure and excellent properties [1-3]. The basic and application Research of Graphene has become the current frontier and hot topic. At present, Graphene materials have been widely used in energy storage and conversion [4-6], catalysis [7,8], electronic devices [9,10], high strength materials [11], chemical and biosensor [12,13], biotechnology [14,15] and other fields. Two scientists at the University of Manchester, Andre Geim and Konstantin Novoselov, successfully stripped Graphene from graphite by mechanical means in 2004, causing a worldwide sensation. Research on Graphene shows explosive growth. By the end of May 8, 2017, the Web of Science showed 144925 related reports after searching "Graphene". Graphene materials, the new favorite of the battery industry, are expected to cause a revolution in the battery industry. Graphene materials are considered to be the material with largest strength unit mass. With the increasing energy consumption and the failure of traditional energy sources, the development of unconventional energy and complex wells such as, deep wells, ultra-deep wells, extended reach wells, wells with long horizontal section has increased year by year [16-18]. With the continuous development of oil and gas resources, the grade of conventional oil

and gas resources is getting worse and worse, and the difficulty of development is further increased [19-20]. The development of unconventional energy and wells with complex conditions is limited by existing technology [21]. As the "Blood" of drilling industry, wellbore fluids face great challenges. Graphene material has become the new favorite of the material field after carbon nano tubes, and the continuous innovation of Graphene material will greatly promote the development of the oilfield.

According to the development needs of petroleum industry, this paper discusses the key technology of Graphene materials about applications and prospects on the basis of extensive investigation of research status in oilfield. Four aspects, the characteristics of Graphene materials, research status, key technology of application and the prospect in oilfield are reviewed.

### Characteristics of Graphene material

#### Graphene structural features

Graphene is a monatomic layer of graphite that can exist independently in the external environment [22]. Graphene is obtained by stripping graphite in a physical or chemical manner. At present, the preparation methods of Graphene mainly include epitaxial grown method [23], mechanical stripping method [24], chemical vapor deposition method [25], thermal or oxidation stripping method [26]. The improved Hummer method is adopted by many scholars [27-28]. There are many different groups such as

carboxyl group, epoxy group and hydroxyl group on the surface of Graphene oxide stripped by chemical method, as shown in Figure 1 [29]. Graphene oxide Nano sheets are mainly composed of hexagons which are not oxidized, and some parts are oxidized.

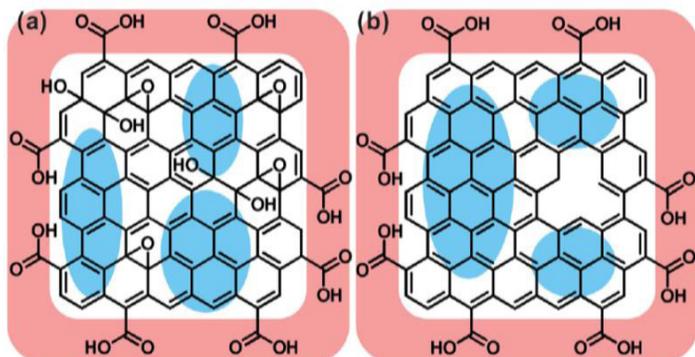


Figure 1: a) Graphene oxide; b) reduced Graphene [29].

The groups such as carboxyl groups are concentrated on the edges of Graphene oxide nano sheets. There are a large number of hydroxyl groups and epoxy groups in the middle zone of Graphene oxide nano sheets. The reduced Graphene is obtained when the Graphene oxide is reduced. The hydroxyl and epoxy groups in the middle zone of reduced Graphene nano sheets are reduced. Hexagonal structure is destroyed and Graphene nano sheets with structural defects are formed. A large number of carboxyl groups, hydroxyl groups and epoxy groups are active groups, which are easy to be functionalized. The structural characteristics of Graphene make it easy to be functionalized. It laid the foundation for the extensive application of Graphene.

### Applications of Graphene

Graphene is a new carbon material after carbon nano tubes. Graphene has maximum strength per unit mass with unique electric conduction and is easy to be functionalized, which all develop the application of grapheme. At present, Graphene composite materials have attracted great attention in the fields of energy storage and conversion, catalysis, electronic devices, high strength materials, chemical and biological sensing, and biological technology and so on. Research and concerns about Graphene continue to heat up.

### Applications in the oil industry

Some scholars have carried out research on the application of Graphene in oilfield because of its excellent performance. In June 2011, James M. Tour invented a patent on the application of Graphene and modified Graphene in drilling fluid [30]. The patent reports the preparation of chemical modified grapheme, as in Figure 2.1.

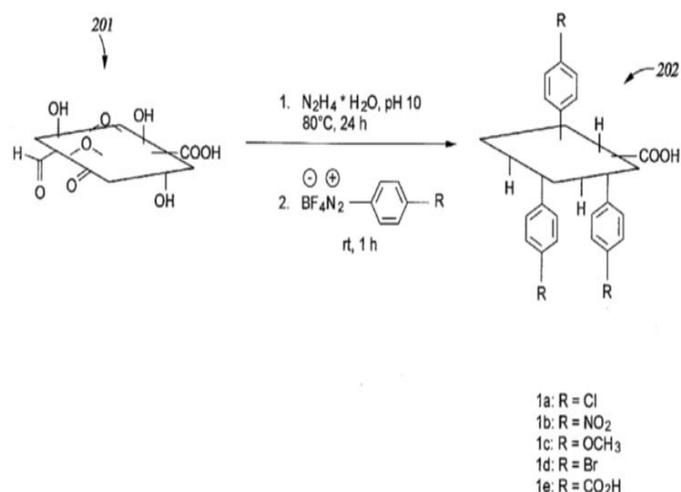


Figure 2.1: preparation of modified Graphene [30].

The benzene was grafted onto the surface of Graphene by using hydrazine hydrate as reducing agent. Graphene and chemical modified grapheme are added to the drilling fluid, and Graphene nano sheets are adsorbed onto the surface of wellbore to reduce drilling fluid into the stratum, as shown in Figure 2.2.

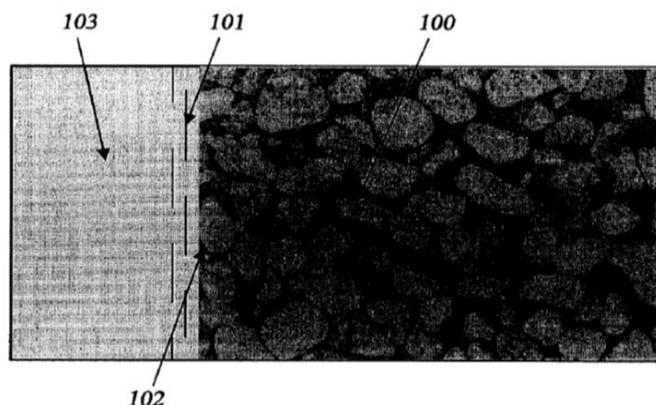
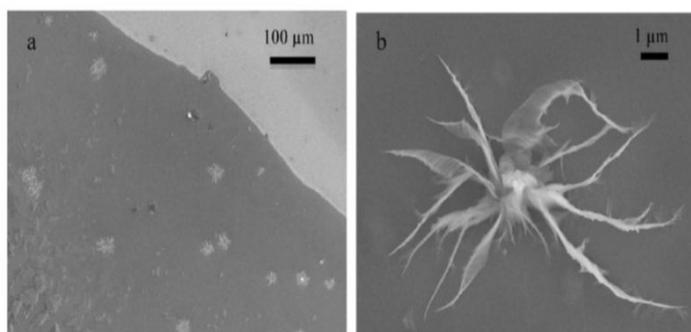


Figure 2.2: Schematic diagram of Graphene and modified Graphene [30].

The cake with the addition of Graphene and modified Graphene is thin and compact. Graphene and modified Graphene can effectively improve the quality of filter cake and reduce drilling fluid into the formation. The same year in September, James M. Tour publishes a paper about the research on Graphene oxide as filtrate reducer of high performance [31] in ACS Applied Materials & Interfaces. The paper describes the process of preparation for Graphene oxide by improved Hummer method in detail. The detailed study on property of Graphene oxide as filtrate reducer

in drilling fluid shows that the filtration is 6.1mL in 0.2 wt% low concentrations which is less than that of conventional filtration reducer, and the average filtration is 7.2 mL. The thickness of the filter cake is about 20  $\mu\text{m}$ , far less than that of conventional filtration reducer which is 280  $\mu\text{m}$ . Flexible Graphene nano sheets can enter pores smaller than their size, and there is a large amount of Graphene nano sheets in the filtration of the drilling fluid, as shown in Figure 2.3. The addition of methanol modified Graphene oxide into drilling fluid results in lower filtration. Graphene oxide has excellent performance on filtration control.



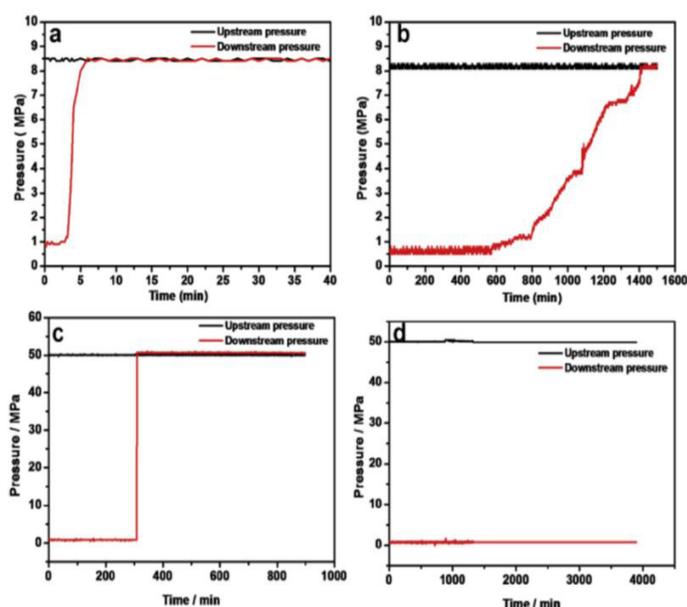
**Figure 2.3:** SEM image of Graphene in mud filtrate [31].

In September 2013, Xuan Yang reported a paper about the preparation and evaluation of nano-Graphene oxide as a high-performance fluid loss additive [32]. Filtration control properties of Graphene oxide according to the API standards are evaluated and the results show that Graphene oxide has excellent fluid loss performance. Compared with conventional filtrate reducers, Graphene oxide has the advantages of low dosage and thin cake.

In October 2013, Steve Young published a patent on Graphene material as shale inhibitor [33]. Based on James M. Tour chemical modified method, the patent evaluates rheological properties and rolling recovery rate after modifying Graphene oxide, the inhibition is characterized by rolling recovery rate. The research about application of Graphene as lubricant was published by Norasazy Mohd Taha in IPTC in September 2015 [34]. Graphene materials can form a dense film on the surface of the metal under the pressure, temperature and mechanical force. This Graphene film is formed under the synergistic action of physical adsorption and chemical adsorption. Compared with traditional lubricants, Graphene materials have much more excellent lubricity. In the aqueous polymer brine system, laboratory tests show that the friction of Graphene materials is at 70%-80% reduction, while it of conventional lubricant materials is generally at only 30%-40% reduction. At the same time, the Graphene material still has excellent lubricity at 176°C. In May 2016, our team studied the inhibition and the plugging performance for the nano pore of shale of amino modified Graphene [35]. As shown in Figure 2.4, we select sandstone with high permeability and shale with ultra-low permeability as cores, downstream pressure is respectively recorded in 4% NaCl

brine system and 0.4% amino modified Graphene solution. The longer time the downstream pressure reaches the upstream pressure, the performance of plugging cores is better. The time which the upstream pressure reaches the upstream pressure in brine system is about 5 minutes when sandstone is tested, while in modified Graphene system the time is about 24 hours.

This result shows that the amino modified Graphene has the ability to seal pores in sandstone. When natural shale is chosen as core, in brine system the time which the upstream pressure reaches the upstream pressure is about 5 hours, while the downstream pressure still does not increase after 66 hours in amino modified Graphene system.



**Figure 2.4:** pressure change in brine system and amino modified Graphene system [35]. a, c) brine system; b, d) amino modified Graphene system.

The ability of Graphene to plug nano pores is further revealed. Amino modified Graphene also has excellent ability to inhibit shale expansion. The mechanism of action between amino Graphene and clay minerals is analyzed in detail in the paper. Graphene is adsorbed on the surface of shale by hydrogen bonding and hydrophobic interaction, and a compact film is formed. This film prevents moisture entry and inhibits the hydration expansion of the clay. The experiment data shows that the amino modified Graphene has excellent ability of plugging the nano pore of shale and inhibiting the hydration expansion of clay.

### Prospects of Graphene in oilfield

Through the domestic and foreign literature investigation, 4 related literatures and 2 patents are retrieved about the application of Graphene materials in oilfield. Many scholars begin to explore the application of Graphene in the petroleum industry. Although a

lot of work can be carried out, it is still in laboratory research now. Lots of work is just test on performance, not a thorough study of mechanism. Graphene, as a new favorite in the field of materials, will have broad application prospects in oilfield. Mainly in the following areas:

### **Drilling Fluid**

Graphene materials as filtrate reducer for drilling fluid, showing excellent fluid loss agent performance, but the mechanism of Graphene materials and clay minerals are not in-depth study, and not study compatibility with other additives for drilling fluid. Graphene material, as a shale inhibitor of drilling fluid, is only used for the determination of rolling recovery. The mechanism of action was not studied. Graphene material is a kind of monolayer graphite with many active groups. It has the following application prospects in drilling fluid.

### **Tackifier and Shear Strength Agent**

Intermolecular weak interaction between active groups of Graphene materials is formed by hydrogen bond, hydrophilic-hydrophobic interaction and  $\pi$ - $\pi$  interaction. Graphene materials have excellent stimuli-responsiveness. High Shear thinning agents with high shear strength and low viscosity can be obtained by molecular design. At high shear rate, the viscosity is low especially near the nozzle. While at low shear rate, the viscosity is high, so it is easy to carry cuttings and prevent the settlement of the weighting materials.

### **Fluid Loss Agent**

Previous work has shown that Graphene is an excellent filtrate reducer. However, the mechanism of action has not been studied deeply. Temperature resistance needs further improvement. Graphene with one single layer, when the salt molecules are close to the edge of Graphene, Graphene will curl to some extent, but the strong  $\pi$ - $\pi$  interaction will limit its curling. So, Graphene materials show excellent salt resistance, especially to divalent metal ions. Graphene materials will be widely used in the fields of filtration control with salt resistance and temperature resistance.

### **Shale Inhibitor**

There are many active groups such as carboxyl and hydroxyl groups on the edge of Graphene materials, and adsorption groups such as amino groups are obtained after being modified. The adsorption of Graphene materials on rocks is enhanced. Large areas of high strength sheet materials are adsorbed onto the rock surface to prevent moisture from entering. Graphene is thin but has high strength, so it can effectively reduce costs with low dosage. Graphene materials are expected to become the unique shale inhibitors through appropriate modification,

### **Nano-Pores Plugging Agent**

For plugging nano-pores in shale, there are no reports of in-

dustrial products at home and abroad. The permeability of shale is low, and the pores are rich. The average size of nano-pores in shale is about 10nm. General rigid nano materials are easy to agglomerate in horizontal solution and difficult to enter nano-pores. Flexible organic materials, with large molecular weight and little interaction with rock, are difficult to adsorb to the surface of shale. By molecular design, strong adsorption groups are introduced to increase the interaction between Graphene and rock. Graphene material is easy to be adsorbed on the surface of rock. It is hopeful to solve the bottleneck of plugging nano-pores in shale because of strong strength of Graphene materials and their pressure-bearing capacity.

### **Lubricant**

By introducing groups which have interaction between metal ions, Graphene materials can be adsorbed onto the surface of the drilling tools and form a flexible film which reduces the friction between drilling tools and drilling fluids, drilling tools and rocks. The lubrication performance of drilling fluids can be effectively improved. The force acting between drilling tools and drilling fluids can be reduced by introducing hydrophobic groups which can prevent bit balling, sticking of tool and other accidents effectively.

### **Wet Ability Reversal Agent**

As hydrophilic materials, the hydrophilicity and hydrophobicity of Graphene can be changed by introducing hydrophobic groups. These modified Graphene can be adsorbed onto the surface of the rocks and change the wettability of rocks. Graphene materials are expected to be an excellent wettability reversal agent

### **Completion Fluid and Work Over Fluid**

Completion fluid and work over fluid generally use brine systems to protect reservoirs. The adsorption of Graphene on the surface of rocks is beneficial to the stability of the borehole. After the operation, the Graphene is desorbed from surface of the rocks under the formation pressure and after encountering the oil layer, then reverse to the ground. Graphene materials are environmentally friendly, low-viscosity and easy to reverse.

### **Acidizing Fluid and Fracturing Fluid**

Diverting acid is the core agent of acidizing fluid. Graphene is oxidized by strong acid and can exist stably under acidic conditions. Calcium sensitive Graphene materials can be prepared with molecular modification. It is expected to become a steering acid with little amount, low cost and excellent performance. Graphene and most polymers can form weak gel systems, which are environmentally responsive by the weak forces through non-covalent bonds. It is expected to become a new generation of fracturing fluid system.

### **Plugging Agent**

There are no mature technical countermeasures to severe leakage. The plugging operation is carried out regardless of cost

and times. Polymer gel has become the new material for plugging because it is not limited by pore size, cross linking time and breaking time are controllable. Graphene can form the gel system with polyacrylamide, poly acrylic acid, polyvinyl alcohol and Carboxymethyl cellulose. Graphene can enhance the strength of gel, and also has excellent adsorption ability. Therefore, Graphene and polymer gel complex are expected to solve the problems of severe leakage.

## Conclusions

The application of Graphene material in oilfield has been preliminarily explored. Many experimental achievements are still in the laboratory research. The research on the mechanism of action is not thorough, and the range of application is still relatively narrow. The following aspects need to be studied:

1. Study the mechanism of action in depth and optimize the design of molecules.
2. Expand the scope of research, conduct researches on drilling fluid, completion fluid, work over fluid, acidizing fluid, fracturing fluid, plugging agent.
3. Accelerate the industrialization of Graphene materials.

Graphene materials with will excellent properties have broad application prospects in oilfield. It is expected to become a new generation of working fluid system. It is hopeful to play a unique role in the exploitation of unconventional oil and gas resources such as shale gas, coal bed methane and tight gas.

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