Multi-functional diamond particles for various applications

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Chapter 5 Discussion

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The studies performed for this dissertation represent stepping towards the application of fluorescent diamonds as sensors for detecting chemical groups in various occasions. The subjects in this thesis include free radical detection in lab samples and clinical samples as well as optimizing diamond surface chemistry by producing an oxidative gradient on diamond plates.

5.1 Free radical detection

The Nitrogen-Vacancy center (NV center) in diamond is most useful when it is applied to quantum measurements, providing extremely high sensitivity at room temperature. Fluorescent nano-diamonds (FNDs) have been used to measure indicators inside the cells, such as free radicals, pH, temperature. Compared to 2′,7,-dichlorodihydrofluorescein diacetate (DCFDA) or similar organic dyes for Ros detection, FNDs have achieved monitoring free radicals specifically rather than all reactive oxygen species (ROS). Meanwhile, the magnetometry values, which reflect the free radical level surrounding FNDs is a real-time indicator. It represents the spin status within FNDs at a specific time point. For several applications of FNDs, the modification on the surface of FNDs is an important step to give the particle more accesses to achieve different goals. In **Chapter 2**, the drug molecule amino diazoxide has been linked to the surface of FNDs. The composite particle can then be used to deliver the drug into cells. We found that the upper limit of diazoxide can be reacted with 70 nm FNDs we used, based on the number of carboxyl from FNDs. Although there is an upper limit to how much diazoxide can be linked per diamond particle, the linked diazoxide provides appreciable improvements for FNDs. The added diazoxide can increase free radical producing inside HeLa cell. As an activator for K_{ATP} channels and an inhibitor of the mitochondrial complex II protein, succinate dehydrogenase (SDH), Diazoxide is able to change the free radical micro-environment in cells[1-3]. Furthermore, FND-Diazoxide provide sustainable drug release in vitro, which suggests that the complex system has a potential for drug delivery. In **Chapter 4**, we focus on free radical detection via diamond magnetometry applied in arthritis patient samples. There are two main kinds of arthritis patients: osteoarthritis and rheumatoid arthritis patients. When we measured the basic radical levels of these two types of samples, there is no significant difference. But after adding Piroxicam, which is a nonsteroidal anti-inflammatory drug (NSAID) used to relieve the symptoms of painful inflammatory conditions from arthritis[4-5], we observed a strong decrease in radical formation in the osteoarthritis samples, the rheumatoid arthritis samples remained unperturbed. These different performances can determine the specific type of arthritis, and provide a different angle to demonstrate the mechanism of Piroxicam. Further, this detection scheme might be useful to predict if a new drug would work in vitro. In this thesis, we have achieved detecting radicals via diamond magnetometry from lab to patient.

5.2 Chemical Gradients on Diamond Surfaces

Due to unique material properties, bulk diamond has been applied widely in different fields for decades. These applications often require control over the surface chemistry. The surface chemistry is especially crucial for quantum sensing since NV centers which are needed for sensing have to be within nanometers from the surface. Thus, there are still some problems in these applications which cannot be ignored. On the one hand, the desired NV centers for quantum sensing are NV^-, but there is charge transfer happening from NV^- to NV^0, whose spin properties are not the same as NV^-. On the other hand, dangling bonds on the surface of diamond is detrimental to the sensing performance of NV centers.

There are many different surface treatments that have been done on nanodiamonds. However, there are different requirements for bulk diamonds. Some work has been done to modify surfaces of bulk diamond. However, due to the relatively high price of bulk diamonds, only a limited number of conditions have been studied. In Chapter 3, air plasma was applied to treat diamond plates with a gradient mask. This mask created a chemical gradient on a single diamond crystal. XPS showed that the more exposed side of diamond has a higher oxygen content. A diamond treated without mask had the highest oxidation levels. The changing trend in contact angle is also consistent. We observed the greatest change in contact angle close to the mask opening. Towards the closed end, the surfaces were less affected by the plasma. To evaluate the defect’s ability for quantum sensing the quantum relaxation time was measured. This time reflects how long an NV^- center can remain in a prepared state before returning to equilibrium. A relaxation rate (T1) measurement in wide-field configuration was performed. The observed decrease in T1 can be explained by dangling bonds which are introduced during the process of plasma treatment. Alternatively, the oxidative etching can bring NV centers closer to the surface and thus shorten the coherence times[25]. But in this work, they used much harsher treatment which can create more obvious etching on the diamond plate. After comparing the T1 values before and after the plasma treatment, we found a gradient in relaxation times over the surface. To be more specific, the relaxation times decrease gradually from the least to the most exposed area of the sample (from about 0.75 ms to 0.4 ms). It means that we are able to investigate hundreds of points under different plasma treatment levels on a single diamond plate. While we have so far not been able to improve relaxation times, this technique is promising for optimization.

5.3 Outlook to the future

Diamonds have drawn attention in several fields based on their unique properties. First of all, NV centers contained in diamonds is a special defect, which not only gives the diamond fluorescent properties, but also can sense magnetic resonances optically. They do so by changing their brightness based on the magnetic surrounding. Besides that, plentiful chemical groups can be attached on the surface of diamond, which can expand the applications of diamond.

In this thesis, the FNDs are applied to detect free radicals in cells and tissue fluid. Making use of FNDs we can detect radical levels in real time. When drugs are linked to the surface of these particles, we can deliver drugs and simultaneously investigate the drug performance. While this was shown here with diazoxide, we believe that FNDs can deliver different drugs and measure clinical samples.

Beside the nano-sized diamond, bulk diamond can also be modified. In this thesis, we use a plasma gradient to treat diamond plates through a triangular mask. This allowed us to study hundreds of different conditions on a single plate. This approach provides a possibility to investigate different reactions on a single diamond plate. Meanwhile, during the process of our study, we also realized that the effect of plasma treatment for bulk diamond is not always permanent. This might be a more general concern in material surface modification that needs to be monitored closely.

5.4 References

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