Solubility of Monolayer MoS$_2$ and Expected Bioabsorbable LED

Dongsheng Peng*, Kailong Liu
College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, China
Email: sbpengds@szu.edu.cn

Abstract. Transient electronic technology is a new technology, which is characterized by the ability to dissolve, decompose in a controlled way. Expected adhibitions include bioabsorbable or biodegradable medical implants, hardware-safe storage devices and biodegradable sensors. 2D materials may play a vital role in these systems due to their unique electrical, thermal, mechanical and optical properties. Monolayer MoS$_2$ is a recently discovered biosoluble two-dimensional material. Monolayer MoS$_2$ has unique semiconductor characteristics and biological absorption properties. Single-layer MoS$_2$ is a direct band gap semiconductor material, and it has a high electron mobility, good current switching ratio, very low power consumption. These characteristics of single-layer MoS$_2$ make it have great potential in electronic/optoelectronic devices, sensors, photothermal therapeutics, and biomedical applications. In this aspect, the ability to dissolve single-layer MoS$_2$ in the biological liquid can be used to regulate the performance and life of the relevant bio-absorbable devices and systems. Based on monolayer MoS$_2$, we designed a bio-absorbable LED. Furthermore, the wet transfer process of single layer MoS$_2$ was optimized to some extent.

Keywords: Monolayer MoS$_2$, dissolve model, wet transfer, bioabsorbable LED.

1. Introduction
Molybdenum disulfide is a pivotal member of the layered transition metal dihalide class (TMDC) of materials. It has attracted great interest in the past few time on account of its applications in electronic, photoelectric, physicochemical and biomedical sensors [1-5].

Single-layer MoS$_2$ can gradually oxidize in air or dissolve in a water solution after a few days, causing its environmental degradation [6-8]. Because of these characteristics, single-layer MoS$_2$ is a well suited material for bioabsorbable electronic devices (for instance biosensors and short time biomedical sensors), they can be completely absorbed after implantation in the human body, and the implant can dissolve in the body without a second operation. The long-term cytotoxicity and immunobiocompatibility of monolayer MoS$_2$ grown by chemical vapour deposited (CVD) have been reported in biological fluids and tissues of live animal models [9, 10]. Temporary monitoring of various intracranial physiological activities in animals of single-layer MoS$_2$ based on bioabsorption and multi-function sensors has also proven that such technology is in the short-term diagnosis/treatment function during the recovery process of traumatic brain injury has a specific clinically relevant role [10].

In previous studies, many bioabsorbable materials have been reported, such as inorganic semiconductors (Si, Ge, ZnO), oxides and nitrides (silicon oxide and silicon nitride), metals (Mg, Zn, W and Mo), polymers and organic materials, and conducted a lot of research [2, 11-13]. This study
intends to manufacture a biodegradable LED based on monolayer MoS$_2$ and some transient electronic materials

2. Dissolve Model

The biodegradation process of single-layer MoS$_2$ crystals in PBS solution is caused by intrinsic defects in the granules or along the grain boundaries (GBs) [14, 15]. In phosphate buffer saline (PBS) solution, the probable reaction during the biodegradation process of MoS$_2$ was studied. Because the dissolution test of single-layer MoS$_2$ involved NaCl, KCl, Na$_2$HPO$_4$, KH$_2$PO$_4$, O$_2$ and H$_2$O in PBS, the possible reactions are as follows [9, 10, 14]:

\[
2\text{MoS}_2 + 7\text{O}_2 \rightarrow 2\text{MoO}_3 + 4\text{SO}_2 \quad (1)
\]

\[
\text{MoO}_3 + 2\text{OH}^- \rightarrow \text{MoO}_4^{2-} + \text{H}_2\text{O} \quad (2)
\]

\[
\text{MoS}_2 + 9/2\text{O}_2 + 3\text{H}_2\text{O} \rightarrow \text{MoO}_4^{2-} + 2\text{SO}_4^{2-} + 6\text{H}^+ \quad (3)
\]

where the molybdate ion ($\text{MoO}_4^{2-}$) is the main Mo-containing byproduct, which has been confirmed by inductively coupled plasma-mass spectrometry (ICP-MS) measurements [9, 14]. Note that Na$^+$ and K$^+$ ions in the PBS solution may lead to lattice distortions of MoS$_2$ and the formation of Na$_2$S (from 2H-MoS$_2$ to 1T-NaMoS$_2$ and then to soluble Na$_2$S). Therefore, the increase of Na$^+$ and K$^+$ concentration will speed up the degradation process. In addition, MoS$_2$ will be oxidized by oxygen in the PBS solution to generate MoO$_4^{2-}$, and MoO$_2^{2-}$ itself is easily dissolved (Eq. 3).

Besides, based on Reaction Eq. 3, the increase in pH caused by increasing the OH$^-1$ concentration can further accelerate the reaction rate. The following empirical kinetic equations regarding pH dependence in room temperature are given [9, 14]:

\[
d\left[\text{MoS}_2\right]/\left[\text{MoS}_2\right]dt = 1.9 \times [\text{OH}^-]^{0.17}, 1/d \quad (4)
\]

Then, Eq.4 can be calculated by ordinary differential transformation:

\[
y = 1 - e^{-1.9\times[\text{OH}^-]^{0.17}t} \quad (5)
\]

where y is the dissolution percentage, the units of the t and OH$^{-1}$ concentration are days and mol/L, respectively. According to Eq.5, the dissolution kinetics simulation shown in figure 1 (a) can be obtained.

![Figure 1](image_url)  
*Figure 1.* (a) Dynamic simulations of pH-dependent of single layer MoS$_2$ oxidative dissolution in room temperature. (b) Dynamic simulations of the temperature dependence of single layer MoS$_2$ in 37°C PBS solutions of pH 7 and pH 12, respectively.
From the previous research report [16], the temperature dependence of the single-layer MoS$_2$ can be derived, the rates can be written as:

$$\ln(r) = (-E_a / K_B)^* (1/T) + C$$

(6)

$K_B$ means Boltzmann constant, $E_a$ means activation energy.

According to the literature, the activation energy at pH 7.4 is ~105 mev and the activation energy at pH 12 is ~147 mev [9]. We can simulate the temperature dependence curve of single layer MoS$_2$ at pH 7.4 and pH 12 in 37 °C PBS solution by Eq.6, as shown in figure 1(b).

3. Transfer of 1L-MoS$_2$ onto Different Substrates

Generally, the necessary step to transfer a single layer of MoS$_2$ grown by CVD using a wet method is to use a polymer layer (such as PMMA) as a support layer [17]. PMMA has many outstanding characteristics, such as relatively low viscosity, excellent wetting ability, flexibility and good solubility in several organic solvents. After a series of experiments, we optimized the single-layer MoS$_2$ wet transfer as follows [18]:

First, clean the silicon wafer: place the silicon wafer in acetone solution and sonicate for 10 minutes, then in ethanol solution for 10 minutes, then rinse with deionized water, and finally dry with nitrogen and plasma cleaner (Enhance the hydrophilicity of the target substrate) for 10 minutes; coat a thin layer of PMMA (950 Å, 40 g/L) to single-layer MoS$_2$ which growing on SiO$_2$ with a dropper. Place the silicon wafer on a heating table (100°C) for 30 minutes to cure PMMA; after cooling to room temperature, float the chip in 30% KOH (aq) for 20 minutes, where the Si substrate sinks due to the etching of SiO$_2$. The PMMA/ MoS$_2$ layer floats on the KOH solution. Next, wash PMMA / MoS$_2$ for 4 times in DI water, use the target substrate remove the molybdenum disulfide film from bottom to top, and dry it naturally for more than 4 hours. Then put it in a drying oven at 100°C for 30 minutes to evaporate the remaining water and improve the combination of MoS$_2$ and substrate. Remove PMMA with warm acetone, soak in ethanol/isopropanol for 30 minutes. In the end, blow dry with nitrogen and store. Figure 2 (a) shows the optical image of monolayer MoS$_2$ continuous film transferred to Si substrate by this way, and figure 2 (b) shows the optical image of monolayer MoS$_2$ continuous film transferred to PDMS substrate. Under the excitation of 473 nm laser, the PL spectra of the transferred monolayers MoS$_2$ transferred to Si substrates were measured, as shown in figure 3. The characteristic peak at 677 nm corresponds to the direct energy band transition between the maximum value of the valence band and the minimum value of the conduction band at the K point of the Brillouin zone. The results show that after transfer to the silicon substrate, the monolayer MoS$_2$ still maintains a strong emission peak, indicating that the monolayer MoS$_2$ is still of high quality.

Figure 2. (a) OM of monolayer MoS$_2$ transferred to Si substrate. (b) OM of monolayer MoS$_2$ transferred to PDMS substrate.
4. LED Device Design

The wide application of light-emitting diodes (LEDs) in displays and lighting sources, the increase in production speed and the shortened lifespan have led to a corresponding increase in concerns about environmental pollution caused by related electronic waste generated [19]. Many components in commercial LEDs, such as organic emitters, metal electrodes, and connecting wires, have high chemical stability, and they have the risk of releasing toxic heavy metals after use [20]. The cost of waste management and potential environmental hazards have prompted research into bio-soluble LEDs that can degrade into non-toxic substances under natural conditions. In addition, biomedical implants, including LEDs, have the potential to provide unprecedented opportunities in diagnostic and therapeutic functions, and biodegradable LEDs can provide useful functions that cannot be provided by existing equipment combinations in this field [21].

The transient effect achieved by bioabsorbable eliminates the traces of the equipment, thereby avoiding the cost, complexity and risk associated with the secondary operation of equipment retrieval. Such a system usually requires a full set of bioabsorbable electronic materials (including semiconductors, dielectrics and conductors) as the basic modules to achieve functions [2, 22]. Moreover, this system must not only consider its basic electrical properties, but also consider the degradation chemistry and biocompatibility of electronic materials and their products after reacting with biological fluids.

Although a lot of research has been done on optical fibers, photovoltaic cells and photodetector cells in the body [1], the development of bioabsorbable optical components has been neglected compared to similar photovoltaic products, and fully bioabsorbable LEDs were not reported until autumn 2019. According to the previously reported bioabsorbable LED, a bioabsorbable LED structure based on a monolayer MoS$_2$ was designed as shown in figure 4.

**Figure 3.** PL spectrum of monolayer MoS$_2$ transferred to Si substrate.

**Figure 4.** Biological soluble LED based on monolayer MoS$_2$. 

![Biological soluble LED based on monolayer MoS$_2$](image-url)
The monolayer MoS$_2$ was transferred to the Si substrate by wet process. The SiO$_2$ pattern layer (20 nm) is deposited on the MoS$_2$ surface, leaving only an opening of 20 um x 20 um as the effective display area of the device, and a uniform thin-film Mo electrode (10 nm) is deposited. A relatively thick layer of lithography W (100 nm) is around the window. Connect the external DC voltage source to the LED through the transient Mg wire and the transient conductive glue. Non-transient power supplies connected to devices that use transient wiring can be used in certain applications, such as bioabsorbable medical implants. The bioabsorbptive properties of such devices have been described in previous studies [19]. The final degradation products are either necessary to life (MoO$_4^{2-}$) or they have low toxicity [WO$_4^{2-}$, Mg(OH)$_2$, Si(OH)$_4$] to biological systems [9, 19, 22]. Therefore, they are also harmless to the environment.

5. Conclusion
The dissolution mechanism of single-layer MoS$_2$ is analyzed. According to the dissolution kinetics equation, the dependence of single-layer MoS$_2$ on temperature and pH dependence curve is simulated. The dissolution rate depends on the temperature, pH value and the type and concentration of ions in the biological fluid. Considering the dissolution kinetics of single layer MoS$_2$ in PBS solution, high pH and high temperature will result in higher dissolution rate. And according to the previously reported bioabsorbable LED, designed a bioabsorbable LED based on a single-layer MoS$_2$. The final degradation products either have low toxicity to biological systems or are necessary for life. Therefore, they are also harmless to the environment. And the wetting transfer process of single-layer MoS$_2$ during device manufacturing was optimized, the substrate transfer film processed by the plasma cleaning machine is better.

Acknowledgements
The authors would like to acknowledge the funding support by the Rising Industry Development Foundation of Shenzhen, China (Grant No. JCYJ20180305124822272)

References
[1] Kenry K, Geldert A, Zhang X, Zhang H and Lim C T 2016 Highly sensitive and selective aptamer-based fluorescence detection of a malarial biomarker using single-layer MoS$_2$ nanosheets ACS Sens. 1: 1315-1321.
[2] Mattina A A L, Mariani S and Barillaro G 2020 Bioresorbable materials on the rise: from electronic components and physical sensors to in vivo monitoring systems Advanced Science 7: 4.
[3] Choi Y, Koo J and Rogers J A 2020 Inorganic materials for transient electronics in biomedical applications MRS Bulletin. 103-112.
[4] Appel, J H et al. 2016 Low cytotoxicity and genotoxicity of two-dimensional MoS$_2$ and WS$_2$ ACS Biomater. Sci. Eng. 2: 361.
[5] Dalila R N, Arshad M K M, Gopinath S C B, Norhaimi W M W and Fathil M F M 2019 Current and future envision on developing biosensors aided by 2D molybdenum disulfide (MoS$_2$) productions Biosens. Bioelectron. 132: 248-264.
[6] Wang Z, et al. 2016 Biological and environmental interactions of emerging two-dimensional nanomaterials Chem. Soc. Rev. 45: 1750.
[7] Gao J, et al. 2017 Aging of transition metal dichalcogenide monolayers ACS Nano. 10: 2628.
[8] Lv D, et al. 2017 Atomic process of oxidative etching in monolayer molybdenum disulfide Sci. Bull. 62: 846.
[9] Chen X, Park Y J, Kang M, et al. 2018 CVD-grown monolayer MoS$_2$ in bioabsorbable electronics and biosensors Nat. Commun. 9: 1690.
[10] Chen X, Shinde S M, Dhakal K P, et al. 2018 Degradation behaviors and mechanisms of MoS$_2$ crystals relevant to bioabsorbable electronics NPG Asia Mater. 10: 810–820.
[11] Yu X, Shou W, Mahajan B K, Huang X and Pan H 2018 Materials, processes, and facile manufacturing for biodegradable electronics: a review Adv. Mater. 30: 27.

[12] Wang S, et al. 2020 Investigation of Mg–Zn–Y–Nd alloy for potential application of biodegradable esophageal stent material Bioactive Materials 5: 1-8.

[13] Chatterjee S, Saxena M. et al. 2019 Futuristic medical implants using biodegradable materials and devices Biosensors and Bioelectronics 142: 111489.

[14] Wang Z, et al. 2016 Chemical dissolution pathways of MoS₂ nanosheets in biological and environmental media Environ. Sci. Technol. 50: 7208-7217.

[15] Kurapati R, et al. 2017 Enzymatic biodegradability of pristine and functionalized transition metal dichalcogenide MoS₂ nanosheets Adv. Funct. Mater. 27: 1605176.

[16] Yin L, et al. 2015 Mechanisms for hydrolysis of silicon nanomembranes as used in biodegradable electronics Adv. Mater. 27: 1857.

[17] Chen Y, Gong X L and Gai J G 2016 Progress and Challenges in Transfer of Large-Area Graphene Films Adv. Sci. 3:1500343.

[18] Lin Z, Zhao Y, Zhou C et al. 2016 Controllable Growth of Large-Size Crystalline MoS₂ and Resist-Free Transfer Assisted with a Cu Thin Film Sci. Rep. 5: 18596.

[19] Lu D, Liu T L, Chang J K, Peng D, Zhang Y, Shin J, Hang T, Bai W, Yang Q and Rogers J A 2019 Transient light-emitting diodes constructed from semiconductors and transparent conductors that biodegrade under physiological conditions Adv. Mater. 31: 1902739.

[20] Gan X R, Zhao H M, Quan X. 2017 Two-dimensional MoS₂: a promising building block for biosensors Biosens. Bioelectron. 89: 56-71.

[21] Tan M J et al. 2016 Biodegradable electronics: cornerstone for sustainable electronics and transient applications J. Mater. Chem. C. 4: 5531-5558.

[22] Choi G J et al. 2017 Polarized light-emitting diodes based on patterned MoS₂ nanosheet hole transport layer Adv. Mater. 29: 1702598.