Notice

DESCRIPTION CN121005443A

Plasma-activated water preparation method based on micro/nano bubble synergistic effect

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基于微纳米气泡协同效应的等离子体活化水制备方法

[0001]

Technical Field

技术领域

[n0001]

This invention relates to a method for preparing plasma-activated water, specifically a method for enhancing the chemical activity of plasma-activated water and extending its storage period through the synergistic effect of micro- and nano-bubbles.

本发明涉及等离子体活化水的制备方法，具体涉及一种通过微纳米气泡的协同效果增强等离子体活化水的化学活性并延长其存储周期的方法。

[0003]

Background Technology

背景技术

[n0002]

Plasma-activated water (i.e., atmospheric pressure cold plasma-activated water) is an aqueous solution with weak acidity and strong oxidizing properties obtained by treating deionized water with atmospheric pressure cold plasma.

等离子体活化水(即大气压冷等离子体活化水)是采用大气压冷等离子体对去离子水处理后得到的具有弱酸性、强氧化性的水溶液。

Atmospheric pressure cold plasma (hereinafter referred to as plasma) generates a large number and variety of gaseous active particles in the gas phase, such as H, O, O₃, OH, NO, NO₂, N₂O, H₂O₂, N₂O₅, etc. When these gaseous active particles come into contact with water, they generate various liquid-phase active particles such as H₂O₂, O₂⁻, OH, NO, ONOO⁻ in the liquid phase.

大气压冷等离子体(以下简称等离子体)会在气相中生成大量且种类丰富的气相活性粒子，例如H、O、O₃、OH、NO、NO₂、N₂O、H₂O₂、N₂O₅等，当这些气相活性粒子与水接触后会在液相中生成H₂O₂、O₂⁻、OH、NO、ONOO⁻等多种液相活性粒子。

These liquid-phase active particles have strong redox properties and can participate in a variety of biochemical reactions, making plasma-activated water prepared based on them play a significant role in biomedical applications such as anti-cancer and sterilization.

这些液相活性粒子因具有较强的氧化还原特性，可以参与多种生物化学反应，使得基于其制备得到的等离子体活化水在抗癌、杀菌等生物医学方面具有明显的作用。

[n0003]

However, during the process of gaseous active particles in plasma transferring into aqueous solution and forming liquid active particles, the mass transfer process at the gas-liquid interface is strongly coupled, which severely hinders the mass transfer process of gaseous active particles. As a result, the concentration of liquid active particles in water is low, ultimately leading to weak chemical activity of plasma-activated water.

然而，等离子体中的气相活性粒子在转移进入水溶液并形成液相活性粒子的过程中，由于气液交界面处的传质过程耦合强烈，使得气相活性粒子的传质过程受到严重的阻碍，水中液相活性粒子的浓度较低，最终导致等离子体活化水的化学活性较弱。

Meanwhile, the strong chemical activity of liquid-phase free radicals makes their lifespan in aqueous solution extremely short. If they are not specially frozen after discharge and are simply placed in a normal room temperature environment, various active particles will react rapidly and consume their respective chemical activity, making it difficult to maintain the chemical activity of the prepared plasma-activated water for a long time. Moreover, the chemical activity will be significantly weakened as the storage time increases, and eventually lose its application effect in the biomedical field.

同时，液相自由基的强化学活性使其在水溶液中的存在寿命极短，若不在放电生成后进行特殊的冻存处理，而仅将其放置于一般的常温环境下，则各类活性粒子之间会迅速地发生反应消耗各自的化学活性，使得制备得到的等离子体活化水的化学活性难以长期保持，且会随着放置时间的增加而出现明显的减弱，最终丧失其在生物医学领域的应用效果。

[n0004]

The aforementioned phenomena have greatly affected the application of plasma-activated water. Therefore, how to increase the number of liquid-phase active particles in plasma-activated water to enhance its chemical activity, and how to extend the survival time of active particles in activated water to enhance its storage effect and extend the "shelf life" of its chemical activity are currently the difficult and hot research topics.

上述现象极大地影响了等离子体活化水的应用，因此，如何提高等离子体活化水中液相活性粒子的数目以增强其化学活性，以及如何延长活化水中活性粒子的存活时间以增强其存储效果、延长其化学活性的“保质期”是目前研究的难点和热点。

[n0005]

Based on the above problems, existing technologies mainly maintain the activity of plasma-activated water over a long period of time by lowering the temperature of the water. The principle is that cooling can suppress the thermal motion of active particles in the water, thereby reducing the probability of particle collisions and reactions and extending the storage time.

基于上述问题，现有技术主要通过降低等离子体活化水的温度来保持其在长时间内的活性维持，其原理是通过降温可抑制水中活性粒子的热运动，从而减少发生粒子碰撞及反应的概率，延长其存储时间。

However, if plasma-activated water is cooled and stored, the process takes a long time, and a large number of active particles can still react rapidly during this period, resulting in the consumption of a large number of active particles.

然而，若对等离子体活化水进行降温存储，由于其所需的时间较长，且在此期间大量的活性粒子仍能快速反应，这使得该过程中依旧有大量的活性粒子被消耗。

If activated water is prepared directly at low temperature, the lower temperature will further reduce the efficiency of gas-liquid mass transfer, thereby affecting the generation efficiency of liquid-phase active particles.

倘若直接在低温环境下制备活化水，则较低的温度会导致其气液传质的效率进一步下降，进而影响液相活性粒子的生成效率。

In addition, many researchers have tried to adjust the discharge parameters to enhance the chemical activity of plasma-activated water and slow down the decay rate of active particles. However, existing technologies make it difficult to fundamentally maintain the chemical activity of plasma-activated water. This means that plasma-activated water may fail to meet the requirements for use in practical applications due to the decay of its chemical activity, thus limiting its actual clinical application.

此外，很多研究学者尝试调控放电参数来提升等离子体活化水的化学活性以及减缓活性粒子的衰减速率。 然而，现有的技术手段很难从根本上维持等离子体活化水的化学活性，这导致等离子体活化水在实际应用中可能因化学活性的衰减而无法满足其使用需求，从而限制了等离子体活化水的实际临床应用。

[0008]

Summary of the Invention

发明内容

[n0006]

The purpose of this invention is to solve the technical problems of low generation efficiency of liquid phase active particles in plasma-activated water prepared by existing methods and difficulty in maintaining the chemical activity of plasma-activated water, and to provide a plasma-activated water preparation method based on the synergistic effect of micro-nano bubbles.

本发明的目的是解决现有方法制备得到的等离子体活化水中液相活性粒子的生成效率较低，以及等离子体活化水的化学活性难以维持等技术问题，而提供一种基于微纳米气泡协同效应的等离子体活化水制备方法。

[n0007]

To achieve the above objectives, the technical solution provided by this invention is as follows:

为实现上述目的，本发明所提供的技术解决方案为：

[n0008]

A plasma-activated water preparation method based on the synergistic effect of micro- and nano-bubbles, characterized by the following steps:

一种基于微纳米气泡协同效应的等离子体活化水制备方法，其特殊之处在于，包括以下步骤：

[n0009]

Micro-nano bubbles are passed through pure water until saturation is achieved to obtain micro-nano bubble water; the gas used for the micro-nano bubbles is one of air, oxygen, nitrogen, or helium.

在纯水中通入微纳米气泡直至饱和，得到微纳米气泡水；所述微纳米气泡采用的气体是空气、氧气、氮气或氦气中的一种；

[n0010]

Plasma activation treatment was performed on micro-nano bubble water within 3 minutes to obtain plasma-activated water based on the synergistic effect of micro-nano bubbles.

于3分钟内对微纳米气泡水进行等离子体活化处理，得到基于微纳米气泡协同效应的等离子体活化水。

[n0011]

Furthermore, saturation refers to pure water appearing completely opaque and milky white.

进一步地，所述饱和是指纯水呈现完全不透明的乳白色。

[n0012]

Furthermore, the micro-nano bubbles are generated by introducing gas into a micro-nano bubble machine, and the gas flow rate into the micro-nano bubble machine is 180-220 sccm, with an introduction time of 1-2 minutes.

进一步地，所述微纳米气泡是将气体通入微纳米气泡机中而产生的，且气体进入微纳米气泡机的流速为180～220sccm，通入时间为1～2分钟。

During this process, the gas flow rate needs to be controlled. If the flow rate is too low, it will draw in ambient air, and if the flow rate is too high, it will damage the micro-nano bubble machine. Therefore, the gas flow rate entering the micro-nano bubble machine should be controlled at 180-220 sccm. At the same time, the gas introduction time also needs to be controlled. If the introduction time is too short, the micro-nano bubble machine will draw in some ambient air and mix it into the working gas, affecting the purity of the introduced gas. If the introduction time is too long, it will easily lead to excessive pressure inside the micro-nano bubble machine, which will affect the normal operation of the machine, and a sharp popping sound will be accompanied when the air tube is pulled out. Therefore, it is advisable to control the gas introduction time to 1-2 minutes.

在此过程中，需对气体的流速进行控制，若流速过低则会吸入周围的空气，流速过高则会损害微纳米气泡机，因此将气体进入微纳米气泡机的流速控制为180～220sccm；同时，气体通入的时间也需进行控制，若通入时间太短，则微纳米气泡机将抽取部分环境中的空气混入工作气体中，影响所通入气体的纯度；若通入时间过长，则易导致微纳米气泡机内部的压力过大，进而影响机器的正常运作，且在拔出气管时会伴随尖锐的爆鸣声，因此，将气体通入时间控制为1～2min为宜。

[n0013]

Furthermore, the plasma activation treatment is performed using one or more plasma jet devices arranged in an array, a coaxial circular tube plasma generator for dielectric barrier discharge, a surface discharge plasma generator, or a sliding arc discharge plasma generator.

进一步地，所述等离子体活化处理采用单个或多个呈阵列排布的等离子体射流装置、介质阻挡放电的等离子体同轴圆管式发生器、沿面放电等离子体发生装置或滑动弧放电等离子体发生装置进行处理。

[n0014]

Furthermore, the plasma activation treatment is carried out using an underwater bubble plasma device. This treatment method involves both dielectric barrier discharge and underwater arc discharge during discharge, making it relatively easy to occur and resulting in high efficiency of plasma activation treatment.

进一步地，所述等离子体活化处理采用水下气泡等离子体装置进行处理，该处理方式在放电时既存在介质阻挡放电，同时也存在水下电弧放电，因此其发生较为容易，等离子体活化处理的效率较高。

[n0015]

Furthermore, the flow rate of the working gas introduced into the underwater bubble plasma device is 500 sccm to 5000 sccm. Too high or too low a flow rate will affect the efficiency of plasma treatment. The working gas is helium doped with nitrogen, and the ratio of the two is 99:1.

进一步地，所述水下气泡等离子体装置中通入的工作气体的流速为500sccm～5000sccm，流速过高或过低均会影响等离子体处理的效率；所述工作气体为氦气掺杂氮气，且二者的比例为99：1。

[n0016]

Furthermore, the flow rate of the working gas is 1000 sccm to 2000 sccm, within which the plasma activation treatment is most effective.

进一步地，所述工作气体的流速为1000sccm～2000sccm，在此范围内，等离子体活化处理的效果最佳。

[n0017]

Furthermore, it also includes the steps of dispensing, sealing, and refrigerating plasma-activated water using centrifuge tubes.

进一步地，还包括利用离心管对等离子体活化水进行分装、密封，并进行低温冷藏的步骤。

[n0018]

Furthermore, the low temperature is 0–10°C.

进一步地，所述低温为0～10°C。

[n0019]

Furthermore, the low temperature is 4°C.

进一步地，所述低温为4°C。

[n0020]

Compared with the prior art, the beneficial effects of the present invention are as follows:

与现有技术相比，本发明的有益效果如下：

[n0021]

1. The present invention provides a plasma-activated water preparation method based on the synergistic effect of micro-nano bubbles, which can improve the generation efficiency and concentration of liquid-phase active particles in plasma-activated water under the synergistic effect of micro-nano bubbles, thereby enhancing its chemical activity.

1、本发明基于微纳米气泡协同效应的等离子体活化水制备方法，能够在微纳米气泡的协同作用下提高等离子体活化水中液相活性粒子的生成效率及浓度，进而增强其化学活性。

[n0022]

2. The present invention provides a plasma-activated water preparation method based on the synergistic effect of micro-nano bubbles. This method can utilize micro-nano bubbles in plasma-activated water to slow down the decay rate of liquid-phase active particles, thereby extending the effective retention time of chemical activity in plasma-activated water.

2、本发明基于微纳米气泡协同效应的等离子体活化水制备方法，能够利用等离子体活化水中的微纳米气泡来延缓其中液相活性粒子的衰减速度，进而延长等离子体活化水化学活性的有效存留时间。

[n0023]

3. In the plasma-activated water preparation method based on the synergistic effect of micro-nano bubbles in this invention, the gas used for micro-nano bubbles is oxygen. The working gas introduced into the underwater bubble plasma device can be helium-doped nitrogen.

Oxygen micro-nano bubbles can dissolve in water through the high internal pressure characteristics of the bubbles themselves, thereby enhancing the oxidizing properties of the resulting plasma-activated water. Nitrogen-doped helium, as the working gas of the underwater bubble plasma device, can enhance the discharge effect through Penning ionization. At the same time, oxygen in the water and nitrogen doped in the gas can undergo a synergistic reaction to generate a large number of peroxynitrite ions in the plasma-activated water to enhance its activity.

3、本发明基于微纳米气泡协同效应的等离子体活化水制备方法中，微纳米气泡所采用的气体为氧气，水下气泡等离子体装置中通入的工作气体可选择氦气掺杂氮气，其中，氧气微纳米气泡可以通过气泡本身的内高压特性溶于水中，增强所得等离子体活化水的氧化性；而氮气掺杂氦气作为水下气泡等离子体装置的工作气体可以通过潘宁电离增强放电效果；同时水中的氧气与气体中掺杂的氮气可发生协同反应作用，在等离子体活化水中产生大量过氧亚硝酸根离子以增强其活性。

[n0024]

4. In the plasma-activated water preparation method based on the synergistic effect of micro-

nano bubbles in this invention, when the micro-nano bubble water is activated by an underwater bubble plasma device, both dielectric barrier discharge and underwater arc discharge exist, thus the efficiency of plasma activation treatment is high.

4、本发明基于微纳米气泡协同效应的等离子体活化水制备方法中，采用水下气泡等离子体装置对微纳米气泡水进行等离子体活化处理时，既存在介质阻挡放电，同时也存在水下电弧放电，因此等离子体活化处理的效率较高。

[n0025]

5. This invention enables the large-scale production of plasma-activated water, which can then be packaged, sealed, and stored; at the same time, the "shelf life" of the chemical activity and biomedical effects of the prepared plasma-activated water is significantly extended.

5、本发明可以实现等离子体活化水的大规模生产，之后可进行分装、密封和存储；同时制备得到的等离子体活化水的化学活性及其生物医学方面作用效果的“有效期”大幅延长。

[n0026]

6. The plasma-activated water prepared by this invention can be further slowed down by low-temperature refrigeration to slow down the decay rate of active particles in the plasma-activated water and increase the preservation time of its chemical activity.

6、本发明制备得到的等离子体活化水可通过低温冷藏进一步延缓等离子体活化水中活性粒子的衰减速度，增加其化学活性的保存时间。

[n0027]

7. The plasma-activated water preparation method based on the synergistic effect of micro-nano bubbles in this invention is simple and easy to implement, which greatly reduces the

cost required for efficient preparation and long-term effective storage of plasma-activated water, and has the characteristics of being economical and efficient.

7、本发明基于微纳米气泡协同效应的等离子体活化水制备方法简单易实现，大大降低了等离子体活化水在高效制备和长期有效存储过程中所需的成本，有经济高效的特点。

[0031]

Attached Figure Description

附图说明

[n0028]

Figure 1 is a schematic diagram of the structure of plasma activation treatment using an underwater bubble plasma device in an embodiment of the present invention.

图1为本发明实施例采用水下气泡等离子体装置进行等离子活化处理的结构示意图。

[n0029]

Figure 2 is a comparison of the appearance changes of pure water before and after the introduction of micro-nano bubbles in the embodiment of the present invention, wherein: (a) shows the pure water after the introduction of micro-nano bubbles, and (b) shows the pure water before the introduction of micro-nano bubbles.

图2为本发明实施例中纯水在通入微纳米气泡前、后的外观变化对比图，其中：(a)图表示通入微纳米气泡后的纯水，(b)图表示通入微纳米气泡前的纯水。

[n0030]

Figure 3 is a comparison of the hydrogen peroxide concentration changes in plasma-activated water prepared by micro-nano bubbles with different gas raw materials under the same plasma treatment conditions according to the embodiments of the present invention.

图3为本发明实施例在相同的等离子体处理条件下，通入不同气体原料的微纳米气泡所制得的等离子体活化水的过氧化氢浓度变化对比图。

[n0031]

Figure 4 is a comparison of the physicochemical properties of pure water before and after underwater bubble plasma treatment and before and after passing through micro-nano bubbles in the embodiments of the present invention. Among them: (a) Figure is a comparison of the pH values of different aqueous solutions, and (b) Figure is a comparison of the ORP values of different solutions.

图4为本发明实施例中经水下气泡等离子体处理前、后的纯水以及通入微纳米气泡前、后纯水的理化特性参数对比图，其中：(a)图为不同水溶液的pH值大小对比图，(b)图为不同溶液的ORP值对比图。

[n0032]

Figure 5 is a comparison of the concentrations of major active particles in four different aqueous solutions before and after the introduction of micro-nano bubbles and before and after plasma treatment according to an embodiment of the present invention. Among them: (a) is a comparison of the concentrations of H₂O₂, (b) is a comparison of the concentrations of NO₂NER16_, (c) is a comparison of the concentrations of ONOO⁻/O₂NER19_, and (d) is a comparison of the concentrations of OH.

图5为本发明实施例对通入微纳米气泡前、后以及等离子体处理前、后的四种不同水溶液中各主要液相活性粒子浓度的对比图，其中：(a)图为H_2O_2的浓度大小对比图，(b)图为NO_2^-的浓度大小对比图，(c)图为$ONOO^-/O_2^-$的浓度大小对比图，(d)图为OH的浓度大小对比图。

[n0033]

Figure 6 shows the changes in the concentration of short-lived active particles with storage time in plasma-activated water prepared according to the embodiments of the present invention and plasma-activated water without the addition of micro-nano bubbles. Among them, (a) is a comparison of the concentration changes of $ONOO^-/O_2^-$, and (b) is a comparison of the concentration changes of OH.

图6为本发明实施例制备得到的等离子体活化水与未加入微纳米气泡的等离子体活化水中各短寿命活性粒子浓度随存储时间的变化曲线图，其中：(a)图是$ONOO^-/O_2^-$的浓度变化对比图，(b)图是OH的浓度变化对比图。

[n0034]

Figure 7 is a comparison of the anticancer effects and storage time of plasma-activated water prepared in the embodiments of the present invention and other plasma-activated waters. In this figure: (a) shows the comparison of cell viability when different plasma-activated waters are directly applied to cancer cells, and (b) shows the comparison of cell viability when different plasma-activated waters are left to stand for a period of time before treating cancer cells.

图7为本发明实施例制备得到的等离子体活化水及其他等离子体活化水的抗癌作用效果及存储时间对比图，其中：(a)图表示将不同的等离子体活化水直接应用于癌细胞时细胞活力对比图，(b)图表示将不同的等离子体活化水静置一段时间后再处理癌细胞时细胞活力对比图。

[n0035]

Figure 8 shows a comparison of the number of cancer cells observed under a microscope after treatment with different aqueous solutions.

图8为经过不同水溶液处理后在显微镜下观察的癌细胞数量对比图像。

[0040]

Detailed Implementation

具体实施方式

[n0036]

To make the objectives, advantages and features of the present invention clearer, the present invention will be further described in detail below with reference to the accompanying drawings and specific embodiments.

为使本发明的目的、优点和特征更加清楚，以下结合附图和具体实施例对本发明作进一步详细说明。

Those skilled in the art should understand that these embodiments are merely used to explain the technical principles of the present invention and are not intended to limit the scope of protection of the present invention.

本领域技术人员应当理解的是，这些实施方式仅仅用来解释本发明的技术原理，目的并不是用来限制本发明的保护范围。

[n0037]

This embodiment provides a plasma-activated water preparation method based on the synergistic effect of micro- and nano-bubbles. The specific preparation method is as follows:

本实施例提供了一种基于微纳米气泡协同效应的等离子体活化水制备方法，具体制备方法为：

[n0038]

Micro-nano bubbles are introduced into pure water until saturation. During this process, the color of the pure water changes from colorless to white and the transparency gradually decreases. When it approaches saturation or even supersaturation, the pure water becomes completely opaque milky white (as shown in Figure 2), at which point micro-nano bubble water is obtained. Then, the micro-nano bubble water is immediately subjected to plasma activation treatment to obtain plasma-activated water based on the synergistic effect of micro-nano bubbles.

对纯水中通入微纳米气泡直至饱和，在此过程中，纯水的颜色由无色转为白色且透明度逐渐下降，当接近饱和甚至过饱和时，纯水呈现出完全不透明的乳白色(图2所示)，此时得到微纳米气泡水；接着，立即对微纳米气泡水进行等离子体活化处理，得到基于微纳米气泡协同效应的等离子体活化水。

[n0039]

After a large number of micro-nano bubbles are introduced to make the pure water turn milky white, the time for it to stand and wait for further treatment should be as short as possible. Ideally, it should be removed and subjected to plasma treatment immediately.

当通入大量微纳米气泡使纯水呈乳白色之后其静置待处理的时间应尽可能短，理想情况下应当取出后立即进行等离子体处理。

Although micro- and nano-bubbles are relatively stable in aqueous solutions, experiments have shown that if left to stand for too long, their color will still fade until they become colorless and transparent, which will greatly weaken the synergistic effect of micro- and nano-bubbles.

虽然微纳米气泡在水溶液中的存在相对稳定，但实验证明若静置时间过长，其颜色依旧会淡化直至无色透明，这将使得微纳米气泡的协同效应大大减弱。

Therefore, the obtained micro-nano bubble water should be subjected to plasma treatment immediately (generally within 3 minutes, preferably within 30 seconds) to ensure the presence of a large number of micro-nano bubbles and maximize their synergistic effect in the plasma treatment process.

因此，应将得到的微纳米气泡水立即进行等离子体处理(一般要求时间间隔在3分钟以内，最好在30s内)，以此保证大量微纳米气泡的存在并最大程度发挥其在等离子体处理过程中的协同作用。

[n0040]

In this embodiment, micro- and nano-bubbles are introduced into the process of plasma treatment of pure water. Through the synergistic reaction of micro- and nano-bubbles during the treatment process, the chemical activity and liquid phase active particle concentration of plasma-activated water are much higher than those of ordinary plasma-activated water.

本实施例在等离子体处理纯水的过程中引入了微纳米气泡，在处理过程中通过微纳米气泡的协同反应，使得等离子体活化水的化学活性和液相活性粒子浓度远高于普通的等离子体活化水。

The synergistic effect of micro- and nano-bubbles described here is intended to emphasize that when a large number of micro- and nano-bubbles are present in plasma-activated water, the inherent characteristics of the micro- and nano-bubbles make the plasma treatment effect stronger and the activity of plasma-activated water maintained for a longer time.

此处所述微纳米气泡的协同效应，意在强调等离子体活化水中存在大量微纳米气泡时，微纳米气泡自身的特性使得等离子体的处理效果更强，也使得等离子体活化水活性的维持时间更长。

The synergistic effect of micro- and nano-bubbles in the preparation of plasma-activated water refers to the fact that after micro- and nano-bubbles are introduced into pure water, their properties are changed to a certain extent. Compared with the prior art, the activated water obtained by plasma treatment under the same conditions in this embodiment has stronger chemical activity.

关于微纳米气泡在制备等离子体活化水过程中的协同作用，指的是在纯水中通入微纳米气泡后，其特性有了一定程度的改变，相比现有技术，本实施例在同等条件下经等离子体处理后得到的活化水拥有更强的化学活性。

[n0041]

In this embodiment, the micro-nano bubbles are generated by introducing gas into a micro-nano bubble machine. The gas flow rate into the micro-nano bubble machine is 200 sccm, and the introduction time is approximately 1 minute.

本实施例的微纳米气泡是将气体通入微纳米气泡机中而产生的，气体进入微纳米气泡机的流速为200sccm，通入时间约为1min。

Regarding the gas feedstock, gases such as air, oxygen, nitrogen, and helium can be selected. Among them, rare gas molecules, as monatomic molecules, undergo more elastic collisions when discharging in water, which greatly improves the energy utilization rate of electrons and thus greatly enhances the discharge. However, their usage cost is relatively high.

关于通入的气体原料，可以选择空气、氧气、氮气、氦气等气体，其中稀有气体分子作为单原子分子，在水中放电时更多地发生弹性碰撞，这使得电子的能量利用率大大提高，从而使放电大大增强，但其使用成本相对较高。

The activation effect of micro-nano bubbles is best when oxygen is introduced, followed by air, while the activation effect of micro-nano bubbles is less than that of air when nitrogen is introduced.

通入氧气微纳米气泡的活化效果最佳，空气次之，通入氮气微纳米气泡的活化效果次于空气。

For the sake of the ease and availability of air, this embodiment uses air as the gaseous raw material to generate micro-nano bubbles.

出于空气简单易得的角度，本实施例采用空气作为气体原料来产生微纳米气泡。

[n0042]

Plasma activation treatment can be carried out using plasma jet devices, plasma surface discharge devices, plasma dielectric barrier discharge devices, or plasma sliding arc discharge devices, or underwater bubble plasma devices. Regardless of the treatment method used, the plasma treatment process after introducing micro-nano bubbles has a significant synergistic promoting effect.

等离子体活化处理可采用等离子体射流装置、等离子体表面放电装置、等离子体介质阻挡放电装置或等离子体滑动弧放电装置等进行处理，也可采用水下气泡等离子体装置进行处理，无论采用何种处理方式，在引入微纳米气泡后进行等离子体处理的过程都具有发现明显的协同促进作用。

[n0043]

Preferably, in this embodiment, an underwater bubble plasma device is selected to perform plasma activation treatment on micro-nano bubble water to improve its gas-liquid mass transfer efficiency. At the same time, the device makes full use of the physicochemical effects of ultraviolet radiation, strong electric field, electrons, and local thermal field that accompany the plasma generation process to maximize the plasma mass transfer efficiency and energy utilization efficiency.

优选地，本实施例选择水下气泡等离子体装置对微纳米气泡水进行等离子体活化处理，以此来提升其气液传质效率，同时该装置尽可能地利用了等离子体产生过程中伴随的紫外辐射、强电场、电子、局部热场的理化效应，最大化地提高等离子体的传质效率与能量利用效率。

[n0044]

Figure 1 shows the underwater bubble plasma device and the container containing pure water to be treated (i.e., micro-nano bubble water), wherein the high-voltage electrode is connected to the iron rod electrode in the underwater bubble plasma device, and the ground electrode is connected to the copper mesh outside the water container.

图1示出了水下气泡等离子体装置和盛有待处理纯水(即微纳米气泡水)的容器组成，其中高压电极接到水下气泡等离子体装置中的铁棒电极上，而地电极接到呈水容器外的铜网上。

Plasma is generated in the air gap between the glass tube and the iron electrode, and then enters the pure water to be treated in the form of plasma bubbles through a small hole in the glass tube, causing changes in the physicochemical parameters of the aqueous solution and generating a large number of liquid-phase active particles.

等离子体在玻璃管与铁电极之间的空气间隙中产生，然后通过玻璃管上开的小孔以等离子体气泡的形式进入到待处理纯水中，使得水溶液理化参数发生改变并产生大量的液相活性粒子。

[n0045]

There are also several options for the working gas introduced into the underwater bubble plasma device.

关于通入水下气泡等离子体装置的工作气体，同样可以有多种选择。

Although rare gases are relatively easy to discharge, their gas cost is relatively high; meanwhile, nitrogen and oxygen each have their own advantages and disadvantages in terms of discharge characteristics and the plasma characteristics they produce.

虽然稀有气体的发生放电比较容易，但其气体成本相对较高；同时氮气与氧气的放电特性以及产生的等离子体特性则各有其优缺点。

In this embodiment, air is used as the working gas for discharge, which is the most economical and efficient way to generate plasma.

本实施例以空气作为放电的工作气体，其产生等离子体是最经济高效的。

Furthermore, when treating pure water containing a large number of micro- and nano-bubbles, the generation rate of plasma bubbles also needs to be controlled. In this process, it is necessary to avoid generating too many plasma bubbles due to excessive airflow, which would make the reaction difficult to complete; at the same time, it is also necessary to avoid generating too few plasma bubbles due to insufficient airflow, which would result in unsatisfactory treatment results. Taking all factors into consideration, the flow rate of the working gas should be controlled between 500 sccm and 5000 sccm during the plasma activation treatment, with the ideal flow rate being between 1000 sccm and 2000 sccm.

此外，在处理含有大量微纳米气泡的纯水时，其等离子体气泡的产生速度也需要进行调控，在此过程中，既需要避免因为气流过大而导致产生的等离子体气泡过多，反应难以进行完全；同时也要避免由于气流过小而导致产生的等离子体气泡过少，处理效果不理想，综合考虑在进行等离子体活化处理的过程中，工作气体的流速控制在500sccm～5000sccm，理想的流速为1000sccm～2000sccm。

[n0046]

In this embodiment, the underwater bubble plasma device is powered by a nanosecond pulse power supply, with air as the working gas. The underwater bubble discharge treatment time is set to 5 minutes, the discharge voltage is set to 10 kV, the air flow rate is set to 1000 sccm, the volume of the pure aqueous solution to be treated is 90 mL, and the ambient temperature during the experimental reaction is room temperature, i.e., 25 °C. In the experiment, the cancer cells treated by plasma-activated water were A549 lung cancer cells.

本实施例水下气泡等离子体装置采用纳秒脉冲电源供电，以空气作为工作气体，水下气泡放电处理时间设置为5min，放电电压设置为10kV，通入空气的流速设为1000sccm，待处理的纯水溶液的体积为90mL，实验反应中环境温度均为室温，即25°C，在实验中等离子体活化水处理的癌细胞为A549肺癌细胞。

[n0047]

The aforementioned underwater bubble plasma generator can be further optimized from a single generator to an array underwater bubble plasma generator composed of multiple generator devices, which is beneficial for large-scale processing of micro-nano bubble water.

上述水下气泡等离子体发生装置可以进一步地从单个发生装置优化为由多个发生器装置组合形成的阵列水下气泡等离子体装置，这有利于对待处理的微纳米气泡水进行大体积大规模的处理。

The power supply for the plasma generator can be a high-voltage sinusoidal power supply or a high-voltage pulse power supply, while the pure water in the micro-nano bubble water can be deionized water, ultrapure water or double-distilled water.

等离子体发生装置的供电电源可选用高压正弦电源或高压脉冲电源，而微纳米气泡水中的纯水可以选择去离子水、超纯水或双蒸水。

The obtained plasma-activated water can be transferred into a storage container for storage and transportation, such as by using centrifuge tubes. Of course, other forms of storage containers can also be selected, and the storage container can even be connected to a container containing the solution to be processed, so that the generated water automatically flows into the storage container for storage.

获得的等离子体活化水可移入存储容器中进行存储和运输，例如采用离心管进行保存，当然也可选择其他形式的存储容器，甚至可以将存储容器与盛有待处理溶液的容器相连，生成后自动流入存储容器进行存储。

Storage and transportation can be further optimized to be carried out in a light-proof or low-temperature environment.

存储和运输可进一步优选得在避光或低温环境下进行。

[n0048]

In this embodiment, air is uniformly selected as the gaseous raw material from the perspectives of economy and universality when selecting the gas to be used.

本实施例在对使用气体进行选择时，从经济性与普适性的角度出发，统一选择空气作为气体原料。

Ideally, micro-nano bubbles containing oxygen can be introduced into pure water, and then helium-doped nitrogen can be used as the working gas for the underwater discharge device. Under these conditions, the chemical activity and anti-cancer effect of the plasma-activated water will be optimal.

理想情况下，可以选择在纯水中通入氧气的微纳米气泡，然后以氦气掺杂氮气作为水下放电装置的工作气体，此条件下制得的等离子体活化水的化学活性与抗癌效果达到最佳。

[n0049]

The plasma-activated water prepared in this embodiment can achieve long-term storage because it contains a large number of micro- and nano-bubbles. The presence of these micro- and nano-bubbles can reduce the probability of collisions and reactions between short-lived active particles in the liquid phase, thereby extending the lifespan of active particles in the liquid phase of the plasma-activated water and thus achieving long-term effective storage of the plasma-activated water.

本实施例制备得到的等离子体活化水可实现长效存储，其原因在于，等离子体活化水中含有大量的微纳米气泡，这些微纳米气泡的存在可以减少液相短寿命活性粒子的碰撞与反应的概率，从而可延长等离子体活化水中液相活性粒子的存在寿命，从而实现等离子体活化水的长期有效存储。

[n0050]

Therefore, the prepared plasma-activated water can be dispensed using centrifuge tubes, then the caps can be tightened and sealed, and stored in a low-temperature environment of 4°C (in a refrigerator) or an ice-water bath. The combined use of low-temperature refrigeration and micro-nano bubbles can further slow down the decay rate of active particles in plasma-activated water and increase the preservation time of its chemical activity.

为此，可将制备得到的等离子体活化水利用离心管进行分装，然后将盖子拧紧密封，并在4°C的低温环境下(冰箱中)或者是冰水浴环境下储存，低温冷藏与微纳米气泡联合使用，可进一步延缓等离子体活化水中活性粒子的衰减速度，增加其化学活性的保存时间。

In addition, during the storage or transportation of this plasma-activated water containing micro-nano bubbles, the container needs to be sealed and the system kept as stable as possible to reduce bubble decomposition caused by vibration or shaking.

此外，在存储或者运输该含有微纳米气泡的等离子体活化水的过程中，需要对容器密封并尽量保持体系稳定，减少振动或摇晃带来的气泡分解。

[n0051]

The micro/nano bubble system introduced in this invention has a significant enhancing effect on the efficient production and long-term storage of plasma-activated water. The reaction mechanism is as follows:

本发明所引入的微纳米气泡体系对于等离子体活化水的高效生产与长效存储都具有明显的增强效果，其反应机制如下：

[n0052]

When the pure water to be treated contains a large number of micro- and nano-bubbles, these micro- and nano-bubbles can have a synergistic effect on plasma treatment of pure water.

当待处理的纯水中含有大量的微纳米气泡时，这些微纳米气泡对于等离子体处理纯水可以起到协同促进的效果。

First, the small size of micro- and nano-bubbles gives them a large specific surface area, which enhances their interaction area with water molecules and improves the gas-liquid mass transfer efficiency of active particles in plasma.

首先，微纳米气泡的小尺寸使其具有极大的比表面积，这增强了其与水分子的作用面积，使得等离子体中活性粒子的气液传质效率得到提高。

Secondly, the surface charge of micro- and nano-bubbles (i.e., the bubble surface carries a negative charge) affects the arrangement of water molecules around them, thereby disrupting the hydrogen bond network between water molecules. The decrease in hydrogen bond strength weakens the surface tension of the aqueous solution, resulting in a weakening of the coupling of the gas-liquid interface mass transfer process, which is beneficial to the gas-liquid mass transfer of active particles.

其次，微纳米气泡的表面电荷(即气泡表面带有负电荷)会影响其周围的水分子排布，进而破坏水分子间的氢键网络，而氢键强度的衰减使得水溶液表面张力减弱，导致气液界面传质过程的耦合减弱，有利于活性粒子的气液传质。

Meanwhile, the ultraviolet radiation and local thermal field generated during underwater bubble plasma treatment can cause the quenching of micro and nano bubbles, thereby inducing a large amount of turbulence and eddies in the aqueous solution, disturbing the boundary layer of the aqueous solution and accelerating the diffusion of gaseous active particles into the liquid phase.

同时，在水下气泡等离子体处理过程中产生的紫外辐射、局部热场等效应会导致微纳米气泡的淬灭，从而在水溶液中引发大量的湍流与涡流，扰动水溶液的边界层且加速了气相活性粒子与液相中的扩散。

The study found that micro- and nano-bubbles in water can promote the generation of liquid-phase active particles during plasma treatment by working synergistically from multiple perspectives, including the effective area, interfacial tension, and liquid disturbance.

总结发现，水中的微纳米气泡可以从作用面积、界面张力、液体扰动等多个角度协同作用促进等离子体处理过程中液相活性粒子的产生。

[n0053]

Meanwhile, when plasma-activated water contains a large number of micro- and nano-bubbles, its special properties and slow-release effect can extend the decay time of liquid-phase active particles, thus greatly extending the retention time of the activity of plasma-activated water.

同时，当等离子体活化水中含有大量的微纳米气泡时，其特殊性质与缓释作用更是可以延长液相活性粒子的衰减时间，使得等离子体活化水的活性可保存时间大大延长。

Firstly, the interfacial adsorption effect of micro- and nano-bubbles causes a large number of active particles to tend to accumulate at the gas-liquid interface, reducing contact with other substances in the liquid phase and thus avoiding rapid reaction consumption.

其一，微纳米气泡的界面吸附效应使得大量活性粒子倾向于在气液界面处富集，减少了与液相中其余物质的接触，因此避免了快速的反应消耗。

Secondly, the surface charge of a large number of micro- and nano-bubbles will form an electric double layer, thereby changing the chemical environment of the active particles, making the distribution of active particles more uniform, reducing free diffusion, and lowering the possibility of collisions or reactions.

其二，大量的微纳米气泡表面电荷会形成双电层从而改变活性粒子的化学环境，使活性粒子的分布趋向均匀，减少了自由扩散，降低了其发生碰撞或者反应的可能性。

Third, the high internal pressure effect inside the micro-nano bubbles can encapsulate some active particles inside the bubbles, reducing their contact with the external environment through the physical protection of the bubbles, and the high pressure environment allows some active particles to exist stably.

其三，微纳米气泡内部的高内压效应可将部分活性粒子包裹在气泡内部，通过气泡的物理保护作用减少其与外界环境的接触，且高压环境使得一些活性粒子可以稳定存在。

The study found that plasma-activated water contains micro- and nano-bubbles that remain after the reaction, which can extend the retention time of active particles in the water through multiple mechanisms such as interfacial adsorption, electrostatic shielding, and high-pressure encapsulation.

总结发现，等离子体活化水中经反应存留的微纳米气泡可以通过界面吸附、静电屏蔽、高压包裹等多重机制延长水中活性粒子的存留时间。

[n0054]

In this embodiment, the synergistic effect of introducing micro-nano bubbles into plasma-treated water is utilized to efficiently generate plasma-activated water during discharge and settling, and its chemical activity and effective storage period are significantly improved.

本实施例在将微纳米气泡引入等离子体处理水的过程中，利用其在放电以及静置过程中发生的协同作用效应，高效产生等离子体活化水，并且其化学活性与有效存储周期均得到大幅提高。

Based on this, the prepared plasma-activated aqueous solution can be applied to the biomedical field, especially in anti-cancer medical applications, and its anti-cancer effect has been greatly improved and optimized.

在此基础上，可将制备得到的等离子体活化水溶液应用于生物医学领域，特别是抗癌方面的相关医学应用之中，其抗癌效果得到了大幅度的提升与优化。

The method of treating cancer cells by mixing plasma-activated water with culture medium adopts the basic methods in this field and will not be described in detail here.

其中，使用等离子体活化水与培养基混合处理癌细胞，其操作方法采用本领域的基本方法，此处不再赘述。

[n0055]

The main objective of this invention is to provide a reaction system for treating water using micro-nano bubbles in conjunction with plasma, thereby achieving efficient generation and long-term storage of plasma-activated water. Specific parameters during the reaction process, such as the volume of the solution to be treated, discharge voltage, discharge time, and working gas, can be selected differently according to application needs and actual conditions to meet various biomedical applications.

本发明的主要目的是提供一种微纳米气泡协同等离子体处理水的反应体系，以此实现等离子体活化水的高效产生与长效存储，其中发生反应过程中的具体参数，如待处理溶液体积、放电电压、放电时间、工作气体等，可根据应用需要和实际情况进行不同的选择，以满足不同的生物医学应用。

[n0056]

Figure 2 shows photographs of pure water before and after the introduction of micro-nano bubbles using a Nikon camera. As can be seen from the figure, there is a significant difference in the appearance of the aqueous solution before and after the introduction of micro-nano bubbles: pure water is colorless and transparent (Figure b), while it is milky white after the introduction of micro-nano bubbles (Figure a).

图2示出了纯水在通入微纳米气泡前、后通过尼康相机拍摄的照片，从图中可看出，通入微纳米气泡前、后水溶液外观存在明显差异：纯水呈无色透明(b图)，而在通入微纳米气泡后呈乳白色(a图)。

[n0057]

Figure 3 shows a comparison of the activity changes of plasma-activated water prepared by micro-nano bubbles with different gas raw materials under the same plasma treatment conditions.

图3示出了在相同的等离子体处理条件下，通入不同气体原料的微纳米气泡所制得的等离子体活化水的活性变化对比图。

There are many indicators for measuring the activity of activated water, among which hydrogen peroxide, as a major liquid-phase active particle product, plays a major role in its activity and anti-cancer effect. Therefore, in this embodiment, the activity of plasma-activated water is approximately compared by measuring the concentration of liquid-phase hydrogen peroxide.

用于衡量活化水活性的指标较多，而其中过氧化氢作为一种主要的液相活性粒子产物对其活性及其抗癌效应起主要作用，因此本实施例通过测量液相过氧化氢的浓度近似地比较等离子体活化水的活性强弱。

As shown in Figure 3, oxygen is the strongest, followed by helium, then air, and nitrogen is the weakest.

由图3可以看出氧气最强，氦气次之，空气再次之，而氮气最弱。

This is because oxygen is the direct raw material in the hydrogen peroxide generation process. The oxygen micro-nano bubbles and the large amount of dissolved oxygen they carry provide a sufficient oxygen source for the plasma discharge region to generate hydrogen peroxide.

这是因为氧气是生成过氧化氢反应过程中的直接原料，氧气微纳米气泡及其附带的大量溶解氧为等离子体放电区域提供了充足的氧源以生成过氧化氢。

[n0058]

The bar charts shown in Figure 4 represent the differences in physicochemical properties of the aqueous solution before and after plasma treatment. In Figure 4(a), the comparison chart corresponds to the pH value, and in Figure 4(b), the comparison chart corresponds to the ORP value.

图4所示柱状图分别代表了等离子体处理前、后水溶液的理化特性差异，其中，图4中的(a)对应的是pH值大小的对比图，图4中的(b)对应的是ORP值对比图。

As can be seen from the figure, the aqueous solution was basically neutral before plasma treatment, while it became weakly acidic after plasma treatment.

由该图可以看到在等离子体处理前水溶液基本呈中性，而在等离子体处理后水溶液呈弱酸性。

Meanwhile, plasma activation and the introduction of micro- and nano-bubbles can both increase the ORP of aqueous solutions, i.e., enhance their oxidizing properties.

同时，等离子体活化与通入微纳米气泡都可以使水溶液ORP升高，即氧化性增强。

[n0059]

Figure 5 shows the concentration comparison of the main active particles in the liquid phase in four different aqueous solutions before and after the introduction of micro-nano bubbles and before and after plasma treatment. Among them: (a) is a comparison of the concentration of H₂O₂, (b) is a comparison of the concentration of NO<sub>2< /sub>NER26_, (c) is a comparison of the concentration of ONOO⁻/O<sub>2< /sub>NER29_, and (d) is a comparison of the concentration of OH.

图5展示了通入微纳米气泡前、后与等离子体处理前、后的四种不同水溶液中各主要液相活性粒子浓度对比，其中：(a)图是H₂O₂的浓度大小对比图，(b)图是NO<sub>2<

/sub>⁻的浓度大小对比图，(c)图是ONOO⁻/O₂⁻的浓度大小对比图，(d)图是OH的浓度大小对比图。

As shown in Figure 5, under the influence of the micro-nano bubble effect, the concentration of H₂O₂ particles in plasma-activated water only increased slightly, while the concentrations of NO₂NER33_, ONOO⁻/O₂NER36_ and OH active particles all increased significantly. Among them, the concentrations of NO₂NER38_ and ONOO⁻/O₂NER41_ increased by about 100%, while the OH concentration increased by nearly 300%.

由图5可以看到在微纳米气泡的作用效应影响下，等离子体活化水中H₂O₂粒子的浓度仅有小幅的增长，而NO₂⁻，ONOO⁻/O₂⁻与OH活性粒子的浓度均大幅度地增长，其中NO₂⁻与ONOO⁻/O₂⁻的浓度约提升100%，而OH浓度提升接近300%。

[n0060]

Figure 6 is a graph showing the change in the concentration of active particles in the plasma-activated water prepared in this embodiment over a certain storage time.

图6为本实施例制得的等离子体活化水在一定存储时间内的活性粒子浓度变化曲线图。

Room temperature storage can be considered to be around 25°C, while low temperature storage refers to storing plasma-activated water in centrifuge tubes under an ice-water bath, generally considered to be at 0°C.

其中，室温保存可以认为是25°C左右，而低温存储是指将等离子体活化水放在离心管中置于冰水浴下保存，一般认为其温度为0°C。

As shown in Figure 6, both micro- and nano-bubbles and low-temperature environments are beneficial for extending the lifespan of active particles and the effective period of chemical activity, and the combined use of the two has an even better effect.

由图6可看到微纳米气泡以及低温环境均有利于延长活性粒子寿命，延长化学活性有效期，而二者结合使用效果更佳。

[n0061]

Figure 7 shows the immediate anticancer effects of different plasma-activated water and the effects after storage for a certain period of time.

图7示出了不同等离子体活化水的即时抗癌效果以及存储一定时间后的效果。

Figure 7(a) shows that plasma treatment of pure water containing micro-nano bubbles can reduce the activity of cancer cells more significantly, while Figure 7(b) shows that plasma-activated water containing micro-nano bubbles still has an inactivating effect on cancer cells after being stored for a certain period of time.

图7的(a)图表明等离子体处理含有微纳米气泡的纯水可以使癌细胞的活性降幅更大，而图7的(b)图表明含有微纳米气泡的等离子体活化水在存储一定时间后依旧对癌细胞有灭活作用。

[n0062]

Figure 8 shows microscopic images of cancer cells treated with different aqueous solutions. The figure shows that activated water with the introduction of micro-nano bubbles significantly reduces the number of cancer cells, demonstrating its stronger anti-cancer effect.

图8示出了采用不同水溶液处理癌细胞的显微镜下图像，由该图可以看到用引入微纳米气泡后的活化水会使癌细胞数目出现明显下降，这证明其抗癌效果更强。

[n0063]

In summary, the plasma treatment under the synergistic effect of micro-nano bubbles described in this embodiment is significantly more effective than plasma treatment without micro-nano bubbles. Therefore, if plasma-activated water with comparable activity is to be prepared, plasma discharge treatment can be carried out under lower treatment conditions under the synergistic effect of micro-nano bubbles. These lower treatment conditions include lower discharge voltage or shorter discharge time.

综上所述，本实施例所述微纳米气泡协同效应下的等离子体处理的效果明显强于无微纳米气泡条件下等离子体处理的效果，因此，若需制备活性相当的等离子体活化水，在微纳米气泡的协同作用下等离子体放电处理可以在更低的处理条件的进行，此处的更低处理条件包括更低的放电电压或者更短的放电时间等。

Experiments show that the required voltage for plasma generation without micro-nano bubbles is 13.2 kV, while the voltage required for plasma generation after introducing micro-nano bubbles is only 12.1 kV. At the same time, the cancer cell viability was measured to be 73% after 5 minutes of plasma treatment without micro-nano bubbles, while the cancer cell viability was measured to be 58% under the same conditions with micro-nano bubbles. If the standard of a 30% decrease in cancer cell viability is taken as the standard, it can be achieved by discharging for about 3 minutes under the condition of containing micro-nano bubbles.

实验表明在无微纳米气泡时等离子体产生的所需电压为13.2kV，而通入微纳米气泡后放电产生等离子体仅需12.1kV；同时无微纳米气泡的等离子体处理5min时测得癌细胞活力为73%，同等条件下有微纳米气泡时测得癌细胞活力为58%，若以测得癌细胞活力下降30%为标准，在含有微纳米气泡条件下只需放电3min左右就能实现。

[n0064]

This invention not only improves the practicality and efficiency of plasma-activated water, but also enhances its long-term storage effect. This is beneficial for the practical application of plasma-activated water and has significant implications for the field of plasma biomedicine, including sterilization, disinfection, anti-cancer, and wound treatment.

本发明不仅提升了等离子体活化水的实用性和高效性，而且加强了等离子体活化水的长期存储效果，这有利于等离子体活化水的实际应用，在等离子体生物医学领域，包括杀菌消毒、抗癌、伤口处理等方面都有着重大意义。

[n0065]

Although the present invention has been described in detail with reference to the foregoing embodiments, those skilled in the art should understand that modifications can still be made to the technical solutions described in the foregoing embodiments, or equivalent substitutions can be made to some or all of the technical features therein; and these modifications or substitutions do not cause the essence of the corresponding technical solutions to deviate from the scope of the technical solutions of the present invention.

尽管参照前述实施例对本发明进行了详细的说明，本领域的普通技术人员应当理解：其依然可以对前述实施例所记载的技术方案进行修改，或者对其中部分或者全部技术特征进行等同替换；而这些修改或者替换，并不使相应技术方案的本质脱离本发明技术方案的范围。