A New Scanning Tunneling Microscope Reactor Used for High Pressure and High Temperature Catalysis Studies

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Abstract

We present the design and performance of a homebuilt high pressure and high temperature reactor equipped with a scanning tunneling microscope for catalytic studies. In this design, the STM body, sample and tip are placed in a small high pressure reactor (~19 cm^{-3}) located within an ultrahigh vacuum (UHV) chamber. A sealable port on the wall of the reactor separates the high pressure environment of reactant gases from the vacuum environment of the STM chamber, and permits the exchange of sample and tip in UHV. A combination of a sample transfer arm, wobble stick, and sample load-lock system allows transfer of samples and tips between the preparation chamber, high pressure reactor and ambient environment. Experiments performed on three samples both in vacuum and in high pressure conditions demonstrate the capability of *in-situ* investigations of heterogeneous catalysis and surface chemistry at atomic resolution at a wide pressure range from UHV to a pressure higher than one atmosphere and a temperature range from 300 K to 700 K.

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I. Introduction

The understanding of heterogeneous catalysis at a molecular level has been one of the central issues of physical chemistry for the past half century.[1] Single crystal surfaces have served as valuable model catalysts providing insights into heterogeneous catalysis under vacuum conditions[1]. This vacuum surface science approach has revealed a tremendous amount of information for a great number of catalytic systems. However, industrial heterogeneous catalytic reactions are usually carried out at high pressure and high temperature. There are considerable experimental challenges in the high pressure studies, which are necessary in order to understand molecular behavior under reactive conditions. The potential difference in catalytic mechanisms between the model studies at low pressure and industrial reactions at high pressure is often referred as the pressure gap.

A key component in studying the pressure gap is to characterize the adsorbed layer of the reactant gases at high pressure during catalytic processes. A simple extrapolation of the insights into the adsorption structure obtained at low pressure and low temperature is not necessarily applicable to high pressure and high temperature systems which could have different energetic pathways. One example is the catalytic activity of Ru catalyst for CO oxidation at different pressures. In a low pressure environment, Ru is inert for CO oxidation.[1] However, it is an extremely active catalyst under high pressure of oxygen due to the formation of RuO_2.[2-4] Thus, to obtain a more complete understanding of catalysis, it is necessary to perform studies of surface catalytic reactions under high pressure of reactants.

STM has the unique capability of studying the catalytic surface atom by atom, which is invaluable for elucidating the adsorption structure and the mobility of reactant molecules during catalysis. This technique can be applied in a pressure range from UHV to atmospheric or higher pressure since the tunneling process between the sample and tip only occurs in a very close range of 5-50 Å. It has been applied to catalytic studies under a condition of relatively high pressure by a few groups[5-8]. In our laboratory we performed high pressure studies of STM using both home made and commercial STM/UHV systems and filling reactant gases into STM chamber connected to the UHV preparation chamber[5]. However, this system has disadvantages such as large volume of reactant gases and has limits in sample heating, reactant gas pressure and spatial resolution. The new high pressure and high temperature reactor STM and UHV system presented here overcome these limitations and allows for catalytic studies under a wide range of pressure and temperature. All parts of this STM and UHV system were designed and homebuilt in the two years of 2006 and 2007. The high pressure reactor is a small cylinder chamber with a volume of approximately 19 cm^3, placed inside the vacuum environment of the UHV chamber by a special docking scaffold and mounting framework. It is vibrationally isolated from the UHV chamber with three springs, offering the capability of imaging surface with atomic resolution. The sample can be heated *in-situ* to 700 K by an external heating lamp installed under the high pressure reactor in the STM chamber. Both the sample and tip can be conveniently placed and transferred using a transfer arm and wobble stick.

II. Apparatus

This section presents the details of our high pressure and high temperature reactor STM. The whole STM system includes sample preparation chamber, STM chamber, and sample/tip loading system (Fig. 1). We will discuss sample preparation and STM chambers, high pressure reactor and gas introduction system, STM body and sample heating, and sample transfer and tip exchange in sections IIA, IIB, IIC, and IID, respectively.

A. Sample Preparation and STM Chambers

The sample preparation chamber is equipped with an Auger electron spectrometer (AES) for analysis of surface composition. It is pumped by a sputtering ion pump and a turbo molecular pump with a base pressure of 5×10^{-11} Torr. Sample cleaning and preparation are carried out by an Argon ion gun for sputtering and an electron bombardment gun for annealing. Sample temperature is monitored by using an *ex-situ* infrared thermometer (pyrometer). During cleaning, the sample holder is placed in a four-finger sample stage fabricated out of alumina for thermal isolation. The sample can be heated to 1000^{o}C with an increase of background pressure less than 1.5×10^{-9} Torr. The four-finger sample stage matches a three-finger stainless steel fork on a transfer rod allowing the sample holder to be transferred to the STM chamber after sample preparation. A universal sample holder and tip exchanger on a wobble stick were designed for engaging with the sample stage, storage slots on a docking disk, and sample stage in the high pressure reactor for rapid transfer of samples and tips.

STM chamber is also a stainless steel chamber pumped by its own sputtering ion pump and turbo molecular pump. It has a base pressure of 1×10^{-10} Torr. This chamber is separated from the sample preparation chamber by an 8" gate valve. A quadrupole mass spectrometer is installed in this chamber for monitoring reactants and products during STM scanning. The STM chamber contains the high pressure reactor Fig. 1 (5), a docking scaffold assembled on a custom-designed sample manipulator, and a wobble stick for sample and STM tip transfer between the transfer rod, high-pressure reactor, and docking disk.

The sample heating source is located outside the high pressure reactor to avoid heating elements in the high pressure environment. It consists of a halogen lamp with an elliptical reflector that focuses the radiation onto the sample through a sapphire window welded at the bottom of the reactor (Fig. 2). The distance between the lamp and reactor can be adjusted to focus the light on the back of the sample for efficient heating. The heating rate can be controlled by adjusting the power supplied to the lamp.

B. High Pressure Reactor and Gas Introduction System

The high pressure reactor is a special vessel designed for assembling the STM body and sample, and providing a high pressure environment of reactant gases. It houses a homebuilt STM body. A sample assembly stage is mounted at the end of the STM body. The sample is thermally isolated and electrically insulated from the STM body. Figure 3a is a picture of the high pressure reactor with a volume of ~ 19 cm^{-3}. The reactor consists of cell lid, cell neck, cell top stage, and cell bottom stage. The cell lid has a set of precisely designed holes to glue a set of pin-socket contacts (set II in Fig. 3a) for assembling a set of male contacts (set I) from the docking scaffold and a set of male contacts (set III in Fig. 3c) for the wiring connections from the shear piezoelectric plates and the scanning tube. These pin-socket contacts provide convenient detachable wiring connections for the high pressure reactor. The contacts (set I) from the docking scaffold can be inserted to the vacuum side of the interfacial contacts (set II) glued on the cell lid. Another set of contacts (set III) is glued on a set of holes of the STM body (Fig. 3b) which have the exact same size and arrangement as the holes on the lid (Fig. 3a). This pin-socket wiring structure (Fig. 3c) makes dismantling and assembling the STM convenient when maintenance is required on the high pressure reactor and STM body.

For sample transfer and tip change, a port is opened on the wall of the bottom stage of the high pressure reactor (Fig. 3a9). A sapphire window is welded at the center of the bottom of the reactor to transmit light to heat the sample. Recesses are fabricated on the cell neck, cell top stage, cell bottom stage, and port of the reactor, hosting Kalrez o-rings forming gas-tight seals. The sealing of Kalrez o-rings allows pressurization of the reactor while maintaining a high vacuum in the surrounding chamber. All four sections of the reactor are assembled together by four venting screws and sealed by these o-rings. A bayonet seal (inset of Fig. 3a) is fabricated to seal the port on the reactor. The reactor was plated with a layer of gold (~5 micron) to avoid possible reactions between the materials of the high pressure reactor and reactant gas.

Figure 4 schematically shows the setup of gas introduction for the high pressure reactor. For gas introduction, the male part of a Swagelok fitting (4 in Fig. 4) is welded on a 1/8" tube of the cell lid (3 in Fig. 4). A 1/32" PEEK tube (7 in Fig. 4) capable of supporting high pressure was glued on a 1/16" stainless steel tube (6 in Fig. 4) assembled into a female part of the Swagelok fitting (5 in Fig. 4). Another end of the PEEK tube is also glued and assembled to another Swagelok fitting welded to a hole of a double side CF flange. This design isolates the reactant gases in the high pressure reactor from the vacuum environment of the STM chamber. The high pressure gases in the reactor can be pumped down by a turbo molecular pump to obtain a UHV environment after completion of a high pressure experiment. Thus, this high pressure reaction system can work under both UHV and high pressure, offering the capability of studying catalysts over a wide pressure range from 1×10^{-10} Torr to 5000 Torr. In addition, the reactions can be carried out with batch or flowing mode.

C. STM Body and Sample Heating

The STM body (Fig. 3b) is the key component of the high pressure reactor. As mentioned above, it is screwed onto the cell neck stage. The STM body includes a coarse approaching system, a scanning tube, a receiver of the tip holder, and wire connections to these parts. The coarse approach is carried out by six sets of shear piezoelectric plates (three of them are schematically shown in a bottom view of STM body in Fig. 3d) located between a hexagonal sapphire (Fig. 3b2) and the wall of the STM body. One side of each shear piezoelectric set is glued on the internal wall of the STM body while the other end contacts the surface of the hexagonal sapphire (Figs. 3d and 3e). By applying negative or positive voltages to the first/third and the second/fourth piezoelectric plates respectively, the lateral force moves the hexagonal sapphire forward and backward (Fig. 3e). A single piezoelectric scanning tube is glued to an alumina disk which is in turn glued to one end of the hexagonal sapphire. Five Kapton wires are glued to the five components (+x, -x, +y, -y, z) of the scanning tube through holes on the alumina disk. Another alumina disk is glued to the other end of the scanning tube onto which a bowl-shaped tip receiver is glued (Fig. 3b4). The central part of this tip receiver is a SmCo magnet. The tip change mechanism is described below. A flexible coaxial wire is glued to this tip receiver for transmitting the tunneling current.

At the front of the STM body one CuBe plate spring (Fig. 3b3) is used to hold two sets of shear piezoelectric plates. The pressure applied to the hexagonal sapphire by the shear piezoelectric sets can be fine-tuned by a screw (Fig. 3b5) in the spring plate. This pressure controls the speed of the coarse approach. A K-type thermocouple is spot-welded to the sample stage for both sample bias and temperature measurements. A second thermocouple is attached to the STM body to monitor the temperature of the shear piezoelectric plates during sample heating. Thus, thermal diffusion and possible increases in the temperature of the STM body can be simultaneously monitored when the sample in the high pressure reactor is heated.

A sample assembly stage is screwed to the end of the STM body (Fig. 3b6), which is thermally and electrically insulated from it by three precisely aligned sapphire balls and insulating washers.

D. Sample Transfer and Tip Change

The sample transfer between STM chamber and sample preparation chamber is carried out by a magnetic transfer rod with a three-finger fork. A wobble stick can transfer the sample and tip between the three-finger fork, the high pressure reactor, and the slots in the docking disk. It can accept and release the sample holder conveniently. In addition, the sample holder and tip exchanger can be introduced or removed from the system through a load-lock system.

Replacement of the STM tip is accomplished by a magnetic tip exchanger with the same geometry as the sample holder (Fig. 5a) and a tip holder (Fig. 5b). The tip exchanger can be easily transferred to and from the high pressure reactor (Fig. 5c), the storage disk, and the load-lock system.

III. Performance

In this section we illustrate the performance of the instrument with two examples of experiments carried out under UHV and high pressure conditions. These include highly ordered pyrolytic graphite (HOPG) and hex-reconstructed Pt(100) single crystal. In section IIIA, the results of a clean HOPG surface and a self-assembled organic monolayer on HOPG under ambient and UHV conditions will be discussed. In section IIIB, STM images of a clean hex-Pt(100) surface with atomic resolution will be presented along with the roughening of the surface upon reaction with high pressure CO.

A. Clean HOPG and Self-assembled Monolayer on HOPG under Both Ambient and UHV Conditions

Atomically resolved images can be routinely obtained on HOPG samples, both under UHV and in ambient condition at a tunneling current of 1.0-2.0 nA and sample bias of 0.1-0.5 volts (Fig. 6a).

To test the behavior of the STM body under high pressure conditions, a HOPG sample deposited with a self-assembled monolayer of hexadecanedioic acid is assembled in the reactor. Then, 760 Torr nitrogen were introduced into the reactor while the STM chamber is pumped down to high vacuum. Images of the self-assembled monolayer with atomic resolution as shown in Fig. 6b can be obtained under an environment of 760 Torr nitrogen. This image has five lamellae. Each lamella in terms of the section between two adjacent blue lines consists of parallel packed molecule. Similar to the self-assembly of other carboxylic acids on HOPG[9], the ordered self-assembled structure is formed through intermolecular hydrogen bonds between two adjacent lamellae. This demonstrates the satisfactory performance of the homebuilt STM body and high pressure reactor.

B. Reactive Surfaces and CO Induced Roughness under High Pressure

CO oxidation is an extremely important industrial catalytic process. Platinum is an active catalyst for this reaction. Here Pt(100) is selected as a highly reactive surface. The CO adsorption on hex-Pt(100) under a wide range of CO pressures was studied with this instrument. As is well known, the top layers of a clean Pt(100) presents a hex-reconstruction with 25% extra Pt surface atoms in contrast to the underlying 1×1 structure. The clean hex-Pt(100) was prepared by the procedure reported in literature[10]. After it is cleaned by a combined Ar^+ sputtering, annealing in oxygen environment, and a final annealing to 1150 K for several minutes in UHV followed by a slow cooling to room temperature, a clean hex-Pt(100) surface is formed. Our STM gives images of the hex-Pt(100) with atomic resolution at room temperature (Fig. 7b). It clearly demonstrates the reliability of the STM body, sample heating, sample sputtering, sample transfer, and tip exchange mechanism of this homebuilt system. Upon exposed to an environment of ~700 Torr CO, the clean hex-Pt(100) significantly restructures and presents as a surface covered with clusters with sizes ranging from 2 to 5 nm. Figure 10 is one image of the highly roughed surface formed in an environment of high pressure CO. A more extensive account of these results will be reported elsewhere[11].

Summary

A new high pressure and high temperature reactor STM was homebuilt with the purpose of simulating industrial catalysis reaction conditions. This STM is housed in a high pressure reactor equipped with *in-situ* heating and convenient sample transfer and tip change. We have demonstrated the good performance of this instrument with examples that include HOPG, both clean and with adsorbed hexadecanedioic acid. We have also shown results of the CO induced reconstruction of Pt(100) over a wide range of CO pressures, demonstrating the capability of studying catalytic reactions at atomic resolution in a high pressure environment. This STM will serve as an important tool in the effort to overcome the pressure gap in surface science and catalysis.

Acknowledgements

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Figure Captions

FIG. 1. STM and UHV system schematic. (1) view window, (2) mounting framework, (3) docking scaffold, (4) docking disk, (5) high pressure reactor (STM body housed within), (6) bayonet seal, (7) guide rod of docking scaffold, (8) sample/tip load-lock system, (9) transfer rod, (10) gate valve, (11) four-finger sample stage, and (12) sputtering ion gun.

FIG. 2. STM chamber *in-situ* sample heating system. (1) Halogen lamp, (2) elliptical reflector, (3) sapphire window welded at the center of the bottom of the high pressure reactor, (4) the assembled sample, (5) high pressure reactor. Turquoise dashed line shows the alignment of light beam and sample center.

FIG. 3. High pressure reactor and STM body. (a) A view of the whole reactor: (1) cell lid, (2) cell neck, (3) middle stage, (4) bottom stage, (5) pin-socket contacts for wiring of STM body at the interface of high vacuum and high pressure environment, (6) a pin on the lever of the cell lid for mounting, (7) Swagelok fitting welded on the tube of the cell lid for gas introduction, (8) Swagelok fitting welded on the button stage of reactor for gas exit, (9) port of reactor for sample and tip transfer. (b) Side view of the STM body: (1) Wall of STM body coated with a layer of gold, (2) hexagonal sapphire, (3) CuBe spring plates, (4) receiver of tip holder, (5) screw to adjust the pressure applied to hexagonal sapphire, (6) hole to assemble sample stage to STM body. (c) Scheme of pin-socket alignment for wiring. Set III is the contacts glued to the holes on top of STM body; Set II is the contacts glued to the holes on top of cell lid of the reactor; Set I is the contacts glued to wires from docking scaffold. (d) Scheme showing the assembly of three packs of shear piezoelectric plates between the hexagonal sapphire and the wall of the STM body and the assembly of the scanning tube: (1) a set of piezoelectric plates, (2) wall of STM

body, (3) hexagonal sapphire, (4) scanning tube. (e) Scheme showing how the four shear piezoelectric plates of one set work for coarse approach.

FIG. 4. Scheme showing the introduction of high pressure reactant gases to reactor when the reactor is under UHV environment of the STM chamber. (1) STM chamber, (2) high pressure reactor, (3) stainless steel tube (ID=1/8″), (4) and (10) male part of a Swagelok fitting, (5) and (9) female part of a Swagelok fitting, (6) and (8) silica-coated stainless steel tube (ID=1/16″), (7) PEEK tubing (OD=1/16", ID=1/32"), (11) double side CF flange, (12) and (13) angle valves, (14) angle valve for pumping reactant gases after completion of a batch mode high pressure experiments, (15) vessel for mixing different reactant gases, (16) and (17) variable leak valves, (18) Bararton capacitance manometer for pressure measurements, (19) and (20) gas filters, (21) and (22) gas cylinders, (23) angle valve.

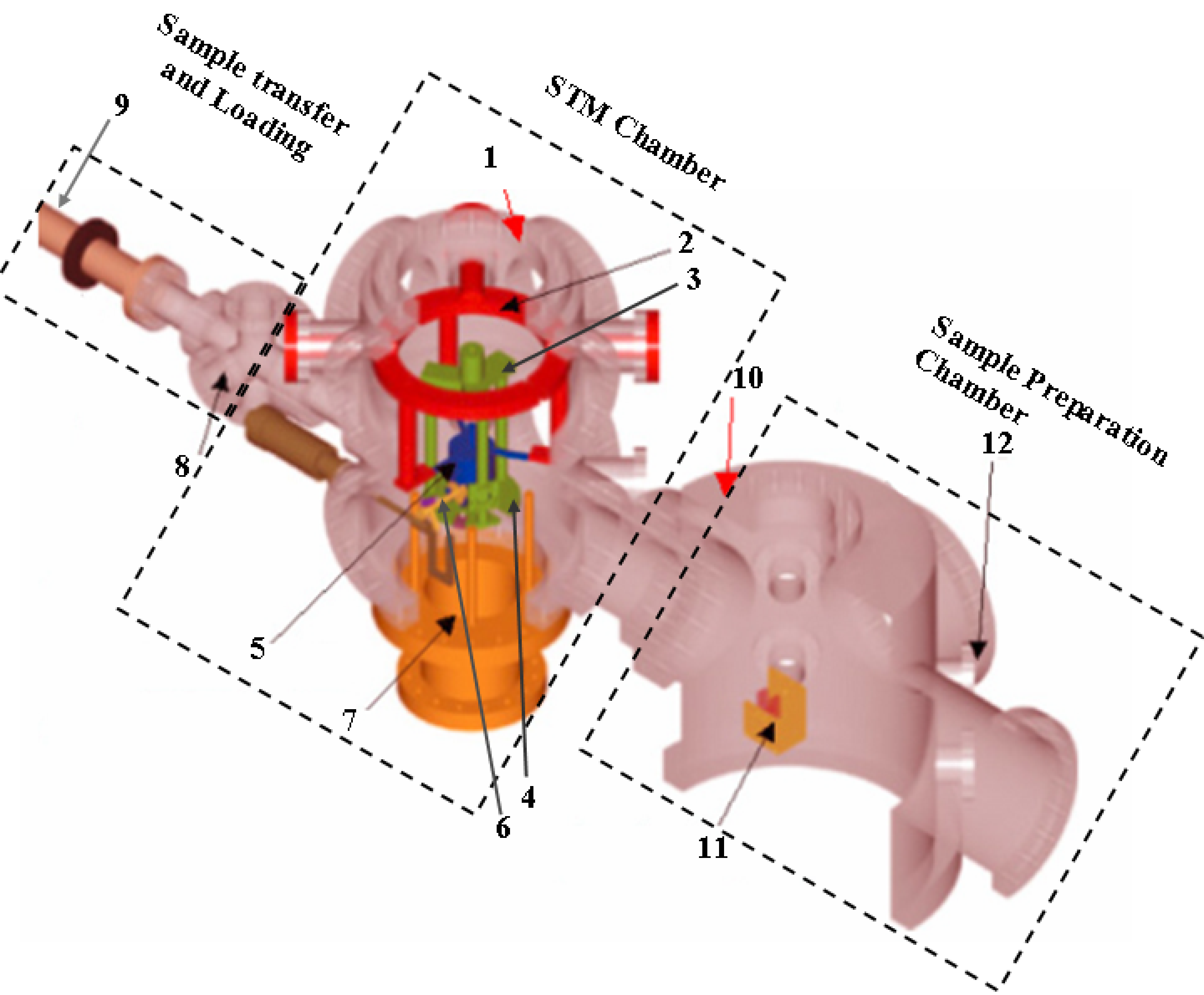
FIG. 5. Parts used for a convenient tip exchange. (a) Tip exchanger; (1) the central slot which has a size between the stopping disk and outer diameter of the tube of the tip holder, (2) magnets. (b) Tip holder with an empty tube for placing a tip; (1) empty tube for placing a STM tip, (2) stopping disk. (c) Magnetic bowl glued at the end of the scanning tube. The arrow shows the hidden bowl at the end of the scanning tube.

FIG. 6. (a) STM image of a clean HOPG surface. (b) STM image of a self-assembled monolayer of hexadecanedioic acid deposited on HOPG under an environment of 760 Torr nitrogen; the bottom is the structure of the molecules self-assembled on HOPG..

FIG. 7. (a) Large-size STM image of a clean surface of hex-Pt(100) with step height of a single atom collected under UHV condition at 300 K. (b) Small-size atom-resolved image of this surface under UHV.

FIG. 8. STM image of a highly roughed Pt(100) formed in an environment of 700 Torr CO.

FIG. 1


Sample transfer and Loading
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Sample Preparation Chamber
1
2
3
4
5
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11
12

FIG. 2

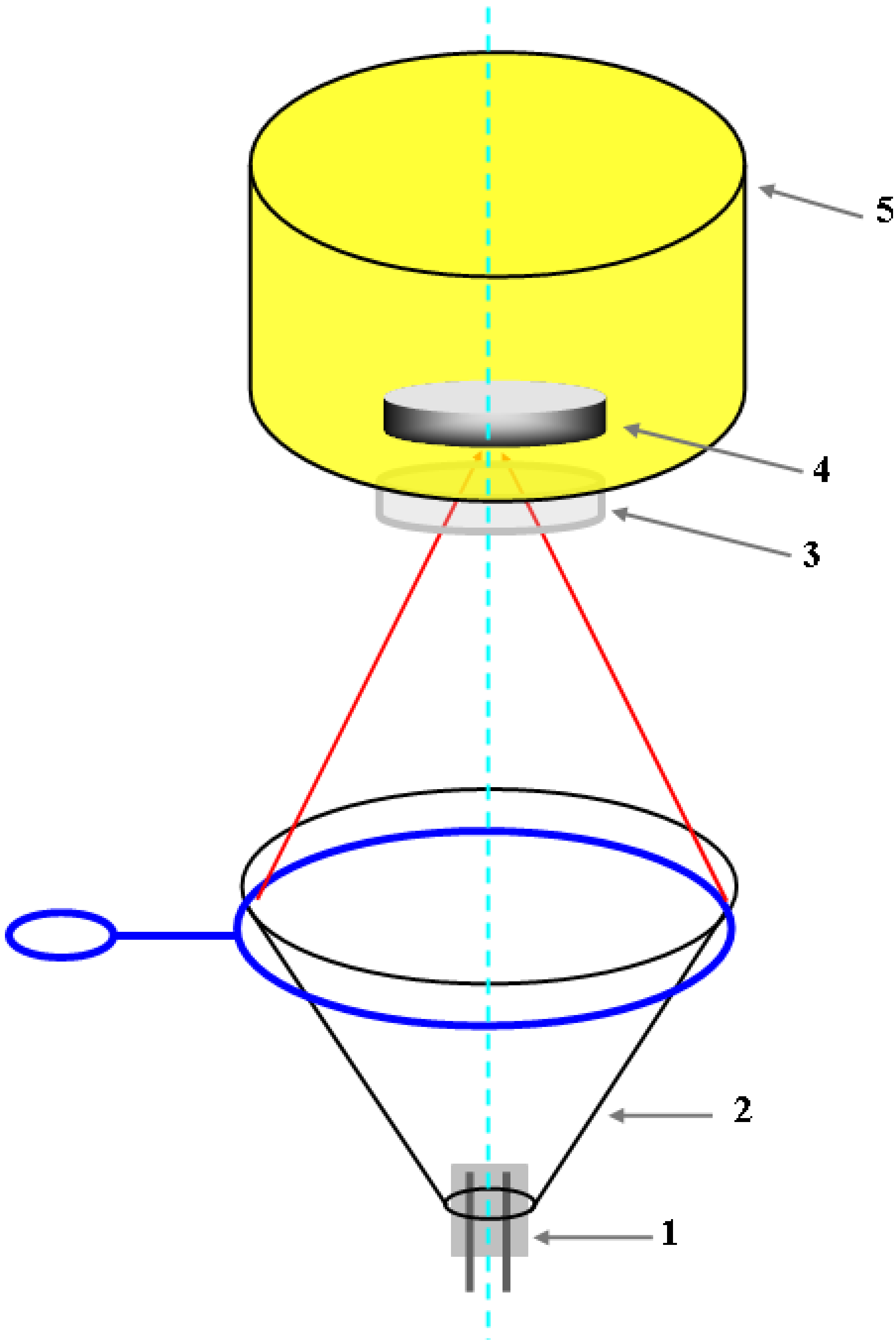


FIG. 3

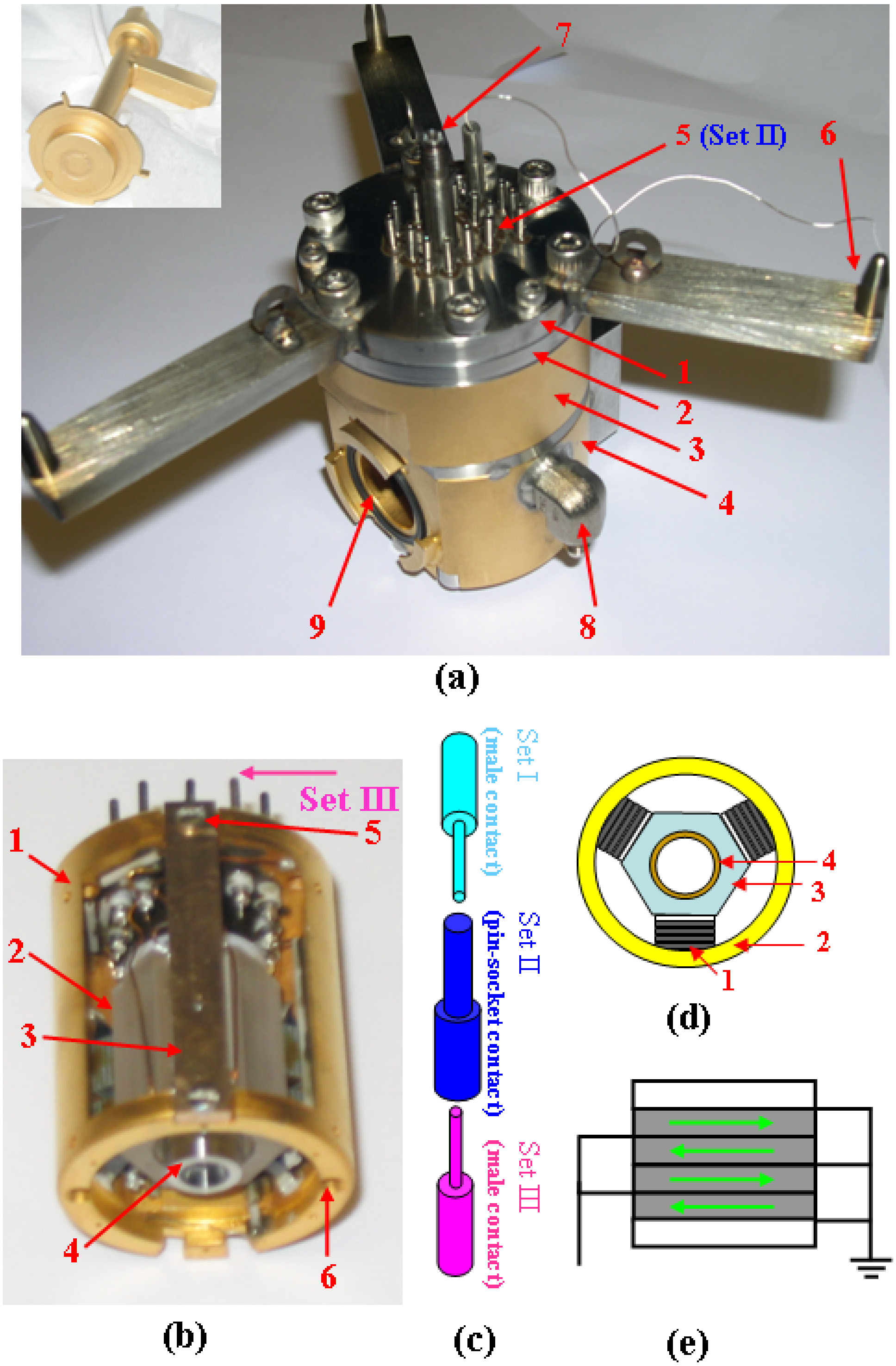

7
5 (Set II)
6
1
2
3
4
9
8
(a)
Set III
5
1
2
3
4
6
(b)
Set I
(male contact)
Set II
(pin-socket contact)
Set III
(male contact)
(c)
4
3
2
1
(d)
(e)

FIG. 4

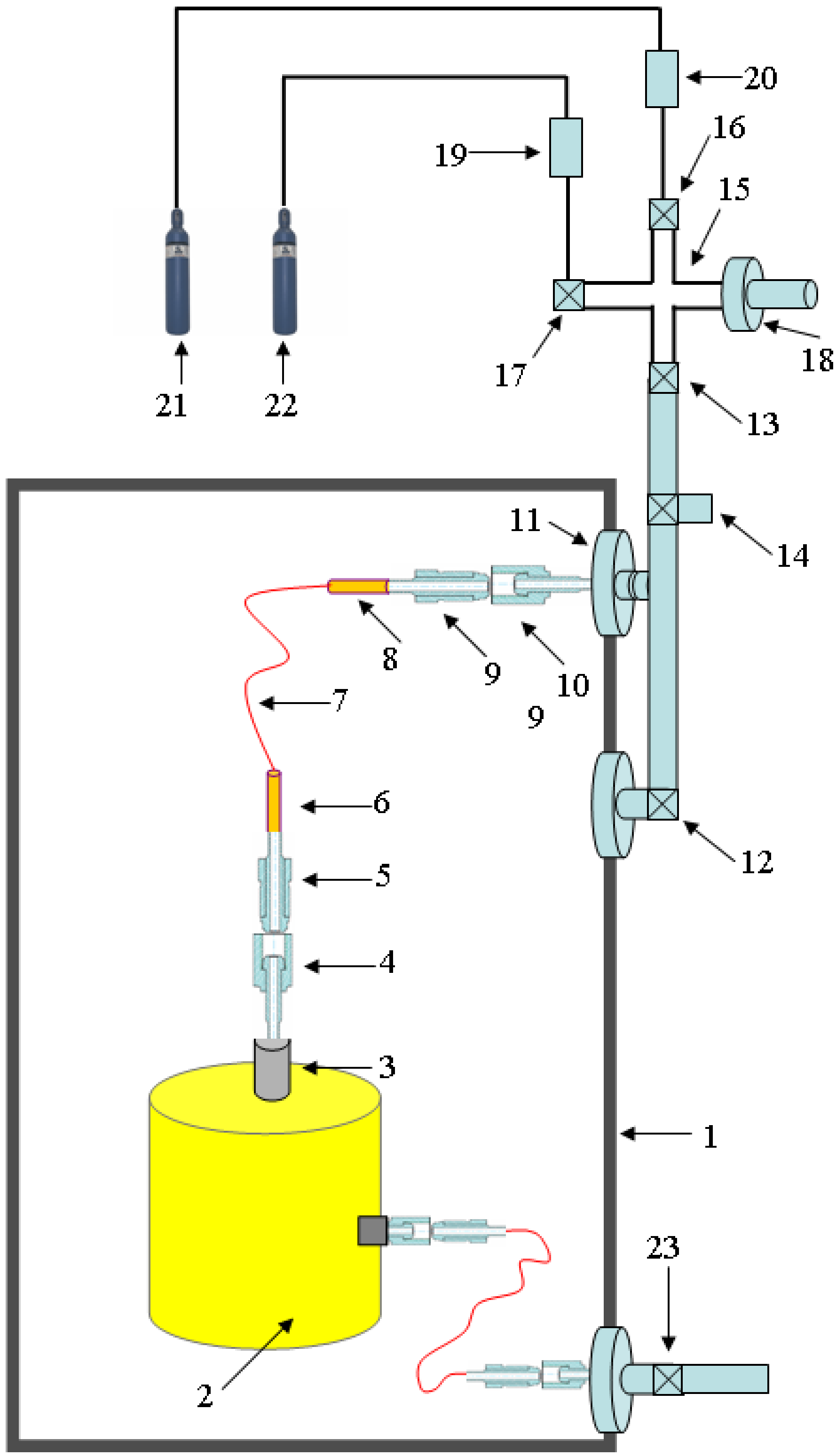
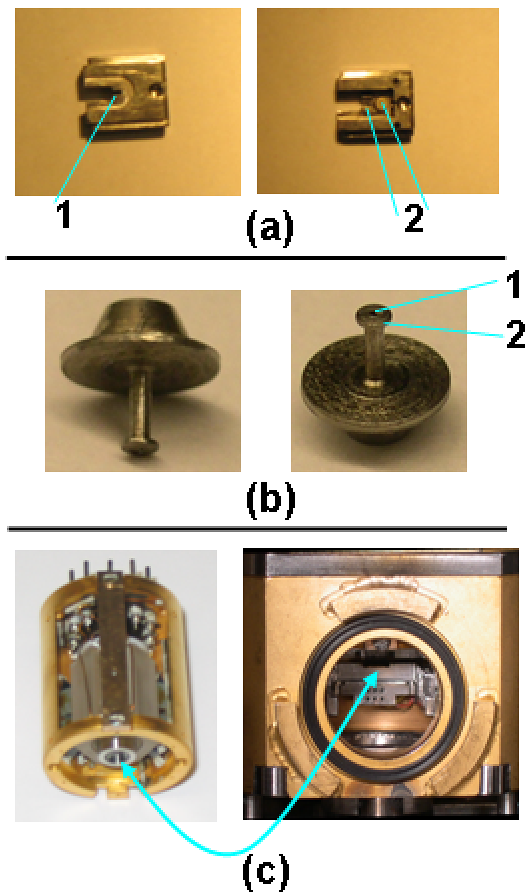
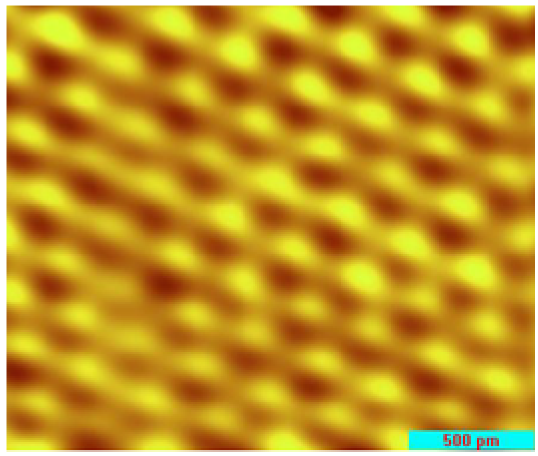
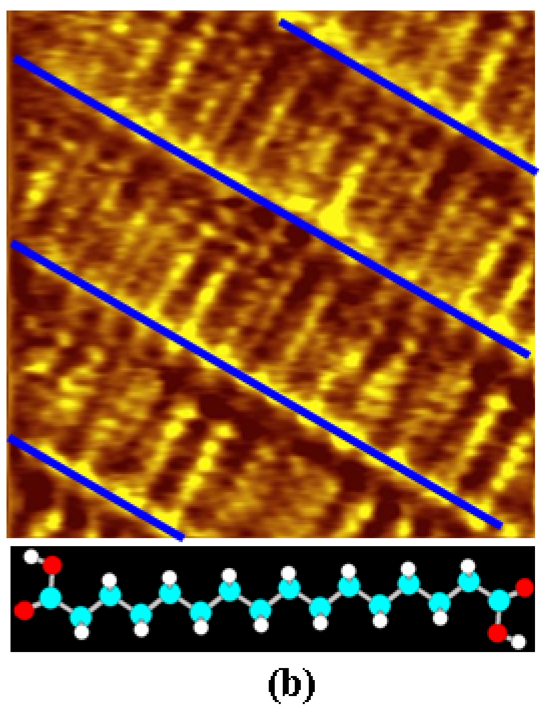


FIG. 5



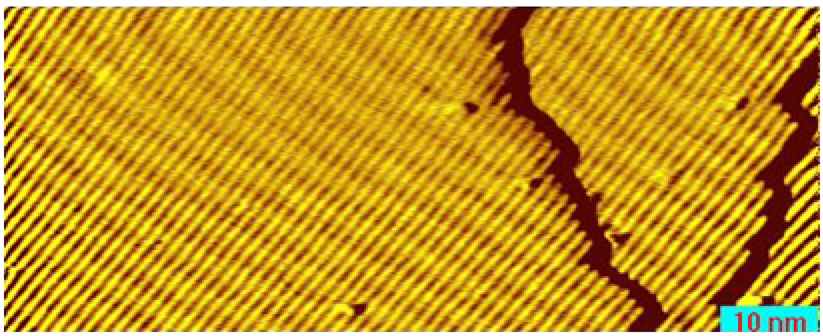


(a)



(b)

FIG. 7



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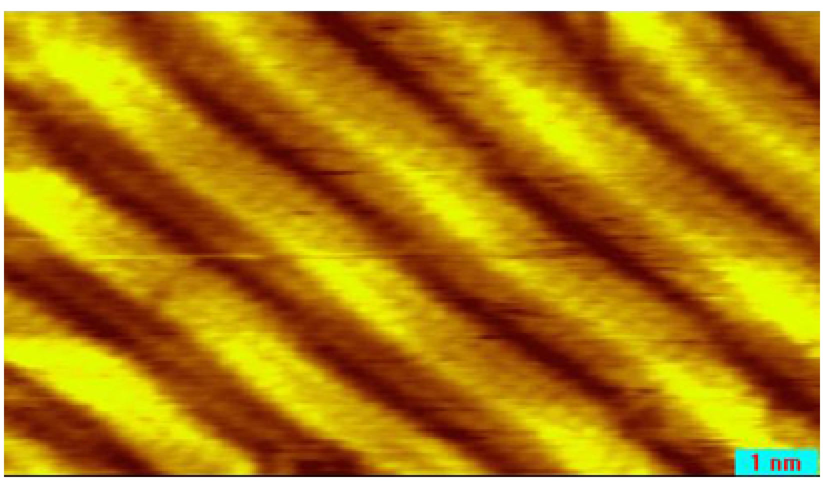

(b)

FIG. 8