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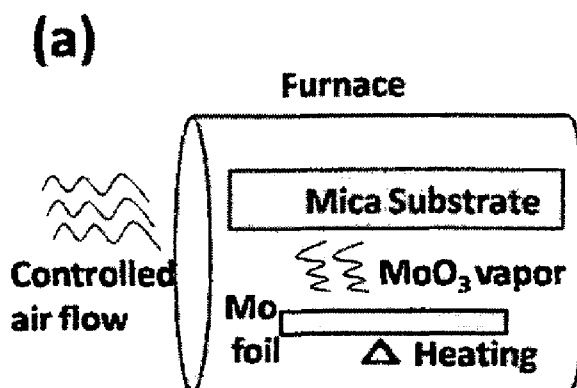
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(54) Title: A MOLYBDENUM OXIDE PHOTOTRANSISTOR AND METHOD OF SYNTHESIS THEREOF



(57) Abstract: A method of synthesizing a molybdenum oxide phototransistor, the method comprising: placing a foil of molybdenum in a furnace; placing a sheet of muscovite ($K(Al_2)(Si_3Al)O_{10}(OH)_2$) at a predetermined distance from the foil of molybdenum in the furnace; controlling airflow into the furnace to provide sufficient oxygen for crystalline growth of potassium-intercalated molybdenum oxide (K_xMoO_3) while maintaining a preset temperature of the furnace for a time period to produce the K_xMoO_3 nanowire; transferring the K_xMoO_3 nanowire onto a substrate; and forming a covering of electrodes on the nanowire to produce the molybdenum oxide phototransistor.

A MOLYBDENUM OXIDE PHOTOTRANSISTOR AND METHOD OF SYNTHESIS THEREOF

FIELD OF THE INVENTION

5 This invention relates to the development of a molybdenum oxide phototransistor and its method of synthesis, in particular, to a potassium-intercalated molybdenum oxide phototransistor.

Throughout the specification, the terms 'nanowire' and 'nanobundle' are used
10 interchangeably to refer to the same structure.

BACKGROUND OF THE INVENTION

Molybdenum oxide and its derivatives have been a subject of increasing research interests due to their broad technological applications, such as electrochromic devices, batteries, photochromic devices, field emission devices, and gas sensors.³⁵⁻⁴⁰ Bulk MoO_3 exhibits a
15 layered structure, which is well suited for intercalation of ionic species, such as Li^+ , to achieve novel physical and chemical properties.^{41,42} The intercalation becomes more facile in nanostructures than in bulk due to the high surface-to-volume ratio of the nanostructures, which provides large contact surface areas for ion insertion, high flexibility, and adequate
20 toughness for accommodating strains induced by ion insertion.⁴³ For small ions (such as Li^+), the self-diffusion method can be utilized to prepare intercalated MoO_3 nanostructures by immersing MoO_3 nanobelts in LiCl solution.⁴⁴ However, the efforts to intercalate large ions such as K^+ into the MoO_3 nanostructure without damaging the integrity of the well-aligned
25 layered structure has essentially never been successful due to the large size of these ions compared to the size of the gap between layers. Indeed, in a MoO_3 thin film, the attempt to intercalate K^+ ions in galvanostatic mode using the standard electrode configuration has failed to maintain the layered structure; instead, transformation from the crystalline structure to an amorphous structure occurred.⁴⁵ Insertion of K^+ ions in the synthesis of bulk potassium
30 molybdenum bronze ($\text{K}_{0.3}\text{MoO}_3$) by electrolytic reduction of potassium molybdate and molybdenum oxide mixtures also gives rise to a substantial structural distortion. The compound becomes infinite sheets consisting of clusters of 10 edge-sharing molybdenum octahedrals linked by corners in the $[010]$ and $[102]$ directions with the adjacent sheets held together by potassium ions.⁴⁶ The structural deformation from the layered structure inevitably leads to undesired physical properties, such as quasi-low-dimensional conductivity,
35 semiconductor–conductor transition, etc.^{47,48} To date, intercalating large cationic species into MoO_3 nanostructures without giving rise to severe structural deformation of the layered MoO_3 structure has remained a great technical challenge.

Photoconductivity is one of the most studied phenomena in nanowires (NWs) mainly due to their large surface to volume ratio, nanosize spatial constraints and quantum confinement. They facilitate the applications of the NWs as photodetectors,^{1,2} photovoltaics,³⁻⁵ optical switches,⁶ and optical interconnects. Among these, phototransistor is one of the basic building blocks for nanoelectronic circuits. Ever since the concept of the phototransistor was first proposed by William Shockley, great attentions have been given to such device due to its much higher sensitivity and lower noise than those of other counterparts.^{7,8} However, previous reported phototransistors either could not achieve saturated output current^{9,10} or the working voltage required is excessively high (>10V) to achieve the saturation.^{11,12} Besides, the relatively slow response rate (ca. 100 Hz) is also an issue restraining the performance of the photoelectric devices.^{9,13-15} On the other hand, metal oxide nanowires form an extremely important class of photoconductors. Molybdenum oxide (MoO₃), a wide-band-gap (3.2eV) *n*-type semiconductor, has been drawing increasingly attention in field emission devices (FED),^{16,17} photodetectors, batteries,^{18,19} catalysts,²⁰ sensors,^{21,22} photochromic and electrochromic materials.^{23,24} Like other metal oxide nanowires, the main applications of MoO₃ in photoelectronics are limited by its wide bandgap. Its low electrical *n*-type conductivity (the resistivity is of the order of 10¹⁰ Ω·m) always inhibits its practical implementation as well.²⁵ Impurity doping is one of the most common way used to modify the electrical properties of the material and one advantage about MoO₃ is its rich intercalation chemistry made possible by its layered structure. However, due to the size limitation of the gap between layers, only small ions, such as lithium has been successfully intercalated through immersing MoO₃ nanostructure in LiCl solution.²⁶

SUMMARY OF INVENTION

The present invention demonstrates the feasibility in intercalating large ions such as potassium without damaging the integrity of the layered structure of MoO₃. A surprisingly simple procedure is developed to synthesize potassium-intercalated MoO₃ nanobundles with the integrity of the layered structure remaining intact. While the material displays semiconductor-like behavior, dramatic enhancement of the electric conductivity from 10⁻⁶ S m⁻¹ of MoO₃ to 24 S m⁻¹ upon potassium uptake was observed. Density functional theory calculations were performed to assist in structural determination and to elucidate the electronic property of the nanobundles. It was found that the K atoms occupy the oxygen vacancy sites in the lattice. The ionization of the K atoms gives rise to the reduction of the adjacent Mo atoms, leading to electron population in the conduction band.

With the intercalation of the foreign atoms, the electron donor level became extremely shallow and the photocurrent response became ultra-sensitive at sub-millisecond level. These effects result in a phototransistive process which gives rise to a very high responsibility and extended response spectral range. On top of this, saturation for the light-intensity gated output current was achievable within 1 volt which makes the device a promising phototransistor. Upon analysis of the charge transport in both negative and positive directions under different temperatures, it was found that the transportation can be separated into a unidirectional, thermal activated part together with the photosensitive part. K-enriched MoO_3 nanowires is thus demonstrated to have potential in nano/micro scaled photoelectric applications.

An ultrasensitive phototransistor was fabricated based on K-intercalated MoO_3 single nanowire. Devices with ultrafast photoresponse rate, high responsivity, and broad spectral response range were demonstrated. Detailed analysis of the charge transport in the device revealed the coexistence of both thermal-activation and photoactivation mechanisms. The promising results are expected to promote the potential of this material in nano/micro-scaled photoelectronic applications.

According to a first aspect, there is provided a method of synthesizing a molybdenum oxide phototransistor, the method comprising: placing a foil of molybdenum in a furnace; placing a sheet of muscovite ($\text{K}(\text{Al}_2)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) at a predetermined distance from the foil of molybdenum in the furnace; controlling airflow into the furnace to provide sufficient oxygen for crystalline growth of potassium-intercalated molybdenum oxide (K_xMoO_3) while maintaining a preset temperature of the furnace for a time period to produce the K_xMoO_3 nanowire; transferring the K_xMoO_3 nanowire onto a substrate; and forming a covering of electrodes on the nanowire to produce the molybdenum oxide phototransistor.

The preset temperature may range from about 300 °C to about 900 °C.

The time period may range from about 10 minutes to about 12 hours.

The predetermined distance may be about 1 mm.

Forming the covering of electrodes may comprise using photolithography to form a design of metal finger electrodes.

The method may further comprise thermal evaporating aluminium to form the metal finger electrodes.

5 The crystalline growth may comprise growth from grain boundaries via thermal evaporation to incorporate K atoms from the muscovite into a MoO_3 lattice.

The crystalline growth may be in a [001] direction.

10 According to a second aspect, there is provided a molybdenum oxide phototransistor comprising: a substrate; a potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire on the substrate; and a covering of electrodes on the nanowire.

The electrodes may be made of aluminium.

15 The molybdenum oxide phototransistor may be synthesized according to the method of the first aspect.

20 The K_xMoO_3 nanowire may have an intact layered structure comprising K atoms incorporated into a MoO_3 lattice.

The molybdenum oxide phototransistor of any one of claims 12 to 15, wherein the substrate comprises a layer of SiO_2 on a layer of Si.

25 For both aspects, the substrate may comprise a layer of SiO_2 on a layer of Si. The substrate may further comprise a dielectric coating of Si_3N_4 .

Alternatively, the substrate may comprise a bendable plastic.

30 According to a third aspect, there is provided a method of synthesizing a potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire, the method comprising: placing a foil of molybdenum in a furnace; placing a sheet of muscovite ($\text{K}(\text{Al}_2)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) at a predetermined distance from the foil of molybdenum in the furnace; controlling airflow into the furnace to provide sufficient oxygen for crystalline growth of potassium-intercalated molybdenum oxide (K_xMoO_3) while maintaining a preset temperature of the furnace for a
35 time period to produce the K_xMoO_3 nanowire.

The preset temperature may range from about 300 °C to about 900 °C.

The time period may range from about 10 minutes to about 12 hours.

The predetermined distance may be about 1 mm.

- 5 The crystalline growth may comprise growth from grain boundaries via thermal evaporation to incorporate K atoms from the muscovite into a MoO_3 lattice.

The crystalline growth may be in a $[001]$ direction.

- 10 According to a fourth aspect, there is provided potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire synthesized according to the method of the third aspect.

BRIEF DESCRIPTION OF FIGURES

- 15 In order that the invention may be fully understood and readily put into practical effect there shall now be described by way of non-limitative example only exemplary embodiments of the present invention, the description being with reference to the accompanying illustrative drawings.

- 20 FIG. 1 (a) is an SEM image of an individual nanowire; upper right inset shows the EDX spectrum of the nanowire and bottom left inset shows the low magnification TEM image;

- FIG. 1 (b) is a Raman spectra of a K-intercalated MoO_3 nanowire (grey curve) and pure MoO_3 nanobelt (black curve);

- 25 FIG. 1 (c) is an SAED pattern of K_xMoO_3 on a (010) surface;

FIG. 1 (d) is an SEM image of an individual nanowire device;

- 30 FIG. 2 (a) is a typical $I_{\text{DS}}-V_{\text{DS}}$ curve of a single nanowire device in dark field, insets show a schematic symbol of potential applications (diode and phototransistor);

FIG. 2 (b) is an EDX spectra measured at three different spots along a nanowire growth direction;

- 35 FIG. 2 (c) is a typical $I_{\text{DS}}-V_{\text{DS}}$ curve (curve labeled as 1 mW/cm^2) of a single nanowire device in white light illumination, inset is a close up of the dark field curve in $V_{\text{DS}} \leq 0$ region;

FIG. 2 (d) is a graph of output current plotted as a function of light power intensity;

FIG. 2 (e) is a graph of I_{DS} - V_{DS} characteristics of a device under different power illumination at a $V_{DS} \leq 0$ region;

FIG. 2 (f) is a close up of characteristics at a region of $-4.5V \leq V_{DS} \leq 0$;

FIG. 2 (g) is a graph of I_{DS} - V_{DS} characteristics of a device under different power illumination at a $V_{DS} \geq 0$ region;

FIG. 2 (h) is a close up of characteristics at a region of $0 \leq V_{DS} \leq 4.5V$;

FIG. 3 is a schematic illustration of components of an entire output characteristic of a device;

FIG. 4 (a) is a graph of low temperature dependence of output current, $V_{DS} = 2, 3, 4$ V, respectively, inset is a relationship between $\ln(I_{DS})$ and temperature;

FIG. 4 (b) is a graph of typical I_{DS} - V_{DS} characteristics of a device at different temperatures;

FIG. 5 (a) is a graph of photoresponse characteristics of a $K_x\text{MoO}_3$ phototransistor at different optical powers;

FIG. 5 (b) is a graph of photoswitching rate test of the $K_x\text{MoO}_3$ phototransistor mentioned in FIG. 5(a);

FIG. 5 (c) is a graph showing that the $K_x\text{MoO}_3$ phototransistor mentioned in FIG. 5(a) is able to respond to all light wavelengths from 488nm to 1100 nm;

FIG. 5 (d) is a graph of I_{DS} -Time of the $K_x\text{MoO}_3$ phototransistor mentioned in FIG. 5(a) showing consistent device performance;

FIG. 6 (a) is a schematic representation of a synthesis system;

FIG. 6 (b) shows a typical morphology of a single $K_x\text{MoO}_3$ nanobundle, inset image is a close up of the right end of the $K_x\text{MoO}_3$ nanobundle;

FIG. 6. (c) is an electron diffraction pattern of a MoO_3 microbelt on a (010) surface; the highlighted rectangle denotes the orthorhombic lattice structure, the inset image shows a SEM image of a typical MoO_3 microbelt growing in a [001] direction;

FIG. 6 (d) is an electron diffraction pattern of a $K_x\text{MoO}_3$ nanobundle on a (010) surface; the highlighted rectangle formed by large bright spots represents a lattice structure of the K-intercalated MoO_3 , inset image shows a TEM image of a typical $K_x\text{MoO}_3$ nanobundle growing in a [001] direction;

FIG. 7 shows XRD patterns of a mica substrate with MoO_3 microbelts (upper chart) and a mica substrate with both MoO_3 microbelts and $K_x\text{MoO}_3$ nanobundles (lower chart), label peaks with M are muscovite peaks while label peaks without notation are MoO_3 peaks, the three peaks that are labeled with asterisks denote a layered structure of $K_x\text{MoO}_3$ correspond to expand along (020), (040), and (060), the rest of the peaks could be attributed to other faces of $K_x\text{MoO}_3$;

FIG. 8 (a) is a schematic illustration of optimized structure of pure MoO_3 ;

FIG. 8 (b) is a schematic illustration of optimized structure of pure MoO_3 with K as intercalants;

FIG. 8 (c) is a schematic illustration of optimized structure of pure MoO_3 with K as occupants;
 FIG. 8 (d) is a schematic illustration of optimized structure of a mixed case, where the pink
 (lower) and green (upper) balls represent intercalants and occupants, respectively;
 FIG. 9 is an I–V curve of individual K_xMoO_3 nanobundle in different temperatures, the inset
 5 figures show schematic view and SEM image of K_xMoO_3 nanobundle contacted by
 electrodes;
 FIG. 10 is an XPS spectrum of Mo-3d peaks in K_xMoO_3 nanobundle;
 FIG. 11 is a graph of calculated band structure and density of states (DOS) of K_xMoO_3 ;
 FIG. 12 is a schematic illustration of an ultrasensitive phototransistor fabricated based on K-
 10 intercalated MoO_3 single nanowire;
 FIG. 13 (a) and (b) show similar results for a device alternatively made on a substrate of
 PET;
 FIG. 14 is a spectrum of a light source;
 FIG. 15a is a typical IDS–VDS curve of a representative single nanowire device in white light
 15 illumination;
 FIG. 15b is the photoresponse characteristics of the device of FIG. 15a;
 FIG. 16 is long time trace of the photoresponse of the device of FIG. 15a;
 FIG. 17 shows the photoresponse characteristics of the device of FIG. 15a under different
 filters with wavelengths selected centred at (a) 488 nm, (b) 500 nm, (c) 514 nm, (d)
 20 532 nm, (e) 550 nm, (f) 570 nm, (g) 600 nm, (h) 633 nm with light power density
 kept at $2.1 \times 10^{-2} \text{ mW/cm}^2$ after employing the filters;
 FIG. 17i shows photocurrent as a function of wavelength; and
 FIG. 18 shows the photoresponse of the device of FIG. 15a under (a) 325 nm, (b) 532 nm, (c)
 808 nm, and (d) 1064 nm laser illumination with the same power density of
 25 $1.3 \times 10^2 \text{ mW/cm}^2$.

DETAILED DESCRIPTION

Exemplary embodiments of the invention will be described with reference to FIGS. 1 to 18 below.

30 Synthesis of K-intercalated MoO_3 nanowire employed a simple and facile one-step vapor deposition method. Briefly, a piece of molybdenum foil was cleaned and loaded into the center of a horizontal tube furnace. A muscovite mica sheet ($\text{K}(\text{Al}_2)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$) was placed on the top of the molybdenum foil with a gap of ca. 1 mm. The mica sheet not only
 35 acted as the substrate, it also provided the source of potassium. The system was ramped to 600 °C and dwelled for 6 hours with controlled air flow into the chamber. Mo was evaporated from the surface of the foil and oxidized in air flow. At the the substrate surface, the oxidized

Mo vapor reacted with potassium squeezed out from the edges and grain boundaries found on the mica and then intercalated into the growing MoO₃ nanowire simultaneously to form the quasi-one-dimensional nanostructure. After synthesis, the nanowire was transferred to a piece of silicon and the morphology of the product was identified by scanning electron microscopy (SEM).

A typical SEM image of a single nanowire is shown in FIG. 1a. The nanowire displays a needle-like shape with the diameter reduces slightly along the growth direction from the bottom (upper left of FIG. 1a) to the top (lower right of FIG. 1a), the measured average diameter is about 800 nm with the length can be more than 200 μ m. Energy-dispersive spectroscopy (EDX) was carried out on a randomly selected spot of the nanowire and the representative spectrum is as shown in the insert of FIG. 1a. The potassium peaks are clearly demonstrated, which indicates that K atoms have been intercalated into MoO₃ successfully. We denoted the K-intercalated MoO₃ nanowire as K_xMoO₃. The ratio of K/Mo revealed by the EDX spectrum is 23:77. A diode laser (centered at 532 nm) was employed as the excitation source for the micro-Raman (Renishaw inVia) characterization. The Raman spectra of pure MoO₃ (black line) and K_xMoO₃ nanowire (red line) are shown in FIG. 1b. Evidently, the Raman shift of these two spectra are completely different, which demonstrates the modification of the chemical bonds and lattice vibrations by potassium intercalation.²⁷ These characterization results are highly suggestive of a diversification in electrical properties of K_xMoO₃ compared with pure MoO₃.

Transmission electron microscopy (TEM) was carried out to further investigate the crystalline lattice. Inset of FIG. 1a illustrates a low magnification TEM image of a single wire, and the corresponding selected area electron diffraction (SAED) pattern of K_xMoO₃ on the (010) surface is displayed in FIG. 1c. Amazingly, a complicated but clear diffraction pattern was exhibited. A typical rectangular pattern consist of large bright spots is clearly shown with five weaker spots evenly distributed between two bright spots along one direction. Through calculation, the bright spots indicate an orthorhombic configuration with the calculated lattice constants of $a = 0.37 \text{ nm}$ and $c = 0.40 \text{ nm}$. The [001] direction is considered as the growth direction of K_xMoO₃ nanowire. The values are similar with our privously reported data of pure MoO₃ nanobelts²⁸ except that a value shrinks by about 0.02 nm while c expands by about 0.03 nm compared with the K_xMoO₃ nanowire, which is attributed to the intercalation of potassium along [100] direction. Considering the valence of potassium and molybdenum, 6 K⁺ ions exchanging with one Mo⁶⁺ ion from mica to nanowires can sustain the right chemical stoichiometry, which gives rise to the observed superstructure.

Using the surprisingly simple procedure to prepare a stable K intercalated MoO_3 nanostructure with a well-aligned lattice structure according to the thermal evaporation method outlined above, the material prepared was found to be semiconducting with substantially higher electric conductivity among the MoO_3 intercalation compounds that have been made. Density functional theory (DFT) under the generalized gradient approximation (GGA) was utilized to understand the morphology and the electronic structure of the nanomaterials and to explain the semiconductor behavior observed in our experiments.

A synthesis scheme for the K-intercalated MoO_3 nanostructure used in the present study is shown in FIG. 6a. Details of the preparation are as follows: a Mo foil was placed in a ceramic boat as the Mo source in a tube furnace and a muscovite mica sheet $\text{K}(\text{Al}_2)(\text{Si}_3\text{Al})\text{O}_{10}(\text{OH})_2$ was placed 1 mm on top of the Mo foil to provide the source of K. The system was heated for 6 h in ambient at 600 °C with controlled air flow. Mo was evaporated from the foil and oxidized in the air flow. Although the original intention was to study how the morphology and alignment of MoO_3 microbelts change with substrate properties, it was surprisingly found that the subsequent deposition of the oxidized Mo on the substrate yielded two distinctively different types of products, depending on where the substances start to grow. The first type of material grows out from the flat surface of the mica substrate as large sized microbelts with a width of 3–5 μm , a length of 10–15 μm , and a thickness of 1 μm . These microbelts were found to be the dominate product, as expected. However, at the grain boundaries of the mica substrate, growth of a new type of nanobundle with length around 200 μm extending out of the substrate was observed. Since the nanobundles were firmly attached to the substrate, only a segment of a nanobundle was transferred to Si substrate as shown in FIG. 6b with the length, width, and thickness of 87, 0.9, and 0.5 μm , respectively. The inset, which displays the enlarged image of the right end of the nanobundle, indicates that the nanobundle is constructed by several parallel nanobelts. These nanobelts are of the same length as the nanobundle but much thinner with a width and a thickness of approximately 300 and 150 nm, respectively. The EDX spectrum elemental analysis on the two types of products reveals that the microbelts consist of pure MoO_3 and the nanobundles contain a significant percentage of potassium atoms (denoted as K_xMoO_3). Remarkably, the K:Mo ratio in the K_xMoO_3 complex is fixed in the same nanobundle but differs slightly between different nanobundles with x ranging from 0.20 to 0.25. The atomic ratio of O over Mo in the K_xMoO_3 nanobundles is roughly 2.6 ± 0.2 , which is lower than the value in stoichiometric MoO_3 compound, implying that O vacancies may exist. Obviously, the grain boundaries in the mica layers allow the K atoms to be extracted to participate in the nanobundle growth.

The surprisingly simple procedure for the synthesis of $K_x\text{MoO}_3$ nanobundles provides a highly effective approach to intercalate large ions into layered nanostructures. The MoO_3 microbelts and $K_x\text{MoO}_3$ nanobundles were subsequently removed from the substrate and transferred to the TEM grids for further characterization. The selected area electron diffraction (SAED) pattern of the MoO_3 microbelts on the (010) surface orientation is shown in FIG. 6c, and the inset image shows the SEM image of the MoO_3 microbelts along the [001] growth direction. The microbelts exhibit a typical rectangular diffraction pattern on the (010) surface with a lattice adopting an orthorhombic configuration, similar to bulk MoO_3 . The SAED pattern of the $K_x\text{MoO}_3$ nanobundles on the (010) surface is shown in FIG. 6d with the inset image displaying a low-magnification TEM image of the nanobundles along the [001] growth direction. The highlighted yellow rectangular diffraction pattern formed by large bright spots represents K-intercalated MoO_3 structure on the (010) surface. Between two bright spots there are five weaker, evenly distributed spots along the [100] direction of the $K_x\text{MoO}_3$ nanobundles. These smaller diffraction spots suggest that $K_x\text{MoO}_3$ nanobundles possess a periodic superstructure with six primitive cells along the [100] direction. Elemental analysis on the mica grain boundaries upon the product removal indicates that Mo–K exchange occurs during the nanobundle growth. Although the precise exchange rate could not be determined, the fact that one Mo^{6+} ion substitutes six K^+ ions to sustain the right stoichiometry of the substrate can give rise to the observed superstructure upon the uptake of the K atoms from mica in the growth of the nanobundles. During the growth, Mo is oxidized on Mo foil and vaporizes upward to react with surface of mica to form liquid islands of $K_x\text{MoO}_3$. The continuous absorption of K^+ from mica substrate and MoO_3 vapor promotes the growth of $K_x\text{MoO}_3$ nanobundles out of these liquid islands. With the K ions in the nanobundle lattice originated from the mica substrate, the bottom-up growth process forces the nanobundles to grow with a specific orientation. Indeed, compared to the growth pattern of the MoO_3 microbelts, the growth of $K_x\text{MoO}_3$ nanobundles displays a strong orientational preference. The length of the nanobundles can grow as long as 200–300 μm with a width of roughly 700–900 nm.

Because of the relatively larger size of nanobundle width than thickness, the transferred nanobundles were placed on the TEM grid with the [010] direction perpendicular to the grid. Although the grid could be made to tilt by 15° , a clear diffraction pattern that contains information along the [010] direction could not be found. Instead, X-ray diffraction was utilized to further resolve the structure of the $K_x\text{MoO}_3$ nanobundles. Two pieces of mica substrate were used to produce materials at different temperatures for XRD analysis. During the growth, mica substrate A was heated at 500 $^\circ\text{C}$ while mica substrate B was heated at 600 $^\circ\text{C}$. The temperature required to grow $K_x\text{MoO}_3$ nanobundles should be above 600 $^\circ\text{C}$. As

a result, only MoO_3 microbelts were produced on substrate A while both MoO_3 microbelts and K_xMoO_3 nanobundles were observed on substrate B. The upper chart and lower chart in FIG. 7 are the XRD spectra of substrate A and B, respectively. New peaks highlighted by asterisks next to (020), (040), and (060) structures of MoO_3 shown in FIG. 7 arise from the K_xMoO_3 nanobundles. Compared with these three peaks of MoO_3 , the left shifted peaks of K_xMoO_3 nanobundles suggest the expansion of lattice constant b upon K intercalation. On the basis of the TEM diffraction pattern and the XRD analysis, the lattice constants of the MoO_3 microbelts and the K_xMoO_3 nanobundles were derived (Table 1).

		a (Å)	b (Å)	c (Å)
MoO_3	exp	4.01	13.87	3.69
	calc	3.91	13.76	3.71
	rep ⁴⁹	3.96	13.86	3.70
K_xMoO_3	exp	3.69–3.72	14.16	3.97–4.05
	calc ^a	3.82	14.89	3.81
	b	3.73	14.25	3.86
	c	3.8	14.56	3.81

^aK as intercalants. ^bK as occupants. ^cMixed (half intercalants and half occupants).

Table 1. Measured and Calculated Lattice Constants of the MoO_3 Microbelt and the K_xMoO_3 Nanobundle

It was noted that the lattice constants obtained for the MoO_3 microbelts agree well with the reported values of the bulk MoO_3 .⁵⁰ For the K_xMoO_3 nanobundles, considerable lattice relaxation upon the K uptake with shifts of the lattice atoms was observed. The a-axis shrinks by roughly 0.3 Å, while both the b- and c-axes expand by ~0.3 Å. As the K content in the lattice increases, the atomic percentage ratio of K over Mo increases from 0.20 to 0.25 and the lattice constant a decreases further from 3.72 to 3.69 Å while the cell parameter c increases from 3.97 to 4.05 Å. It was noted in particular that the lattice constant b reported in Table 1 in the experiments is the value derived using the apex of the peaks in XRD spectrum from the most abundant nanobundles. The XRD spectrum of the K_xMoO_3 nanobundles clearly indicates that the complex preserves a layered structure as evidenced by the significant peaks located at (020), (040), and (060). This is distinctively different from the XRD analysis reported by Sian et al.,⁴⁵ in which the intensity of all the peaks associated with MoO_3 was reduced with the increase of the K contents and, in particular, all peaks vanished

upon x reaching 0.3, indicating the complete loss of the initially layered structure. The participation of the K atoms from mica in the MoO_3 nanobundle formation is anticipated to take three possible forms: as intercalants between MoO_3 layers or as occupants at the oxygen vacancy sites in the lattice or, possibly, as both. Unfortunately, with the experimental techniques currently available, it was not possible to resolve definitively the specific forms of the K atoms in the lattice and the atomic coordinates in the unit cells.

To interpret the experimental results, functional theory calculations were performed to understand the structures and properties of the pure and K-intercalated MoO_3 materials. Compared with the size of atoms, the thicknesses and widths of the MoO_3 microbelts and the K_xMoO_3 nanobundles are several orders of magnitude larger. Therefore, it is justified to model these nanomaterials with 3-dimensional periodic bulklike structures, assuming that the edge effects on structures and physical properties are insignificant. A $2 \times 1 \times 2$ supercell of the MoO_3 primitive lattice containing 16 Mo atoms and 48 O atoms (FIG. 8a) was first selected to model the MoO_3 microbelts. The fully optimized lattice structure of the MoO_3 supercell, shown in Table 1, is in excellent agreement with the reported experimental XRD data,⁴⁹ suggesting that the present computational method is reliable for structural predictions for the type of materials dealt with here.

Subsequently, various scenarios were explored with K atoms acting as intercalants, as lattice occupants at oxygen vacancies or as both in the supercell for $x = 0.25$. In the case of K intercalation, the K atoms were placed in between the MoO_3 layers. To model the O vacancies in the lattice, one dangling O atom was removed between the layers for each K atom introduced. For K atoms acting as both intercalants and occupants, two terminal O atoms were substituted with K atoms and two K atoms were placed as intercalants in the supercell. In all cases, various K distribution configurations were calculated and, upon full lattice optimization, the lowest energy configurations were obtained. The optimized structures and the cell parameters are shown in FIG. 8 and Table 1, respectively. Clearly, only in the case where the K atoms act as occupants the calculated cell parameters are in good agreement with the experimental data. In the other two scenarios K-uptake in the lattice results in significantly higher lattice expansion than what is observed experimentally. Furthermore, the calculated average cohesive energies of -7.94 eV (occupants), -7.80 eV (intercalants), and -7.88 eV (mixed) indicate that the K occupation at the oxygen vacancy sites is indeed energetically preferred. This is also consistent with the experimental fact that the atomic ratio of O over Mo in the K_xMoO_3 nanobundle is lower than the stoichiometric value due to the existence of O vacancies. It was found in all cases that the K uptake in the lattice forces the lattice to undergo significant relaxations as clearly visible in FIG. 8.

Next, a single nanobundle fabricated device, schematically depicted in the upper inset panel of FIG. 9, was used to measure the I–V curves of the $K_x\text{MoO}_3$ nanobundle. As can be seen, the device comprises a nanobundle on a substrate. In this example, the substrate comprises a layer of SiO_2 on a layer of Si. The lower inset panel of FIG. 9 displays the SEM image of an individual $K_x\text{MoO}_3$ nanobundle contacted by electrodes. For the MoO_3 microbelt, the measured current is on the order of ca. 1 pA at ca. 5 V. From the measured effective length and cross section of this material, the electric conductivity of the MoO_3 microbelt was estimated to be about 10^{-6} S m^{-1} , consistent with the reported value of the MoO_3 nanobelts.⁴⁴ For the $K_x\text{MoO}_3$ nanobundles, at room temperature, the measured current is 6.64 μA at a bias of 5 V and the I–V curve displays typical semiconductor-like behavior. Further field-effect transistor (FET) measurement shows the $K_x\text{MoO}_3$ nanobundles exhibit n-type semiconductor behavior. It is remarkable that the electric conductivity is enhanced substantially by 7 orders of magnitude from 10^{-6} S m^{-1} of the MoO_3 microbelts to 24 S m^{-1} . The magnitude is also 3 orders higher than that of the lithiated MoO_3 bulk ($\text{Li}_{0.25}\text{MoO}_3$, $3.1 \times 10^{-2} \text{ S m}^{-1}$)⁴² and 5 orders higher than that of lithiated MoO_3 nanobelt (10^{-4} S m^{-1}).⁴⁴ The conductivity of the $K_x\text{MoO}_3$ nanobundles increases rapidly upon heating as shown in FIG. 9. At the bias of 5 V, the current increases from 6.64 μA to 0.15 mA as the temperature increases from 23 to 142 °C, raising the conductivity from 24 to 530 S m^{-1} . The thermal enhanced conductivity indicates a very small band gap of the nanobundles.

To understand the significantly enhanced conductivity of $K_x\text{MoO}_3$ nanobundle, Bader charge analysis was performed and the band structure of the $K_x\text{MoO}_3$ nanobundles was calculated in which K atoms act as occupants at oxygen vacancies. It was found that significant charge transfer in the lattice occurs with the K atoms largely ionized. This results in the reduction of the adjacent Mo atoms. To confirm the prediction, an XPS experiment was performed to measure the valence variation of the Mo atoms in the nanobundle upon K intercalation using the transferred $K_x\text{MoO}_3$ nanobundles. In FIG. 10, the black curve shows the measured XPS spectra of the $K_x\text{MoO}_3$ nanobundle. The grey curve was fitted by Mo^{6+} peaks (blue peaks 235.9 eV (Mo 3d 3/2) and 232.7 eV (Mo 3d 5/2)) and Mo^{5+} peaks (green peaks 235.1 eV (Mo 3d 3/2) and 232.0 eV (Mo 3d 5/2)).⁵⁰ The area ratio of Mo^{5+} over Mo^{6+} is around 1.5, suggesting that the valence of Mo is roughly +5.4. The result indicates that the Mo atoms are indeed partially reduced upon K insertion, consistent with the theoretical population analysis.

The electronic structure of MoO_3 is well understood, and the compound is an n-type semiconductor with a band gap of 3.3 eV.⁵¹ The valence band is largely dominated by the 2p orbitals of oxygen, while the conduction band consists of chiefly the 4d states of molybdenum with a significant contribution from the 2p states of oxygen.⁵² Upon potassium

uptake in the lattice, however, the electronic structure undergoes a substantial change due to the charge transfer from potassium to molybdenum, which forces electrons to populate the conduction band. This is clearly seen in the calculated band structure of the $K_x\text{MoO}_3$ lattice depicted in FIG. 11. The projected density of states (PDOS) for the K-4s and Mo-4d states indicates that the electrons from the K atoms are fully transferred to the adjacent Mo atoms. Because of the strong overlap between the Mo-4d orbitals and the O-2p orbitals in the conduction band, in which the transferred electrons are populated and readily delocalized, the electric conductivity is thus significantly enhanced. Therefore, the conductivity enhancement arises solely from the reduced Mo atoms, which are aligned in the [001] direction as highlighted in FIG. 8. Electric conductivity along these rows thus reaches its maximum. Indeed, the calculated band structure displays wide bands across the Fermi level from $G \rightarrow B$ and $Q \rightarrow F$. The energy bands in other directions, particularly those along the [010] direction, are much narrower due to the high oxidation states of the Mo atoms away from the K atoms. Compared with Li, the ionization potential of K is much lower, and thus the adjacent Mo is more readily reduced. This explains nicely the much higher observed electric conductivity of $K_x\text{MoO}_3$ than that of Li_xMoO_3 . It was further noted that the $K_x\text{MoO}_3$ nanobundle crystalline grows along the [001] direction, in which the voltage is also applied in our I-V curve measurement. From the calculated band structure of $K_{0.25}\text{MoO}_{2.75}$, electric conductivity along the rows highlighted in FIG. 8 is the highest. However, even in the [001] direction, the rows in which the Mo atoms remain in the high oxidation states are still semiconducting due to lack of electron occupation in the conduction band. It therefore requires energy to shift electrons from the valence band to the conduction band to gain good conductivity. This explains the semiconductor-like behavior of the nanobundles observed in our I-V curve measurement and is consistent with the fact that the conductivity jumps 30 times higher simply by raising the temperature from 25 to 100 °C.

In summary, there is now devised a simple but effective technique to grow K-intercalated MoO_3 nanobundles with the layered structure remaining essentially intact for the first time. The growth of nanobundles adopts a bottom-up model starting from the grain boundaries via thermal evaporation to incorporate K atoms into the MoO_3 lattice, forcing the lattice to expand modestly. Using a single nanobundle fabricated device, the I-V curves of the $K_x\text{MoO}_3$ nanobundles were measured. It was found that the complex displays substantially higher electric conductivity than the lithiated MoO_3 nanostructures and the conductivity increases significantly with temperature. Density functional theory was used to assist the $K_x\text{MoO}_3$ structural determination and to understand the semiconductor-like behavior of the material. Our results suggest that the K atoms in the nanobundles most likely occupy the O vacancy sites, leading to considerable lattice relaxation due to the large size of potassium.

This structural arrangement allows the K atoms to be intercalated without incurring large distortion of the MoO_3 layered structure. The calculated band structure of the $\text{K}_{0.25}\text{MoO}_{2.75}$ indicates the K atoms are fully ionized, giving rise to the reduction of the adjacent Mo atoms. As a consequence, the conduction band is populated, leading to electron delocalization along the rows containing low oxidation state Mo atoms in the [001] direction. The results are consistent with the measured high conductivity of the nanobundles and the observed variation of the conductivity with temperature. The novel properties of the K-enriched MoO_3 nanobundles are envisaged to significantly enhance the performance of the electronic devices using compounds in the metal-intercalated MoO_3 family, and the simple preparation method opens a new opportunity to develop patterned nanostructured materials of large-ion-intercalated metal oxides.

EXPERIMENTAL SECTION

Sample Synthesis.

K_xMoO_3 nanobundles were synthesized by thermal evaporation method. A Mo foil (5 mm × 5 mm × 0.05 mm in size, from Aldrich Chemical Co., Inc.) was used as the Mo source and placed in ceramic boat, and a muscovite mica sheet ($\text{K}_2\text{O} \cdot 3\text{Al}_2\text{O}_3 \cdot 6\text{SiO}_2 \cdot 2\text{H}_2\text{O}$, 8 mm × 8 mm in size, from Alfa Aesar Co., Inc.) was placed 1 mm on top of the Mo foil as substrate and K source. The ceramic boat containing Mo foil and mica sheet was inserted into furnace (Carbolite MTF 12/25/250). The system was heated for 6 h in ambient at 600 °C, and a fan was used to blow fresh air into the furnace to provide enough oxygen for the growth.

Morphology and Crystalline Characterizations

The nanobundles were characterized by a scanning electron microscope (SEM, JEOL JSM-6700F), a transmission electron microscope (TEM, JEOL JEM-2010F) with built-in energydispersive spectroscopy (EDS), and X-ray diffraction (XRD, Philips X'Pert).

Electrode Fabrication

The single nanobundle device mentioned above was fabricated by transferring individual nanobundles from the growth substrate to SiO_2/Si substrate and utilizing a photolithography method to achieve designed metal ($\text{Au}(500 \text{ nm})/\text{Cr}(10 \text{ nm})$) finger electrodes (of gap $\sim 10 \mu\text{m}$) covering on nanobundle. The electrical measurements were carried out using Keithley 6430 source-measure unit.

Simulation Method

All simulations were carried out using the Perdew–Burke–Ernzerhof (PBE) exchange-correlation functional under the generalized gradient approximation as implemented in the Vienna Ab-initio Simulation Package (VASP). The projector augmented wave (PAW) method was used to describe the core electrons of the atoms, and the valence orbitals were represented with a plane wave basis set with a cutoff energy of 450.0 eV. All calculations were performed using a spin-polarization scheme. The Brillouin zone integration was performed using a $4 \times 2 \times 4$ Monkhorst–Pack k-point mesh. For calculations of the band structure (BS) and density of states (DOS), the k-points mesh was doubled. The conjugate gradient algorithm was selected to optimize both the ion positions and the lattice parameters with no constraint. The energy and SCF convergence threshold was set to be 5.0×10^{-5} and 1.0×10^{-5} eV, respectively.

Device fabrication

A single $K_x\text{MoO}_3$ nanowire was transferred to a silicon substrate coated with a 200 nm thick Si_3N_4 dielectric for device fabrication and subsequent electrical characterization. A UV-laser lithography system (Heidelberg Instruments μPG101) was employed to develop the device architecture. The fabrication was completed by thermal evaporating aluminum as the source-drain electrodes.

The SEM image of an individual nanowire device with four electrodes is shown in FIG. 1d. Both the electrode width and the separation between two electrodes are designed to be 10 μm . The typical $I_{\text{DS}}\text{-}V_{\text{DS}}$ curve is displayed in FIG. 2a, with V_{DS} ramping from -10V to 10V. The blue curve indicates the dark current which was carried out without any light illumination. Different from common semiconductors, the output current of $K_x\text{MoO}_3$ nanowire exhibited an obvious unidirectional property. The current is minimal with the rising reverse bias while at forward range, output current increased dramatically with the voltage and almost a linear relationship was shown in the high voltage region. This curve is a typical I-V characteristic curve of a diode. The equivalent circuit is diagramed in the top inset of FIG. 2a, which indicates the current is only allowed to flow from positive to negative electrode. The turn-on voltage (beyond which, the output current displays a significant positive value) of $K_x\text{MoO}_3$ nanowire diode is measured as $V_{\text{d(on)}} = 0.4$ V, which is even lower than that of silicon diode ($V_{\text{d(on)}} = 0.5\sim 0.6$ V). The unidirection of the output characteristic implies the existence of intrinsic barrier in the nanowire device. Further investigation through systematical EDX spectra along the $K_x\text{MoO}_3$ nanowire growth direction was carried out. And as labeled in FIG. 1d, three representative spots were selected and the corresponding EDX results are shown in FIG. 2b. Evidently, from bottom to top spot along the wire growth direction, the potassium concentration decreases gradually (from Mo:K=75:25 to Mo:K=81:19). Therefore, the

formation of intrinsic barrier is attributed to the nonuniform distribution of K composition which favors the unidirectional fluxion of the electrons and inhibits the reverse channel. This property demonstrates the great potential of $K_x\text{MoO}_3$ nanowire as a intrinsic barrier diode for nanoscale electronics application.

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Besides the diode property, $K_x\text{MoO}_3$ nanowire also exhibits high sensitivity to light, even under weak light intensity. A halogen lamp with the main spectrum ranging from 400-1100 nm (the spectrum of the lamp was captured using a spectrometer and result is shown in FIG. 14) was employed as white light to study the photo-response of the nanowire device during I-V measurement. The pink curve shown in FIG. 2c displays the typical $I_{\text{DS}}-V_{\text{DS}}$ curve under 1 mW/cm^2 of broad beam white light illumination. Obviously, the output current increased sharply beyond 4 V (-4V for backward) and subsequently reached saturation before 5 V for both voltage direction. The current saturation is attributed to the higher density of states in the conduction band than that of the excited electron. The rapid increase and saturation of the photo-related current suggests the potential of $K_x\text{MoO}_3$ nanowire as a ultrasensitive phototransistor. In FIG. 2d, the current magnitude as a function of white light power was also recorded, in which case, the voltage was kept at -10 V (black square) and 10 V (red circle) respectively. The output current increased dramatically with the light power rising, and a linear relationship is shown. The larger values of current at 10 V were caused by the original dark current at positive voltage region. This typical illumination characteristic curve demonstrates the good performance of $K_x\text{MoO}_3$ single nanowire phototransistor.

Phototransistors are built on photo-related free carriers under illumination. Hence, two working mechanisms may occur in this phototransistor device. One is photovoltaic effect which depends on the light absorption, exciton dissociation, electron and hole diffusion and electrode collections.⁹ The other possible mechanism is photoconductive effect which results in a huge increase of carrier density in the nanowire ($\sigma = nq\mu$, where σ is the conductivity, μ is the carrier mobility of the material, n is the carrier density and q is the charge of electron). Refer to the present system, no photovoltage was observed in the device despite a large photocurrent was formed. Hence the photoconductive effect is more significant and can be described by^{14,29}

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$$I_{pc} = (q\mu nE)WD = AP_{power} \quad (1)$$

where E is the electrical field in the nanowire, W is the gate width and D is the active layer thickness. While P_{power} is the incident light power and A is a fitting parameter. Evidently, the experiment data in FIG. 2d is well fitted with Eq. 1. This confirms that the photocurrent of $K_x\text{MoO}_3$ single nanowire device was driven by photoconductive effect.

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The output characteristics under different intensities of illumination at the negative voltage direction is shown in FIG. 2e. With the increase of incident light power, the drain current raised gradually. Actually, the drain current was controlled by the optical power density and the curves displayed good transistor behavior, consisting of a rapidly increased linear regime and a fully saturated regime, which is similar to the output characteristics of a traditional field effect transistor modified by gate voltage. Except here the light intensity plays the role of voltage gating. The results suggest that the incident light could be employed to replace the gate voltage, V_{DS} , as an additional terminal to control the output level of the transistor, indicating an effective approach to achieve current modification and signal magnification in a single nanowire device for future low-cost, nano-scale photoelectric integration. Under 4mW/cm^2 illumination, the I_{DS} is measured to be $-5.6\text{ }\mu\text{A}$ at $V_{DS} = -10\text{ V}$ with the electric conductivity estimated to be about 3.3 S/m . The responsivity, R_{res} , an important parameter of phototransistors, could be calculated by³⁰

$$R_{res} = \frac{I_{ph}}{P_{opt}} = \frac{(I_{DS,illum} - I_{DS,dark})S^{-1}}{P_{inc}} \quad (2)$$

where P_{opt} is the light power, $I_{DS,illum}$ and $I_{DS,dark}$ are the drain-source current under illumination and in dark, respectively, S is the effective area of nanowire device, and P_{inc} is power density of the incident light. It is very attractive that the R_{res} value of the nanowire phototransistor could reach as high as $1.75 \times 10^7\text{ mA/W}$. This value is much higher than that of graphene ($\sim 1\text{ mA/W}$),³¹ MoS_2 (7.5 mA/W)¹⁰ and organic phototransistors (PPEs, 36 mA/W).¹⁴ It is even comparable with those of the ZnO nanowires ($1.29 \times 10^4\text{ A/W}$)¹⁵ and vertically aligned Si nanowire arrays ($\sim 10^5\text{ A/W}$)³². The high responsivity of the nanowire device enables a large on/off ratio, indicating the potential applications of the nanowire transistor in photoelectronic devices such as retro sensors, optoisolators^{9,30} and photoamplifiers. The related diagram and equivalent circuit of the K_xMoO_3 nanowire transistor are illustrated in the right inset of FIG. 2a, where R is the intrinsic resistance of K_xMoO_3 nanowire. The output characteristics of I_{DS} under illumination at positive V_{DS} direction is shown in FIG. 2g. Similarly, the device also showed a good phototransistor behavior. The output current was well controlled by incident light power and saturation is achieved at higher voltage regime. Again, the unidirectional property of the existing current in K_xMoO_3 nanowire resulted in the slightly higher output current compared with the negative voltage region. Careful analysis of the output characteristics could indicate more details about the phototransistor mechanism, as shown in FIG. 2f and h. The regions for $-4.5\text{V} \leq V_{DS} \leq 0$ and $0 \leq V_{DS} \leq 4.5\text{V}$ were zoomed in and it is clear that the photo-related current is only available in the case of drain voltage beyond 4 V (or -4V). This is attributed to the Schottky barrier formed by the connection of K_xMoO_3 nanowire and aluminum electrode (the

work function of Al is about 4.2 eV³³). Moreover, the magnitude of the output current shows little increase with the increasing light power in the $0 \leq V_{DS} \leq 4V$ region, which indicates the current output related to intrinsic barrier distribution is not photo-activated. Therefore, there should be another output current mechanism which is highly sensitive to light power.

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To illustrate this concept, the existing output curve under dark field was further investigated. As shown in the inset of FIG. 2c which is the zoom in of the negative voltage regime of the dark characteristics, a small current was detected at around 4 V and increased with the increasing voltage thereafter, which indicates a typical Schottky contact characteristic curve.

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Therefore, the whole output characteristic is predicted to be the combination of two possible mechanisms: one is the unidirectional output caused by nonuniform intrinsic potential distribution (denoted as part I) and the other is a normal semiconductor output with Schottky contact (part II), as shown in FIG. 3. Since the magnitude of the output current related to part I is much higher than that of part II, part I dominated the output characteristic curve in dark condition by showing the unidirectional tendency of the entire output current.

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Although the output of part I showed little fluctuation with incident light power, it changed dramatically with thermal variation. The output current was measured with temperature varying from 77 K to 330K and the corresponding I_{DS} curves were recorded. As shown in FIG. 4a, the V_{DS} values were kept at 2 V, 3 V and 4 V respectively at which region I_{DS} is hardly affected by the incident light. An exponential behavior of the output current with increasing temperature is demonstrated for various applied bias. The electron movement almost came to a stop below 100K and increased rapidly with rising temperature from 200 K to 330 K. The corresponding values of $\ln(I_{ds})$ display a quasi-linear relationship with the increasing temperature, as shown inset of FIG. 4a. As expected, the current-temperature dependence of the nanowire follows the thermal-activation model,^{32,34}

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$$I_{DS} = \sigma_0 \frac{V_{ds} S_{cross}}{W} e^{\frac{\Delta E}{k_B T}} \quad (3)$$

where W is the width of the transistor channel, S_{cross} is the cross sectional area of the K_xMoO_3 nanowire, k_B is the Boltzmann constant and ΔE is activation energy. The fitted results of the phototransistor at various applied bias were shown as solid lines in FIG. 4a. Evidently, all the output current at V_{DS} below 4 V region were fitted well with the thermal-activation model, indicating the thermal activation characteristic of K_xMoO_3 nanowire in part I rather than opto activation. On the other hand, FIG. 4b exhibits the typical characteristic curves under 3 mW/cm² illumination at different temperature (part II). Obviously, the photocurrent change was not significant and the amplitude of fluctuation was much lower

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than that of part I, indicating that photo-activated process dominates part II (at high voltage bias) under illumination conditions. The obvious thermal- and photo-activation process demonstrated the great potential of $K_x\text{MoO}_3$ nanowires in both thermal-electronic and photoelectronic applications dependent on different bias applied.

5 The promising phototransistor performance is also supported by the ultra-fast photo-response of the $K_x\text{MoO}_3$ nanowire to light. The time responses of the transistor have been investigated under applied bias $V_{DS} = 10$ V with light power densities of 0.1, 1, 2, 3, and 4 mW/cm^2 . The light source was turned on and off for 5 s respectively. As shown in FIG. 5a, 10 the device presented a perfect switching on/off behavior. Each photoresponse cycle consists of three distinct stages: a sharp rise, a steady state and a sharp decay process to original state with an on/off current ratio of about 10^4 under $4 \text{ mW}/\text{cm}^2$ illumination. Five single nanowire devices have been tested and the on/off ratio ranges from 1×10^4 to 5.6×10^4 . One more representative device's photoresponse behavior is shown in FIG. 15. As shown in FIG. 15 5b, both the response and recovery process were completed very fast. The rapid response time (ca. 5 ms) was tested by an oscilloscope (DSO-X 3024A, 200MHz) associated with an electronic chopper. As shown in FIG. 5b inset, the recovery rate was tested as short as 0.3 ms, which is even faster than the rising response process, 5 ms. To the best of our knowledge, this value is much faster than that of the reported organic and inorganic phototransistors or photoswitches. The device also exhibited high stability and reproducibility. 20 Almost no degradation of the current was observed regardless of several tens of cycles of continuous work, as shown in FIG. 16. Moreover, the phototransistor is demonstrated to response to full spectrum regime. The photoresponse characteristics were investigated through employing a series of filters with wavelengths of 488 nm, 500 nm, 514 nm, 532 nm, 25 550 nm, 570 nm, 600 nm, 633 nm and lasers with wavelengths of 325 nm, 532 nm, 808 nm and 1064 nm. As can be seen in FIG. 5 (c), the phototransistor is able to respond to all light wavelengths from 488-1100nm using a light filter and 532, IR (808, 1064) laser for verification. The representative results and photocurrent as a function of wavelength are shown in FIGS. 17 and 18. As can be seen in FIG. 17, the photoresponse of the device does 30 not show obvious fluctuation in the visible spectrum regime. Evidently, the $K_x\text{MoO}_3$ nanowire device is much more sensitive for the visible spectrum regime which promotes this kind of devices toward a myriad of applications in daily life. As can be seen in the I_{DS} -Time graph of FIG. 5 (d), the $K_x\text{MoO}_3$ phototransistor shows consistent device performance.

35 In summary, K-intercalated MoO_3 nanowire has been successfully synthesized through a simple but effective one-step vapor deposition method. EDX analysis confirmed the decreasing trend of K concentration along the nanowire growth direction which enables the

unidirectional, diode-like behavior of the dark current. This part of current is found to be irresponsive to the change of light intensity but to the temperature. The extreme shallow donor created by the intercalation of K enables an ultra-sensitive and sub-millisecond photocurrent response. On top of this, fabrication and characterization of the single-wire device demonstrated that the saturation of the output current can be achieved within 1 volt and light was able to serve as a reliable control over the current level with the on/off ratio as high as 10^4 , which confirms the application of the devices as promising phototransistors and light sensors. Moreover, the high responsivity and broad spectral response further illustrate the great potential of this material in the nano-sized, photoelectronic applications of communications, sensing and imaging.

Whilst there has been described in the foregoing description exemplary embodiments of the present invention, it will be understood by those skilled in the technology concerned that many variations in details of design, construction and/or operation may be made without departing from the present invention. For example, besides the exemplary temperature of 600 °C of the furnace and dwelling time of 6h used to synthesize the nanowire, the nanowire may also be synthesized at a furnace temperature ranging from 300 to 900 °C at a dwelling time ranging from 10 minutes to 12 hrs.

Also, other alternatives may be used as the substrate for the molybdenum oxide phototransistor, such polyethylene terephthalate (PET), and other low-cost plastic and bendable substrates. Similar results for a device made on PET are shown depicted in FIG. 13.

REFERENCES

- (1) Soci, C.; Zhang, A.; Bao, X. Y.; Kim, H.; Lo, Y.; Wang, D. L. *J. Nanosci. Nanotechnol.* **2010**, *10*, 1430.
- (2) Soci, C.; Zhang, A.; Xiang, B.; Dayeh, S. A.; Aplin, D. P. R.; Park, J.; Bao, X. Y.; Lo, Y. H.; Wang, D. *Nano Lett.* **2007**, *7*, 1003.
- (3) Hu, L.; Chen, G. *Nano Lett.* **2007**, *7*, 3249.
- (4) Tian, B.; Kempa, T. J.; Lieber, C. M. *Chem. Soc. Rev.* **2009**, *38*, 16.
- (5) Huynh, W. U.; Dittmer, J. J.; Alivisatos, A. P. *Science* **2002**, *295*, 2425.
- (6) Kind, H.; Yan, H. Q.; Messer, B.; Law, M.; Yang, P. D. *Adv. Mater.* **2002**, *14*, 158.
- (7) Seeds, A. J.; De Salles, A. A. A. *Microwave Theory and Techniques, IEEE Transactions on* **1990**, *38*, 577.
- (8) Saragi, T. P. I.; Pudzich, R.; Fuhrmann, T.; Salbeck, J. *Applied Physics Letters* **2004**, *84*, 2334.

- (9) Tang, Q. X.; Li, L. Q.; Song, Y. B.; Liu, Y. L.; Li, H. X.; Xu, W.; Liu, Y. Q.; Hu, W. P.; Zhu, D. B. *Adv. Mater.* **2007**, *19*, 2624.
- (10) Yin, Z.; Li, H.; Li, H.; Jiang, L.; Shi, Y.; Sun, Y.; Lu, G.; Zhang, Q.; Chen, X.; Zhang, H. *ACS Nano* **2011**.
- 5 (11) Singh, T. B.; Koeppe, R.; Sariciftci, N. S.; Morano, M.; Brabec, C. J. *Adv. Funct. Mater.* **2009**, *19*, 789.
- (12) Guo, Y.; Du, C.; Di, C.-a.; Zheng, J.; Sun, X.; Wen, Y.; Zhang, L.; Wu, W.; Yu, G.; Liu, Y. *Applied Physics Letters* **2009**, *94*, 143303.
- (13) Varghese, B.; Tamang, R.; Tok, E. S.; Mhaisalkar, S. G.; Sow, C. H. *J. Phys. Chem. C*
10 **2010**, *114*, 15149.
- (14) Dong, H.; Li, H.; Wang, E.; Nakashima, H.; Torimitsu, K.; Hu, W. *The Journal of Physical Chemistry C* **2008**, *112*, 19690.
- (15) Weng, W. Y.; Chang, S. J.; Hsu, C. L.; Hsueh, T. J. *ACS Applied Materials & Interfaces* **2011**, *3*, 162.
- 15 (16) Zhou, J.; Xu, N. S.; Deng, S. Z.; Chen, J.; She, J. C.; Wang, Z. L. *Adv. Mater.* **2003**, *15*, 1835.
- (17) Zhu, Y. W.; Yu, T.; Cheong, F. C.; Xu, X. J.; Lim, C. T.; Tan, V. B. C.; Thong, J. T. L.; Sow, C. H. *Nanotechnology* **2005**, *16*, 88.
- (18) Juárez Ramírez, I.; Martínez-de la Cruz, A. *Materials Letters* **2003**, *57*, 1034.
- 20 (19) Reddy, C. V. S.; Qi, Y. Y.; Jin, W.; Zhu, Q. Y.; Deng, Z. R.; Chen, W.; Mho, S. I. *J. Solid State Electrochem.* **2007**, *11*, 1239.
- (20) Ohler, N.; Bell, A. T. *Journal of Catalysis* **2005**, *231*, 115.
- (21) Barazzouk, S.; Tandon, R. P.; Hotchandani, S. *Sensors and Actuators B: Chemical* **2006**, *119*, 691.
- 25 (22) Hussain, O. M.; Rao, K. S. *Materials Chemistry and Physics* **2003**, *80*, 638.
- (23) Hsu, C.-S.; Chan, C.-C.; Huang, H.-T.; Peng, C.-H.; Hsu, W.-C. *Thin Solid Films* **2008**, *516*, 4839.
- (24) Mahajan, S. S.; Mujawar, S. H.; Shinde, P. S.; Inamdar, A. I.; Patil, P. S. *Applied Surface Science* **2008**, *254*, 5895.
- 30 (25) Wisitsoraat, A.; Phokharatkul, D.; Tuantranont, A.; Saikaew, C.; Ieee *Effect of Carbon Doping on Gas Sensing Properties of Molybdenum Oxide Nanoneedles*; Ieee: New York, 2009.
- (26) Mai, L. Q.; Hu, B.; Chen, W.; Qi, Y. Y.; Lao, C. S.; Yang, R. S.; Dai, Y.; Wang, Z. L. *Adv. Mater.* **2007**, *19*, 3712.
- 35 (27) Hu, Z.; Zhou, C.; Zheng, M.; Lu, J.; Varghese, B.; Cheng, H.; Sow, C. H. *The Journal of Physical Chemistry C* **2011**.

- (28) Xie, Y. L.; Cheong, F. C.; Zhu, Y. W.; Varghese, B.; Tamang, R.; Bettiol, A. A.; Sow, C. H. *The Journal of Physical Chemistry C* **2009**, *114*, 120.
- (29) Sze, S. M. **1988**, *In Physics of Semiconductor Devices*, 744.
- (30) Hamilton, M. C.; Martin, S.; Kanicki, J. *IEEE Trans. Electron Devices* **2004**, *51*, 877.
- 5 (31) Xia, F.; Mueller, T.; Lin, Y.-m.; Valdes-Garcia, A.; Avouris, P. *Nat Nano* **2009**, *4*, 839.
- (32) Zhang, A.; Kim, H.; Cheng, J.; Lo, Y.-H. *Nano Letters* **2010**, *10*, 2117.
- (33) Bennette, C. J. S., L. W.; Charbonnier, F. M. *J. Appl. Phys.* **1967**, *28*, 634.
- (34) Ma, Y. *Solid State Communications* **2004**, *130*, 313.
- (35) Hsu, C. S.; Chan, C. C.; Huang, H. T.; Peng, C. H.; Hsu, W. C.; *Thin Solid Films* **2008**,
10 516, 4839–4844.
- (36) Kanno, H.; Holmes, R. J.; Sun, Y.; Cohen, S. K.; Forrest, S. R.; *Adv. Mater.* **2006**, *18*,
339–342.
- (37) Reddy, C.V. S.; Deng, Z. R.; Zhu, Q. Y.; Dai, Y.; Zhou, J.; Chen, W.; Mho, S.-I. *Appl. Phys. A* **2007**, *89*, 995–999.
- 15 (38) Zhang, G. J.; Yang, W. S.; Yao, J. N. *Adv. Funct. Mater.* **2005**, *15*, 1255–1259.
- (39) Zhou, J.; Xu, N. S.; Deng, S. Z.; Chen, J.; She, J. C.; Wang, Z. L.; *Adv. Mater.* **2003**, *15*,
1835–1840.
- (40) Wang, J. Z.; Matsubara, I.; Murayama, N.; Woosuck, S.; Izu, N.; *Thin Solid Films* **2006**,
514, 329–333.
- 20 (41) Ohtsuka, H.; Sakurai, Y. *Solid State Ionics* **2001**, *144*, 59–64.
- (42) Hashem, A. M.; Askar, M. H.; Winter, M.; Albering, J. H.; Besenhard, J. O. *Ionics* **2007**,
13, 3–8.
- (43) Maier, J. *Nature Mater.* **2005**, *4*, 805–815.
- (44) Mai, L. Q.; Hu, B.; Chen, W.; Qi, Y. Y.; Lao, C. S.; Yang, R. S.; Dai, Y.; Wang, Z. L. *Adv.*
25 *Mater.* **2007**, *19*, 3712–3716.
- (45) Sian, T. S.; Reddy, G. B. J. *Electrochem. Soc.* **2005**, *152*, A2323–A2326.
- (46) Graham, J.; Wadsley, A. D. *Acta Crystallogr.* **1966**, *20*, 93–100.
- (47) Greenblatt, M. *Chem. Rev.* **1988**, *88*, 31–53.
- (48) Fogle, W.; Perlstein, J. H. *Phys. Rev. B* **1972**, *6*, 1402–1412.
- 30 (49) JCPDS (Card No. 89-5108), International Centre for Diffraction Data, 2002.
- (50) Anwar, M.; Hogarth, C. A.; Bulpett, R. J. *Mater. Sci.* **1989**, *24*, 3087–3090.
- (51) Bouzidi, A.; Benramdane, N.; Tabet-Derranz, H.; Mathieu, C.; Khelifa, B.; Desfeux, R.
Mater. Sci. Eng., B **2003**, *97*, 5–8.
- (52) Sha, X. W.; Chen, L.; Cooper, A. C.; Pez, G. P.; Cheng, H. S. J.; *Phys. Chem. C* **2009**,
35 113, 11399–11407.

CLAIMS

1. A method of synthesizing a molybdenum oxide phototransistor, the method comprising:
 - 5 placing a foil of molybdenum in a furnace;
 - placing a sheet of muscovite ($K(Al_2)(Si_3Al)O_{10}(OH)_2$) at a predetermined distance from the foil of molybdenum in the furnace;
 - controlling airflow into the furnace to provide sufficient oxygen for crystalline growth of potassium-intercalated molybdenum oxide (K_xMoO_3) while maintaining a preset
 - 10 temperature of the furnace for a time period to produce the K_xMoO_3 nanowire;
 - transferring the K_xMoO_3 nanowire onto a substrate; and
 - forming a covering of electrodes on the nanowire to produce the molybdenum oxide phototransistor.
- 15 2. The method of claim 1, wherein the preset temperature ranges from about 300°C to about 900°C.
3. The method of claim 1 or claim 2, wherein the time period ranges from about 10 minutes to about 12 hours.
- 20 4. The method of any preceding claim, wherein the predetermined distance is about 1 mm.
5. The method of any preceding claim, wherein forming the covering of electrodes comprises using photolithography to form a design of metal finger electrodes.
- 25 6. The method of claim 5, further comprising thermal evaporating aluminium to form the metal finger electrodes.
7. The method of any preceding claim, wherein the crystalline growth comprises growth from grain boundaries via thermal evaporation to incorporate K atoms from the
- 30 muscovite into a MoO_3 lattice.
8. The method of any preceding claim, wherein the crystalline growth is in a [001] direction.
- 35 9. The method of any preceding claim, wherein the substrate comprises a layer of SiO_2 on a layer of Si.

10. The method of claim 9, wherein the substrate comprises a dielectric coating of Si_3N_4 .

11. The method of any one of claims 1 to 8, wherein the substrate comprises a bendable plastic.

12. A molybdenum oxide phototransistor comprising:

a substrate;

a potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire on the substrate;

and

a covering of electrodes on the nanowire.

13. The molybdenum oxide phototransistor of claim 12, wherein the electrodes are made of aluminium.

14. The molybdenum oxide phototransistor of claim 12 or claim 13, synthesized according to the method of any one of claims 1 to 11.

15. The molybdenum oxide phototransistor of any one of claims 12 to 14, wherein the K_xMoO_3 nanowire has an intact layered structure comprising K atoms incorporated into a MoO_3 lattice.

16. The molybdenum oxide phototransistor of any one of claims 12 to 15, wherein the substrate comprises a layer of SiO_2 on a layer of Si.

17. The molybdenum oxide phototransistor of any one of claims 12 to 16, wherein the substrate comprises a dielectric coating.

18. The molybdenum oxide phototransistor of claim 17, wherein the dielectric coating comprises Si_3N_4 .

19. The molybdenum oxide phototransistor of any one of claims 12 to 15, wherein the substrate comprises a bendable plastic.

20. A method of synthesizing a potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire, the method comprising:

placing a foil of molybdenum in a furnace;

placing a sheet of muscovite ($K(Al_2)(Si_3Al)O_{10}(OH)_2$) at a predetermined distance from the foil of molybdenum in the furnace;

controlling airflow into the furnace to provide sufficient oxygen for crystalline growth of potassium-intercalated molybdenum oxide (K_xMoO_3) while maintaining a preset temperature of the furnace for a time period to produce the K_xMoO_3 nanowire.

21. The method of claim 20, wherein the preset temperature ranges from about 300°C to about 900°C.

22. The method of claim 20 or claim 21, wherein the time period ranges from about 10 minutes to about 12 hours.

23. The method of any one of claims 20 to 22, wherein the predetermined distance is about 1 mm.

24. The method of any one of claims 20 to 23, wherein the crystalline growth comprises growth from grain boundaries via thermal evaporation to incorporate K atoms from the muscovite into a MoO_3 lattice.

25. The method of any one of claims 20 to 24, wherein the crystalline growth is in a [001] direction.

26. A potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire synthesized according to the method of any one of claims 20 to 25.

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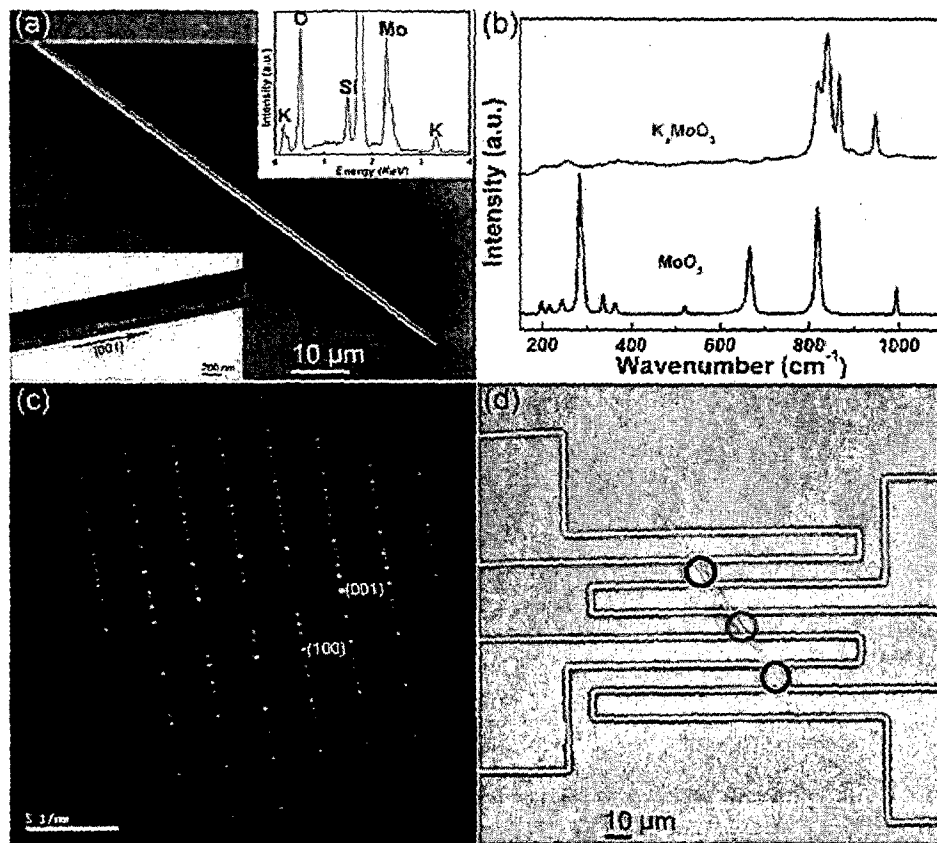


FIG. 1

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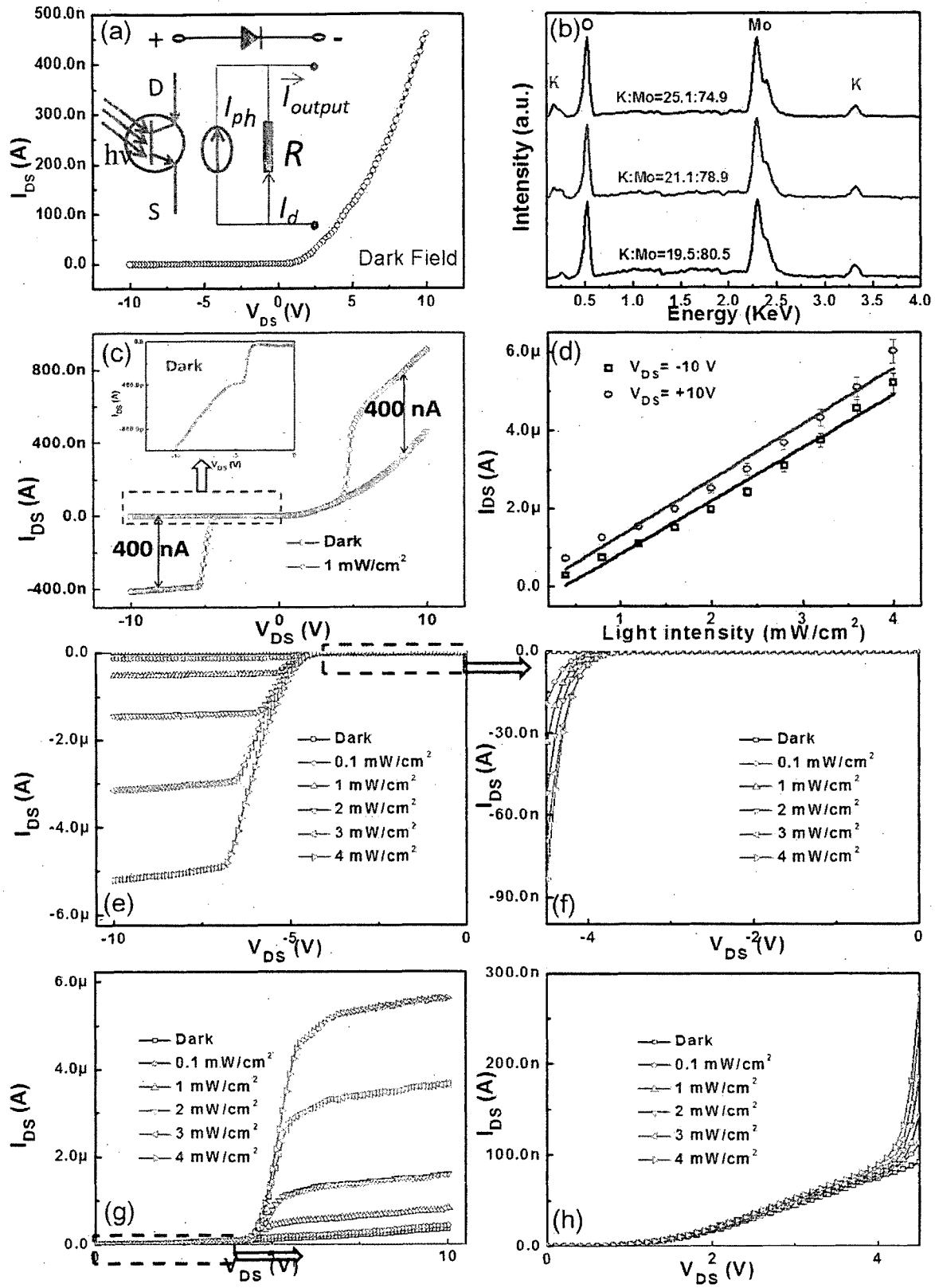


FIG. 2

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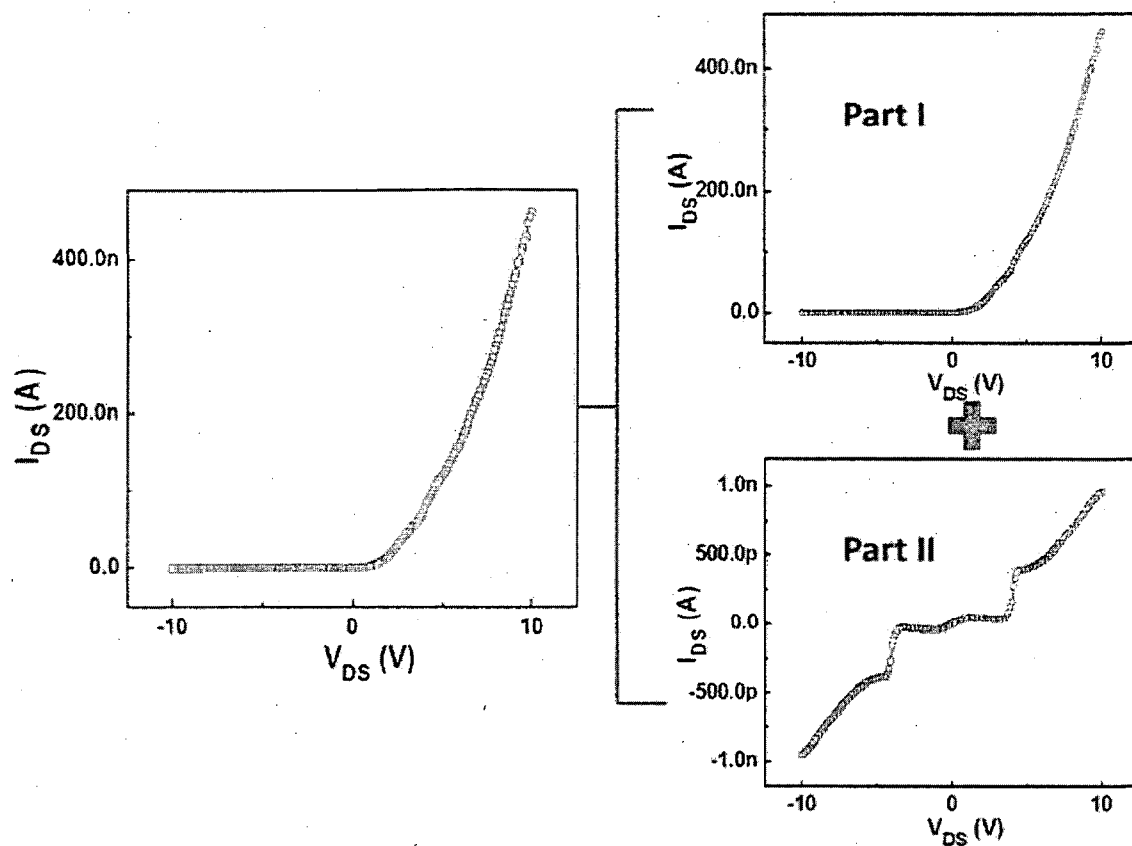


FIG. 3

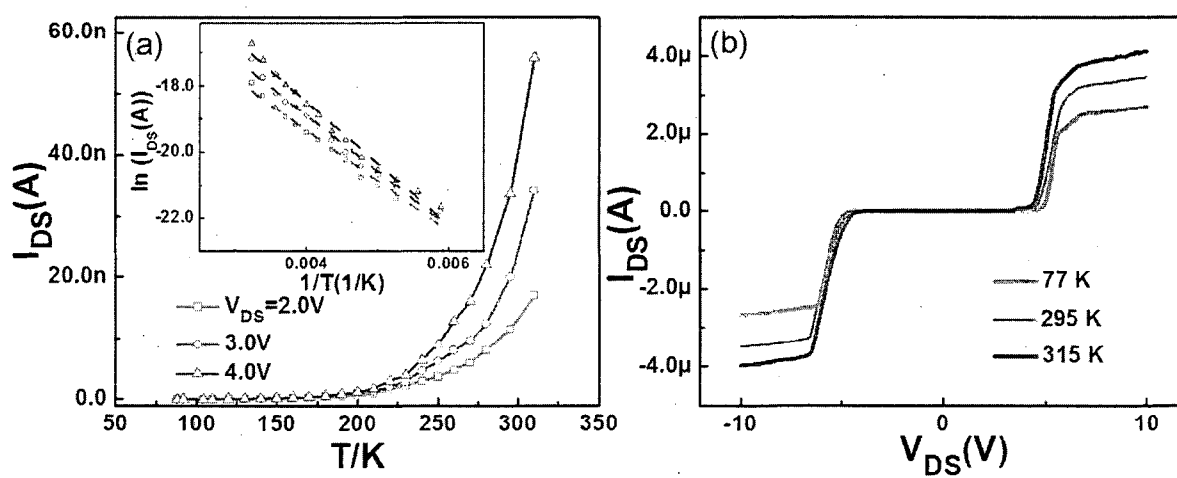


FIG. 4

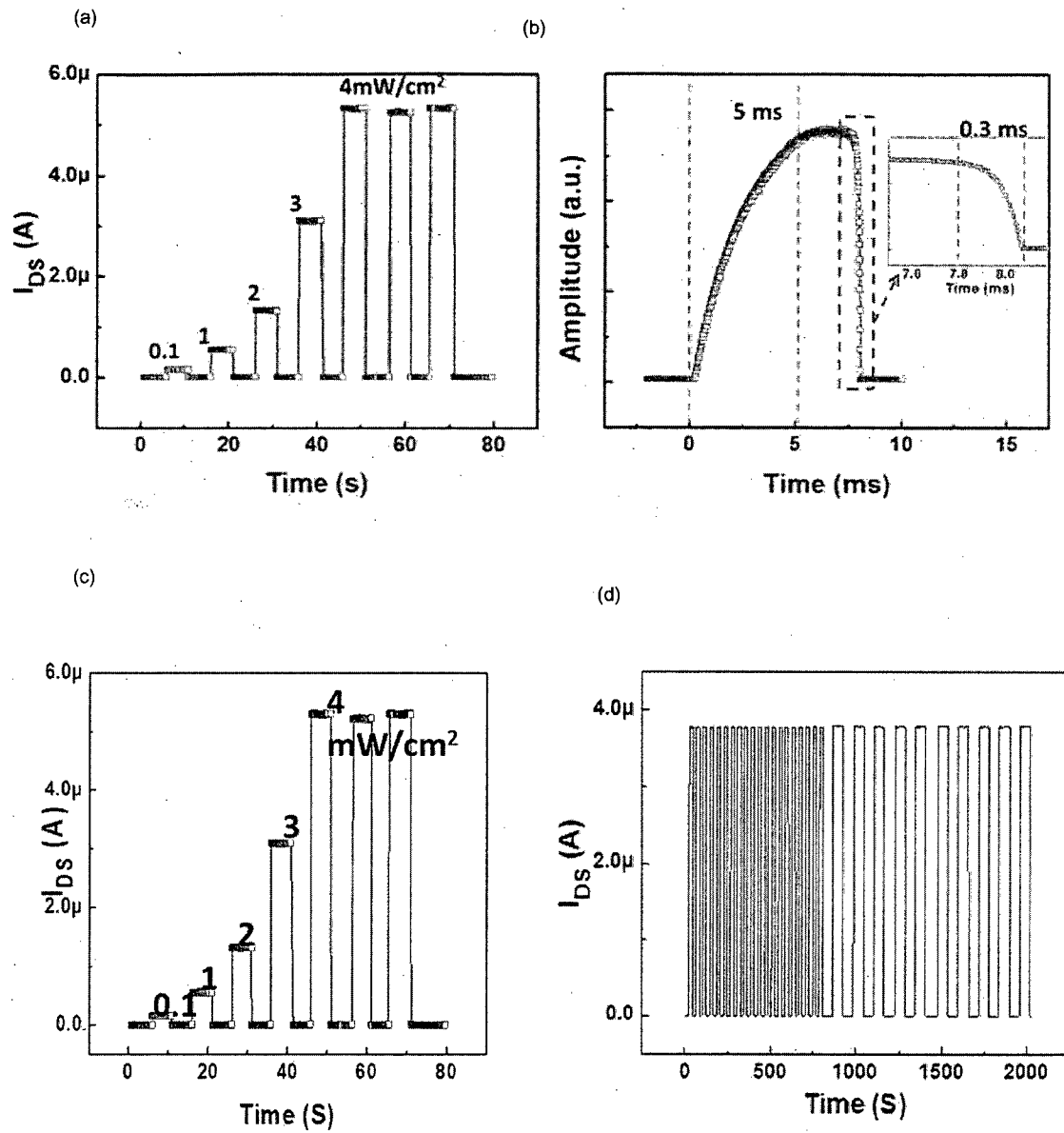


FIG. 5

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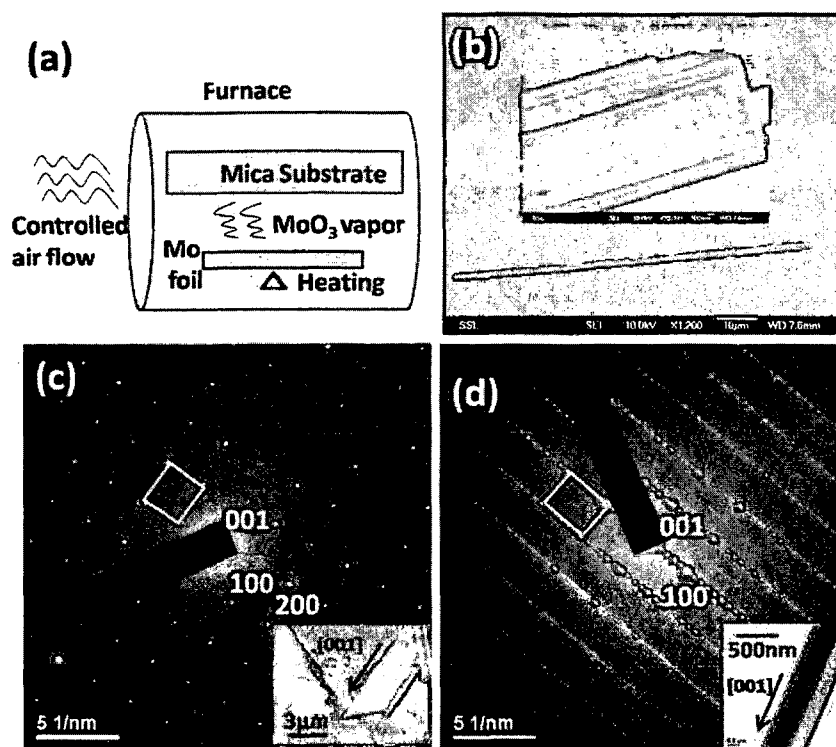


FIG. 6

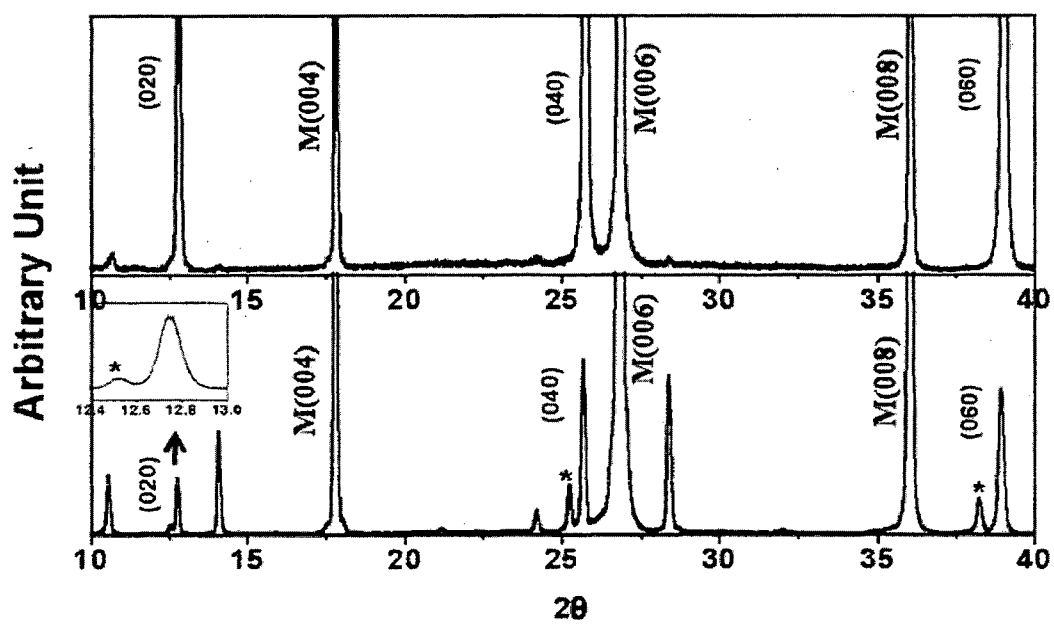


FIG. 7

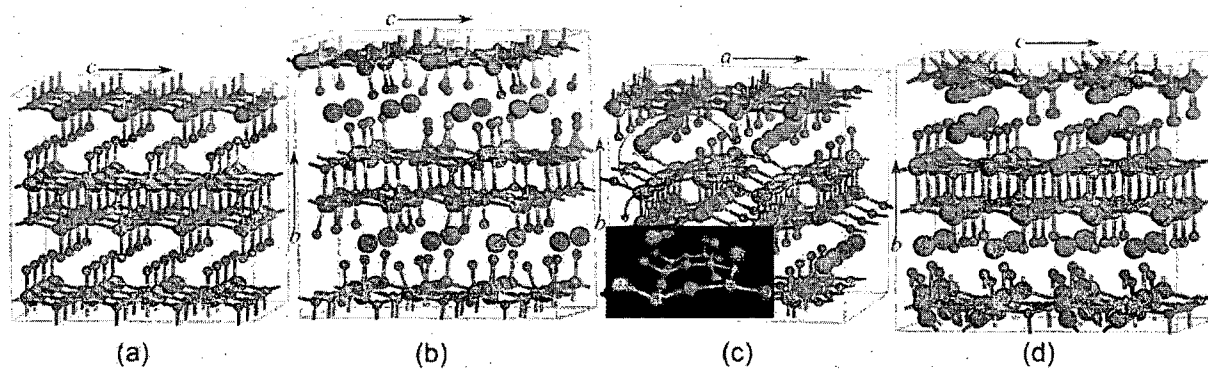


FIG. 8

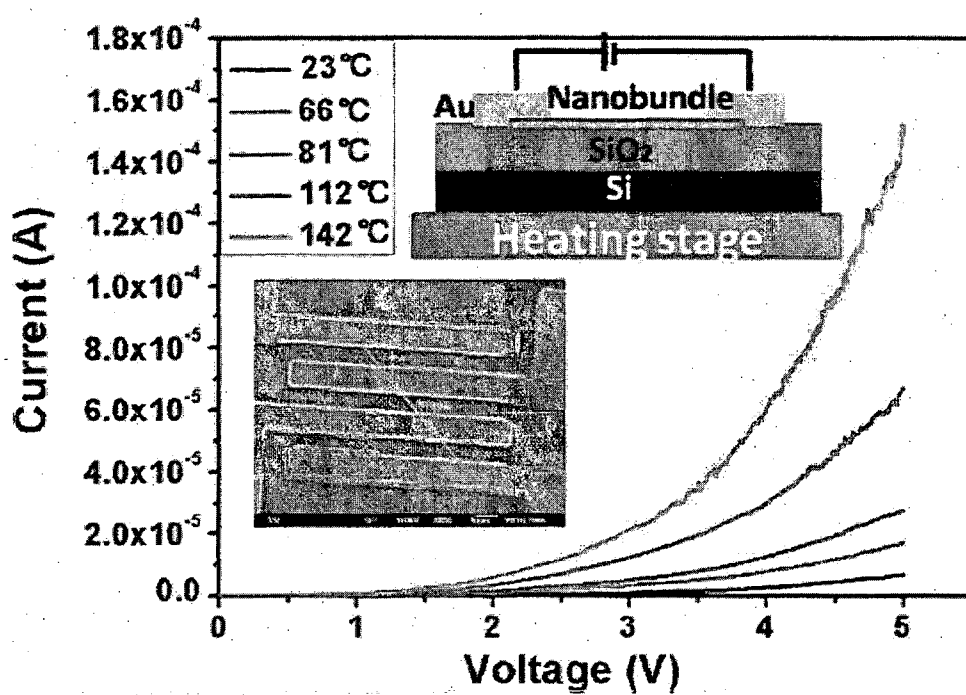


FIG. 9

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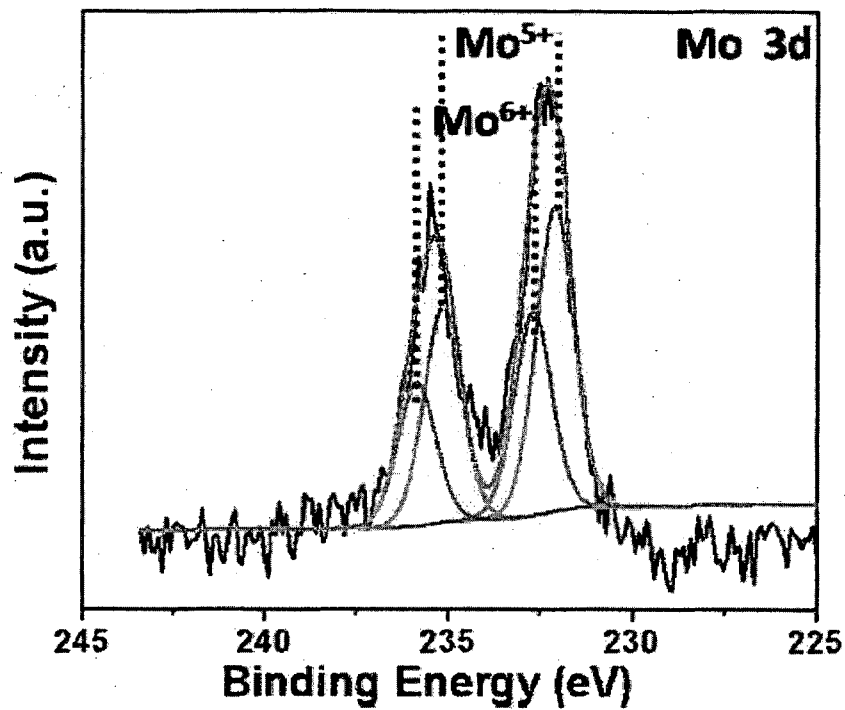


FIG. 10

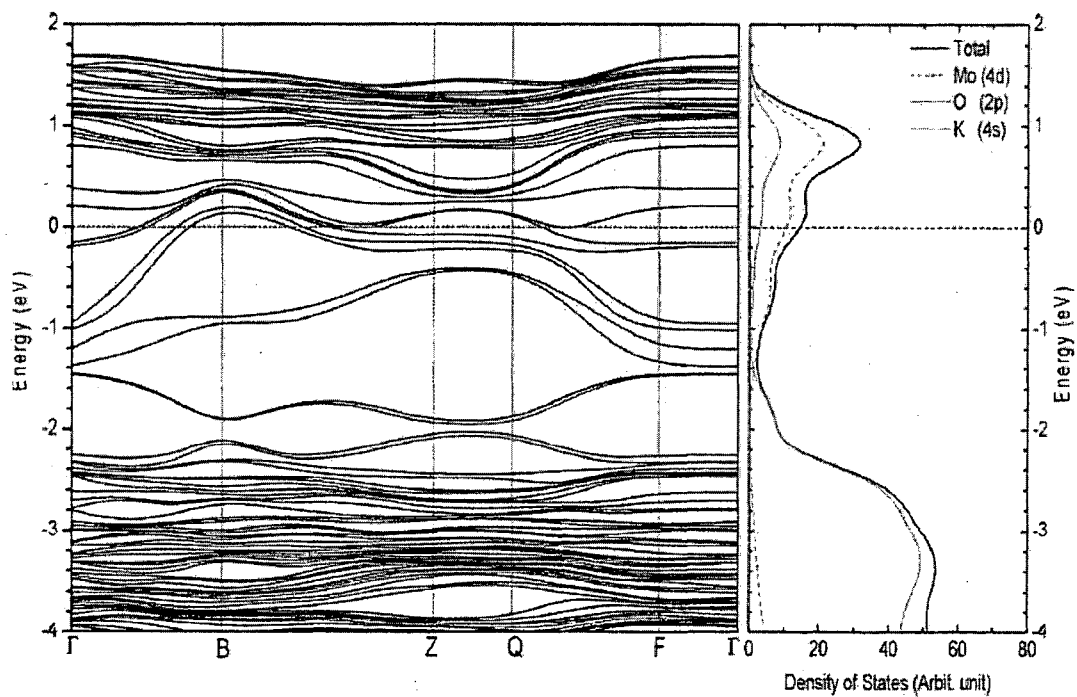


FIG. 11

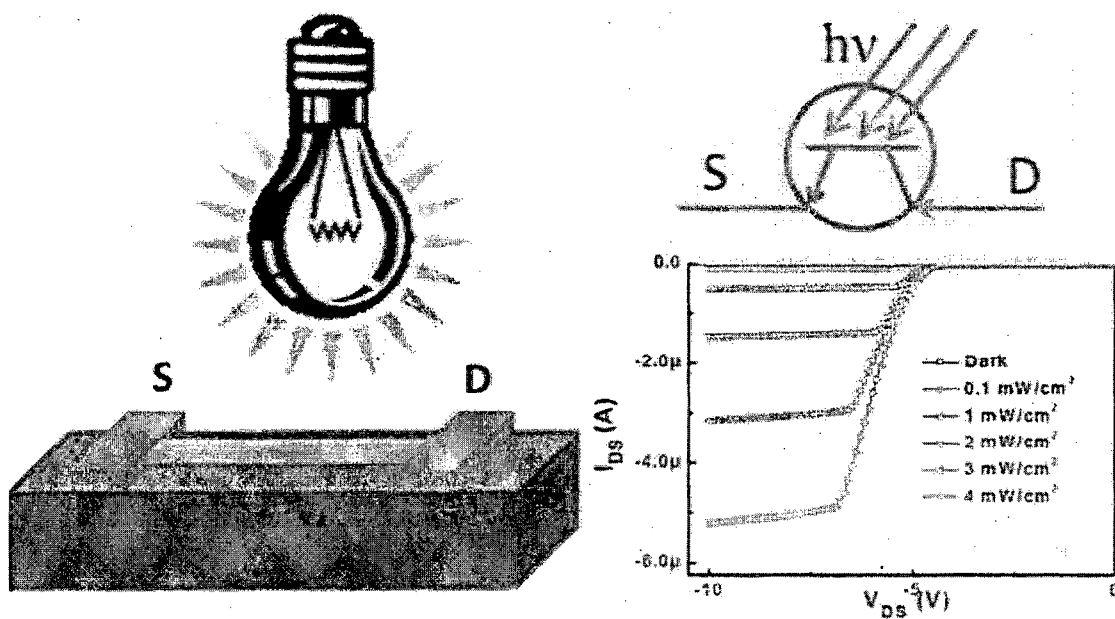


FIG. 12

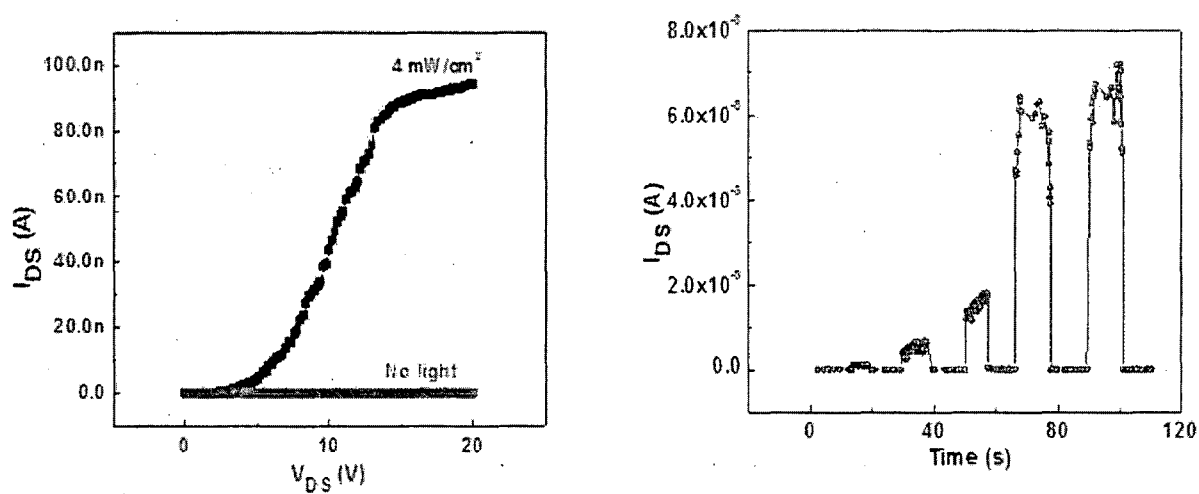


FIG. 13

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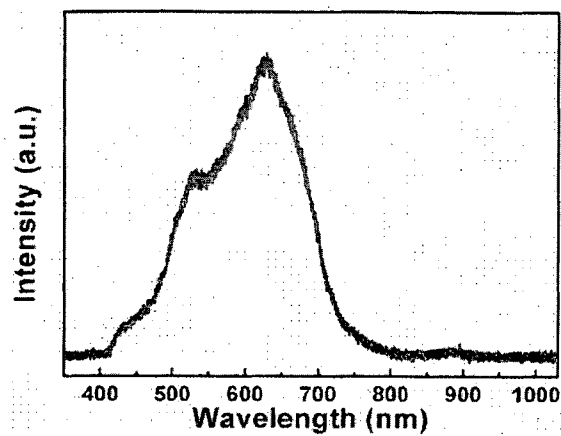


FIG. 14

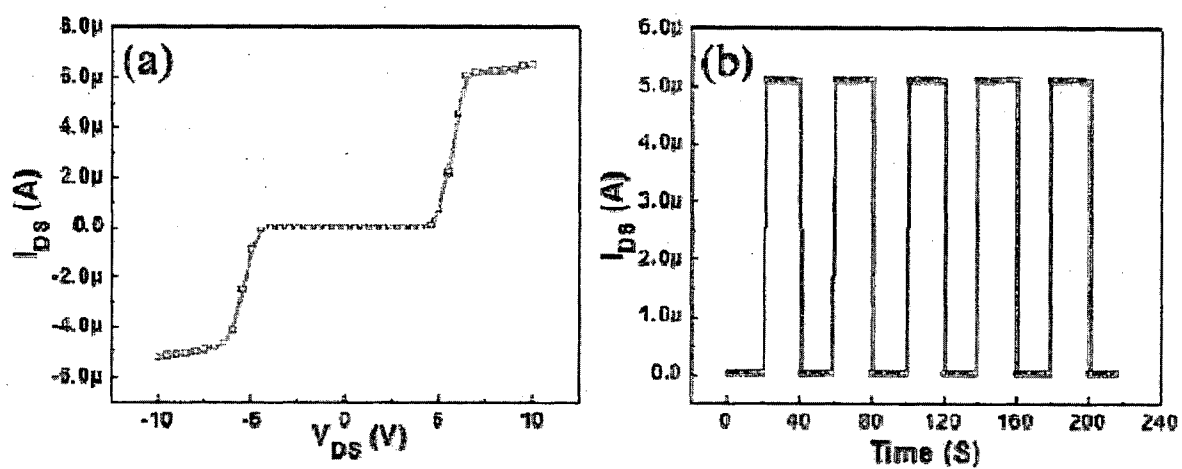


FIG. 15

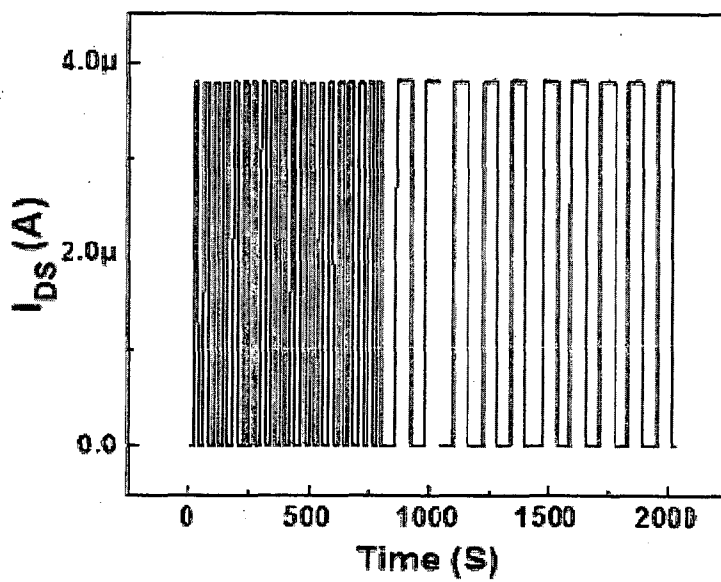


FIG. 16

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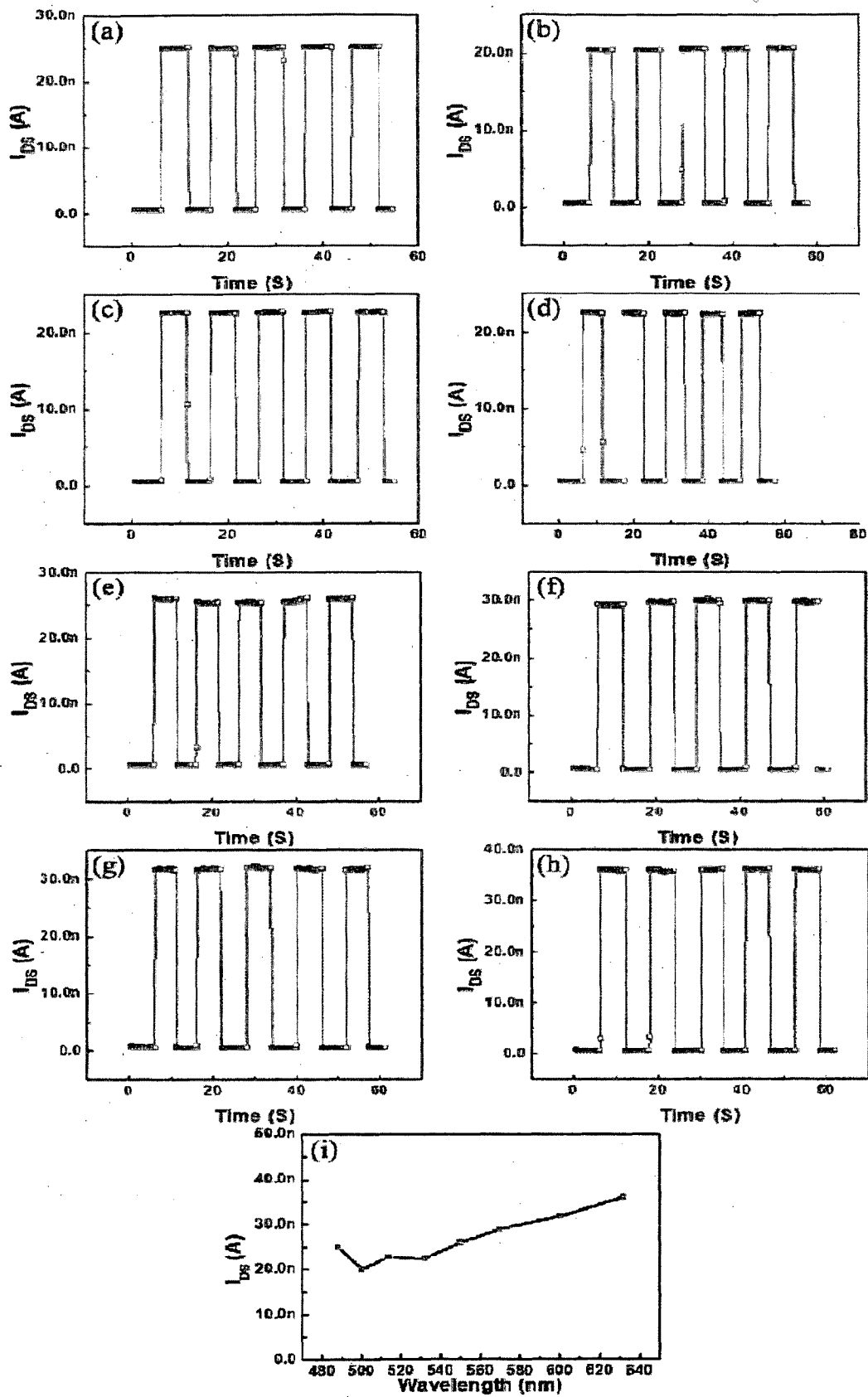


FIG. 17

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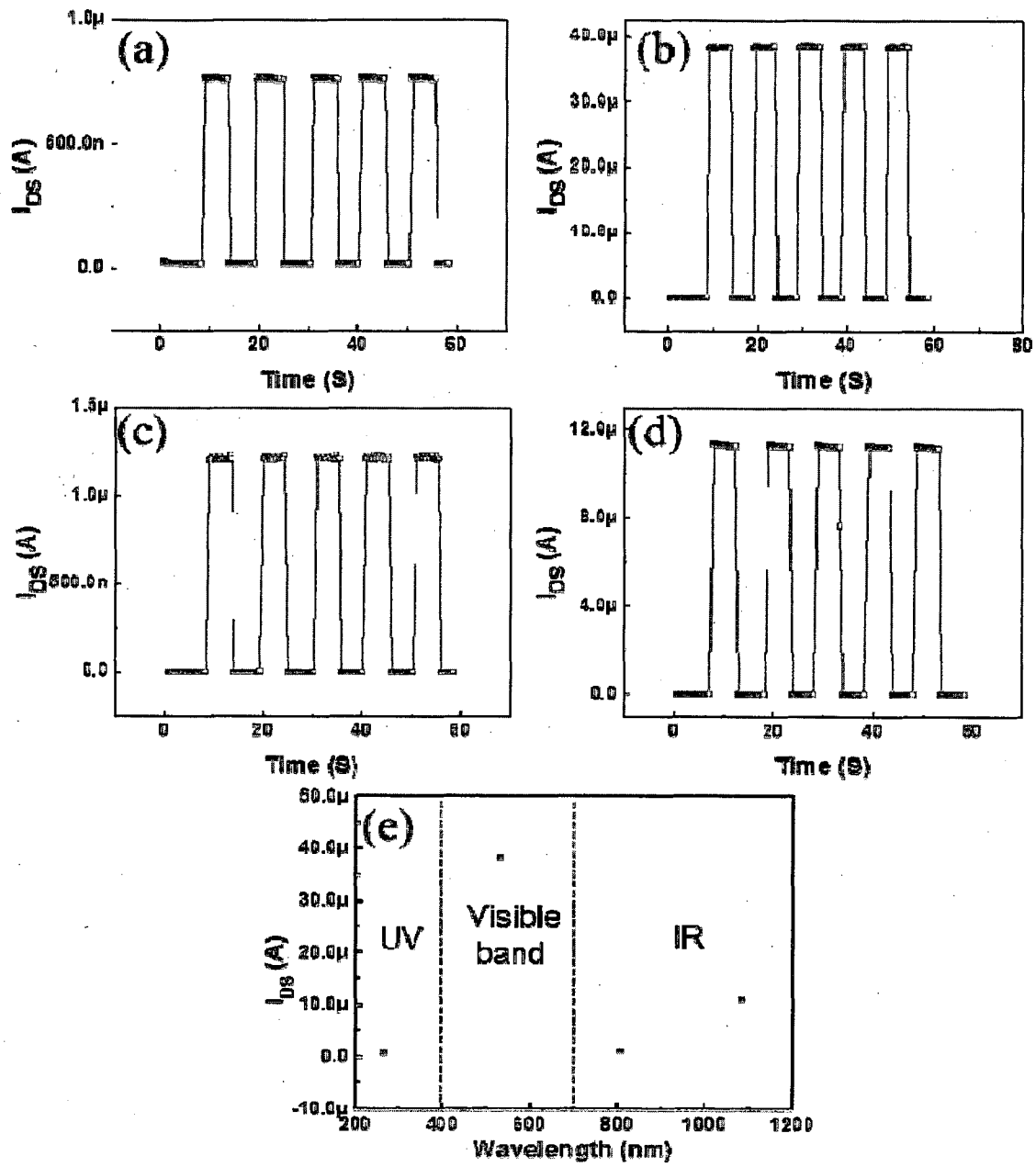


FIG. 18

INTERNATIONAL SEARCH REPORT

 International application No.
PCT/SG2013/000096

A. CLASSIFICATION OF SUBJECT MATTER

H01L 29/775 (2006.01) H01L 31/10 (2006.01) H01L 31/18 (2006.01) G02B 1/02 (2006.01) C01G 39/02 (2006.01) B82Y 20/00 (2011.01)

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, INSPEC, GOOGLE: (OR PHOTO_TRANSISTOR?, OPTO_COUPLER?, (PHOTONIC 2W DEVICE?), H01L31/IC/EC/CC, H01L29/775/CC/IC/EC); (OR INTERCALAT+, LAYER+, INTER_LAYER+, SPACING, SPACE+, DISTORT+, LAMELLAR); (OR (MOLYBDENUM W +OXIDE?), MOO3, MOO6, MO4O12, MOO5, C01G39/02/IC/CC/EC); (OR B82Y20/IC/CC/EC, B82Y30/00, +NANO+, B82Y40/IC/CC/EC); (OR HEAT+, FURNACE?, TEMPERATURE, THERMAL+); (OR AIR_FLOW, AIR, VOLATILIZ+, VOLATILIS+, SUBLIMAT+, VAPO?R, OXYGEN) 3D (OR (ALKALI W METAL?), POTASSIUM, SODIUM, LITHIUM, LI, NA, MUSCOVITE, K_ENRICH+, K_CONTAIN+, KXMOO3, K_INTERCALAT+, MUSCOVITE, MICA, ISINGLASS, PHYLLOSILICATE?); and similar terms

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	Documents are listed in the continuation of Box C	



Further documents are listed in the continuation of Box C



See patent family annex

* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E"	earlier application or patent but published on or after the international filing date	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O"	document referring to an oral disclosure, use, exhibition or other means	"&"	document member of the same patent family
"P"	document published prior to the international filing date but later than the priority date claimed		
Date of the actual completion of the international search 27 May 2013		Date of mailing of the international search report 27 May 2013	
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA Email address: pct@ipaustalia.gov.au Facsimile No.: +61 2 6283 7999		Authorised officer Firoozeh Rabbani AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No. 0262832287	

INTERNATIONAL SEARCH REPORT		International application No.
C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		PCT/SG2013/000096
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HU Z. et. al.: "K-Enriched MoO ₃ Nanobundles: A Layered Structure with High Electric Conductivity", J. Phys. Chem. C, 2012, 116, 3962–3967. Published 29 December 2011. Refer to the whole document and in particular to Figs. 1 & 4 and pages pg. 3964 -3966	1-26
A	W. GONG et. al., "Room temperature synthesis of K ₂ Mo ₃ O ₁₀ •3H ₂ O nanowires in minutes", Nanotechnology, 2009, 20, 215603 Refer to the whole document	1-26
A	US 2008/0257204 A1 (ORIAKHI et. al.) 23 October 2008 Refer to the whole document	1-26

Form PCT/ISA/210 (fifth sheet) (July 2009)

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See Supplemental Box for Details

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☒ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- ☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- ☐ No protest accompanied the payment of additional search fees.

Supplemental Box

Continuation of: Box III

This International Application does not comply with the requirements of unity of invention because it does not relate to one invention or to a group of inventions so linked as to form a single general inventive concept.

This Authority has found that there are different inventions based on the following features that separate the claims into distinct groups:

- Claims 1-11 & 20-26 are directed to a method of synthesizing a molybdenum oxide phototransistor or potassium-intercalated molybdenum oxide using muscovite ($K(Al_2)(Si_3Al)O_{10}(OH)_2$). The feature of "placing a sheet of muscovite at a predetermined distance from the foil of molybdenum in the furnace; controlling airflow into the furnace to provide sufficient oxygen for crystalline growth of potassium-intercalated molybdenum oxide (K_xMoO_3) while maintaining a preset temperature of the furnace for a time period to produce the K_xMoO_3 nanowire" is specific to this group of claims.
- Claims 12-19 are directed to a molybdenum oxide phototransistor comprising a potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire. The feature of "a potassium-intercalated molybdenum oxide (K_xMoO_3) nanowire" is specific to this group of claims.

PCT Rule 13.2, first sentence, states that unity of invention is only fulfilled when there is a technical relationship among the claimed inventions involving one or more of the same or corresponding special technical features. PCT Rule 13.2, second sentence, defines a special technical feature as a feature which makes a contribution over the prior art.

When there is no special technical feature common to all the claimed inventions there is no unity of invention.

In the above groups of claims, the identified features may have the potential to make a contribution over the prior art but are not common to all the claimed inventions and therefore cannot provide the required technical relationship. The only feature common to all of the claimed inventions and which provides a technical relationship among them is "a potassium intercalated molybdenum oxide (K_xMoO_3) nanowire"

However this feature does not make a contribution over the prior art because it is disclosed in:

HU Z. et. al.: "K-enriched MoO_3 Nanobundles: A layered Structure with High Electric Conductivity", The Journal of Physical Chemistry C, 2012, 116, 3962-3967

Therefore in the light of this document this common feature cannot be a special technical feature. Therefore there is no special technical feature common to all the claimed inventions and the requirements for unity of invention are consequently not satisfied *a posteriori*.

INTERNATIONAL SEARCH REPORT Information on patent family members		International application No. PCT/SG2013/000096	
This Annex lists known patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.			
Patent Document/s Cited in Search Report		Patent Family Member/s	
Publication Number	Publication Date	Publication Number	Publication Date
US 2008/0257204 A1 23 Oct 2008 US 2008257204 A1 23 Oct 2008 US 7641728 B2 05 Jan 2010 WO 2008131394 A1 30 Oct 2008			
End of Annex			
Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001. Form PCT/ISA/210 (Family Annex)(July 2009)			