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[Continued on next page]

(54) Title: PROCESS FOR PRODUCING AROMATIC COMPOUNDS USING LIGHT ALKANES

(57) Abstract: There is provided a new process using heat or photoenergy for catalizing the production of aromatic compounds such as benzene, toluene and xylene from C_1-C_6 alkanes or cycloalkanes. The process is carried out in presence of a type IIIA metal nitride such as Ga N as the catalyst.

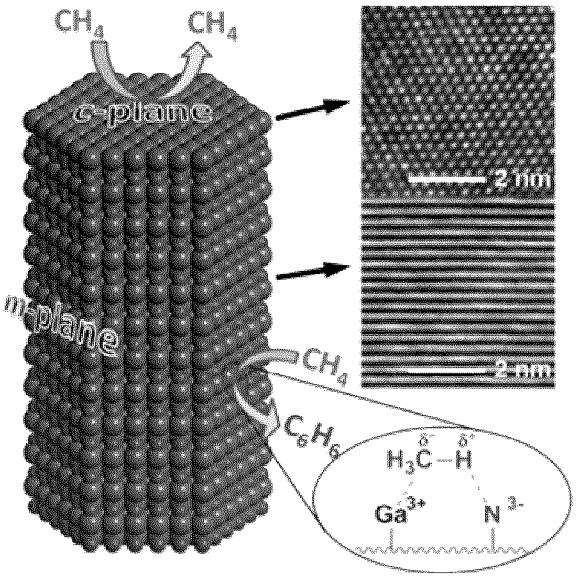

Figure 6

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PROCESS FOR PRODUCING AROMATIC COMPOUNDS USING LIGHT ALKANES

FIELD OF THE DISCLOSURE

[0001] The invention relates generally to a process for the conversion of light alkanes into aromatic compounds.

BACKGROUND OF THE DISCLOSURE

[0002] As one of the key building blocks in the chemical industry, aromatic compounds are mainly derived from the catalytic reforming of petroleum-based long chain hydrocarbons (Ahuja, R. *et al.*, Nature Chem. 3, 167-171 (2010)). There are only few examples of forming aromatic compounds directly from short-chain alkanes (Zheng, H. *et al.*, J. Am. Chem. Soc. 130, 3722-3723 (2008) and Luzgin, M. V. *et al.*, Angew. Chem. Int. Ed. 47, 4559-4562 (2008)). However, an elevated temperature, owing to the large positive Gibbs free energy as per equation (1) below, is required to promote the equilibrium conversions of methane.

$$6\ CH_4 \rightarrow C_6H_6 + 9\ H_2, \quad \Delta G_{(298\ K)} = 434\ kJ/mol \qquad (1)$$

[0003] This caused a major concern of great shortage of aromatic compounds for shale-gas-based future chemical industry. New catalysts, either thermocatalysts or photocatalysts would be useful for in an attempt to cut down on the energy required to produce such aromatic compounds. Compared to the thermal strategies, a compelling approach is using photoenergy to drive the conversion of methane under mild conditions (Yuliati, L. & Yoshida, H. Chem. Soc. Rev. 37, 1592-1602 (2008)). The energy of input photons can break the thermodynamic barrier and make it possible to realize methane conversion reactions even at room temperature. Recently, various researchers (Yoshida, H., *et al.*, J. Phys. Chem. B 107, 8355-8362 (2003); Yuliati, L., *et al.*, J. Catal. 238, 214-220 (2006); Li, L. *et al.*, Angew. Chem. Int. Ed. 50, 8299-8303 (2011); and Li, L. *et al.*, Angew. Chem. Int. Ed. 51, 4702-4706 (2012)) developed several photocatalysts for methane conversion, respectively, such as SiO_2-Al_2O_3 oxides with highly dispersed Ti and Zn^+ modify ZSM-5 zeolite. However, none of these powdered photocatalysts previously reported can produce aromatic compounds and the methane conversion rate is still low (< 10 $\mu mol \cdot h^{-1} \cdot g^{-1}$). It is noted that most of these photocatalysts are insulator-supported (SiO_2 or zeolites) materials, which have large band gap and low optical adsorption. Nevertheless, the widely used metal oxide semiconductors (such as TiO_2, ZnO and Cu_2O) are not suitable supports for the methane conversion reaction, simply because they are not stable and the lattice oxygen can be abstracted by the produced hydrogen in the harsh gas-solid environment (Yuliati *et al.*, and Li *et al.*, *supra*).

SUMMARY

[0004] The present invention therefore provides a new process for producing aromatic compounds from light alkanes, using a group IIIA metal nitride catalyst with either thermal energy or photonic energy.

[0005] In an aspect of the disclosure, there is provided a photocatalytic process for the conversion of a light alkane into an aromatic compound and molecular hydrogen, said process comprising the steps of:

a) combining a gaseous light alkane with a catalyst comprising at least a group IIIA metal nitride as a reaction mixture, and

b) adding to the reaction mixture, photoenergy absorbable by said catalyst to yield an aromatic compound and molecular hydrogen.

[0006] The catalyst can be gallium nitride.

[0007] The catalyst can also be doped, and is preferably Si-doped n-type gallium nitride.

[0008] The catalyst has preferably a nano or microstructured material, such as a nanowire. The catalyst can also be film or a powder.

[0009] The photoenergy can be solar illumination. It can also be UV illumination between 290-380 nm, preferably between 290 nm and 360 nm or between 360-380 nm. Solar illumination can also be in the visible light between 400 nm and 550 nm.

[0010] The light alkane can be methane, ethane, propane, butane, pentane, hexane, cyclohexane or a mixture thereof, but is preferably methane, ethane, propane, butane, or a mixture thereof, and is more preferably methane, ethane, or a mixture thereof. Most preferably, the light alkane is ethane or methane.

[0011] The aromatic compound that can be produced with the process can be benzene.

[0012] In accordance with a further embodiment, there is provided a process for the conversion of a light alkane into an aromatic compound, said process comprising the steps of:

a) combining a light alkane with a catalyst comprising at least a group IIIA metal nitride as a reaction mixture, and

b) heating the reaction mixture to a temperature above 250°C to yield an aromatic compound.

[0013] The reaction mixture is preferably heated at a temperature above 300°C, more preferably above 350°C, or above 400°C, and most preferably between 375 to 425°C, between 395 and 405°C, between 450°C and 550°C, or between 650°C and 700°C .

[0014] The catalyst can be dried before the reaction.

[0015] The catalyst can be gallium nitride.

[0016] The catalyst can also be doped, and is preferably Si-doped n-type gallium nitride.

[0017] The catalyst has preferably a nano or microstructured material, such as a nanowire. The catalyst can also be film or a powder.

[0018] The light alkane can be methane, ethane, propane, butane, pentane, hexane, cyclohexane or a mixture thereof, but is preferably methane, ethane, propane, butane, or a mixture thereof, and is more preferably methane, ethane, or a mixture thereof. Most preferably, the light alkane is ethane or methane.

[0019] The aromatic compound that can be produced with the process can be benzene.

[0020] In accordance with a further embodiment, there is provided the use of the process as described above for producing molecular hydrogen.

[0021] Still in accordance with the present invention, there is provided the use of the process as described above for producing an aromatic compound.

[0022] The aromatic compound can be at least on of benzene, toluene and xylene.

BRIEF DESCRIPTION OF THE FIGURES

[0023] Further aspects and advantages of the present invention will become better understood with reference to the description in association with the following drawings in which:

[0024] Figs. 1A to 1F illustrate the characterization of the as-synthesized GaN samples by SEM (1A), by low- (1B) and high-resolution (1C) TEM images, by diameter distribution (1D), by room temperature photoluminescence (PL) spectrum (1E) of the as-synthesized GaN nanowires GaN 800nm, and by powder X-ray diffraction patterns of wurtzite GaN samples in the forms of nanowire, thin-film and powder (1F, from top to bottom);

[0025] Figs 2A and 2B illustrate the photocatalytic performances of different GaN samples for converting methane (2A) and ethylene (2B) for different forms and the total surface area of GaN catalysts used in the test;

[0026] Fig. 3 illustrates the UV-vis absorption spectrum of GaN thin-films grown on sapphire;

[0027] Fig. 4 illustrates the TEM image of the commercial GaN powdered samples;

[0028] Figs. 5A to 5C illustrates the TEM image of the exposed c- and m-planes in GaN powders (5A) and the corresponding electron diffraction patterns of c- (5B) and m-planes (5C);

[0029] Fig. 6 illustrates a schematic diagram for the interaction between m-plane and adsorbed methane and the C-H bond polarization on the surface of GaN m-plane;

[0030] Fig. 7 illustrates the methane consumption curve upon the initial irradiation time;

[0031] Figs. 8A and 8B illustrates SEM images of Mg-doped p-type (8A) and Si-doped n-type (8B) GaN nanowires;

[0032] Fig. 9 illustrates the methane conversion rate and benzene selectivity over a slice (each of an area of 3.5cm^2) of intrinsic GaN NWs, n-type GaN NWs, p-type GaN NWs and pure Si substrate under UV irradiation (290-380 nm) for 12 hours;

[0033] Fig. 10 illustrates the proposed mechanism of the photocatalytic methane dehydroaromatization reaction;

[0034] Fig. 11 illustrates the amount of converted CH_4, C_2H_6, C_2H_4 and C_2H_2 as a function of the UV irradiation time for the dehydroaromatization reaction over n-type GaN NWs;

[0035] Fig. 12 illustrates a plot of the methane consumption and quantum yield (inset) over n-type GaN NWs in 12 h as a function of the light intensity;

[0036] Fig. 13 illustrates the XRD patterns of GaN nanowires before (bottom) and after (top) the oxygen plasma treatment;.

[0037] Fig. 14 illustrates the equilibrium conversions of non-oxidative dehydroaromatization of various light alkanes as a function of temperature;

[0038] Figs. 15A and 15B illustrate the product distributions obtained in the light alkane aromatization reaction over GaN powders in the absence of any oxidant (15A) and the benzene yield as a function of time, using pure n-hexane over GaN powders (15B); and

[0039] Figs. 16A and 16B illustrate the conversion of methane (16A) and propane (16B) as a function of time over GaN (top curves) and Ga_2O_3 (bottom curves) powders under 400°C, respectively.

DESCRIPTION OF THE EMBODIMENTS

[0040] This invention is not limited in its application to the details of construction and the arrangement of components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments and of being practiced or of being carried out in various ways. Also, the phraseology and terminology used herein is for the purpose of description and should not be regarded as limiting. The use of "including", "comprising", or "having", "containing", "involving" and variations thereof herein, is meant to encompass the items listed thereafter as well as, optionally, additional items. In the following description, the same numerical references refer to similar elements. In the drawings, like reference characters designate like or similar parts.

[0041] The term "light alkane" represents a linear or branched C_1-C_6 alkane or cyclohexane. Examples of "light alkane" include but is not limited to methane, ethane, propane, butane (or n-butane), pentane (or n-pentane) and hexane (or n-hexane). The term "alkane" is also meant to include alkanes such as n-butane or isobutane, isopentane, neopentane, isohexane, and neohexane.

[0042] The term "aromatic" represents a carbocyclic moiety containing at least one benzenoid-type ring. Examples include but are not limited to benzene, xylenes, toluene, hemilitene, pseudocumene, and mesitylene.

[0043] The term "nano material" represents materials with any external dimension in the nanoscale or having internal structure or surface structure in the nanoscale. Examples of "nano materials" include but are not limited to nanoparticles, nanowires, nanotubes, nanoribbons, nanocrystals, nanorods, and metal-organic frameworks (MOFs).

[0044] The term "microstructured material" represents materials that have on their surface structures can be revealed using a range of microscopy techniques. Examples of "microstructured materials" include but are not limited to sheets, rods, crystals, amorphous solids, and micro and mesoporous solids.

[0045] The term group IIIA metal represents the metal in the group IIIA of the periodic table of elements. In one embodiment, the preferred group IIIA metal is aluminum, gallium, or indium. In another embodiment, the preferred metal is aluminum. In a further embodiment, the preferred metal is gallium. In still another embodiment, the preferred metal is indium.

[0046] GaN semiconductors are known in the art, and GaN nanowires are well characterized in the art. However, the present invention unveils for the first time the use of the GaN nanowires as catalist for in a process for producing aromatic compounds from light alkanes. Gallium is a

group IIIA compound. Other group IIIA metal nitride compounds are also known in the art to have similar properties as GaN, such as AlN and InN. Hence, although the experiments illustrated herewith were conducted with GaN, the person of the art will appreciate that the results reported herein are directly extrapolated to other group IIIA nitride compounds, and that such other group IIIA nitride compounds will also be useful as GaN for converting light alkanes into aromatic compounds according to the process described herein.

[0047] The recent discovery of an enormous amount of shale gas is projected to change the landscape of the future chemical industry (Richard, A. K., Science 328, 1624-1626 (2010)), since through suitable conversions shale gas may replace the dwindling petroleum resources as a carbon-based feedstock (Choudhary, V. R., *et al.*, Science 275, 1286-1288 (1997); Lunsford, J. H., Catal. Today 63, 165-174 (2000); Periana, R. A., *et al.*, Science 301, 814-818 (2003); Holmen, A., Catal. Today 142, 2-8 (2009); Balasubramanian, R. *et al.*, Nature 465, 115-119 (2010); and Schwarz, H., Angew. Chem. Int. Ed. 50, 10096-10115 (2011)). Unfortunately, due to the inert C-H bonds in methane and other light alkanes (Bergman, R. G. Nature 446, 391-393 (2007)), there has been no easy way of turning shale gas into synthetically useful compounds such as olefins and aromatics, especially hard for the latter (Wang, D. J., *et al.*, J. Catal. 169, 347-358 (1997)). Herein there is reported the new use of well-defined semi-conductor compounds as catalysts for producing from light alkanes and cyclohexane, aromatic compounds and molecular hydrogen. Indeed, the design and synthesis of well-defined group IIIA metal nitride, such as gallium nitride (GaN) semiconductors that can directly convert light alkanes such as methane (or ethane) into benzene and molecular hydrogen at room temperature for the first time, and also converting methane and other light alkanes into benzene at temperature under thermal conditions. The process can thus be a photocatalytic process or a thermal process.

[0048] Mechanistic studies suggest that the exposed m-plane of GaN exhibited particular activity toward methane C-H bond cleavage process and the overall quantum efficiency increased linearly as a function of light intensity. The incorporation of dopants into GaN also has a large influence on the photocatalytic performance. Therefore, the optimized Si-doped GaN nanowires with 97% rationally constructed m-plane can convert methane to benzene at a very fast rate of 325 $\mu molh^{-1}g^{-1}$ with 94% selectivity in 36-hour with near ultraviolet (UV) illumination (290-380 nm). The results demonstrate that the polarizing ability of catalysts is highly beneficial to methane C-H bond activation. It is anticipated that the low synthetic cost of the wafer-based GaN nanowires and the power-dependent feature of the quantum efficiency pave the way to large-scale methane to benzene conversion under concentrated solar power.

[0049] With dopants, it is now possible to modulate the amount of energy, or the type of energy (from UV to visible wavelengths) required to carry out the process. As an example, InN has a K_{ev} of 0.67 eV. However, In can be combined with Ga to form $In_xGa_{(1-x)}N$ with a band

spanning from 0.7 eV to 3.4eV, spanning over the UV-visible spectrum. Hence irradiation with visible light is also contemplated with such compounds or with a n-type doped group IIIA metal nitride calalyst. The band gap of InN allows for wavelengths as long as 1900 nm to be used. Still doping the GaN with erbium for example would allow a band gap near 1000-1500 nm. Such Group IIIA metal nitride, their synthesis and the method for doping them to obtain modified properties have been well studied and characterized.

[0050] GaN is a well-known group IIIA nitride semiconductor commercially available with the direct energy band gap of ~3.4 eV at room temperature (Han, W. Q., et al., Science 277, 1287-1289 (1997)). Compared with metal oxide semiconductors, the controlled n- and p-type doping and the inherent chemical stability make GaN a suitable electronically active support for the photocatalytic reaction under harsh conditions (Schäfer, S. et al. J. Am. Chem. Soc. 134, 12528-12535 (2012)). Furthermore, compared with conventional powdered photocatalysts, nanowires are preferred for their large surface-to-volume ratios and superior photoelectric properties (Garnett, E. & Yang, P. D. Nano Lett. 10, 1082-1087 (2010)). Consequently, the inventors synthesized pure (intrinsic) GaN nanowires (GaN NWs) with a length of 800 nm grown on a silicon substrate by plasma-assisted molecular beam epitaxy (MBE) under nitrogen-rich conditions. Scanning electron microscopy (SEM, Fig. 1A) and transmission electron microscopy (TEM, Figs. 1B and 1C) images of the as-synthesized GaN NWs revealed that the nanowires possess hexagonal cross sections (see the inset of Fig. 1A showing the top view of one nanowire) and are vertically aligned to the substrate, with the morphology slightly tapered from top to bottom. Electron diffraction pattern indicates that the wires are of single crystal wurtzite structure and the growth direction is $(000\ \bar{1})$, with the top facet of c-plane and lateral facet of m-plane. The diameter distribution of the top facets derived from SEM measurements fits well in a logarithmic normal distribution with a mean diameter of $d_{NWs} = 100 \pm 5$ nm (Fig. 1D). Fig. 1E gives room temperature photoluminescence (PL) spectrum of GaN NWs with an intensive peak around 365 nm, corresponding to the band gap of 3.4 eV. To evaluate the photo-catalytic performance of GaN semiconductor comprehensively, GaN thin-films (Fig. 3) with the thickness of 650 nm grown on sapphire prepared using AlN as the buffer layer by metal organic chemical vapor deposition (MOCVD) and commercial powdered samples (Fig. 4) have also been used. The spectrum illustrated in Fig. 3 is characterized by the well-known oscillations appearing when a transparent thin film of a material of high refractive index (2.29 for GaN) is deposited on a lower refractive index substrate (1.726 for sapphire). As shown in Fig. 1F, due to the orientated growth on the Si substrates, the only reflections of GaN NWs and thin-films obtained from X-ray diffraction (XRD) measurements are 002 and 004 (Chuaha, L.S., *et al.*, J. Alloys Compd. 481, 15-19 (2009)), which further confirm that the top facet of GaN NWs and thin-films is c-plane. The area densities of the nanowires and thin-films are measured to be 0.1 $mg \cdot cm^{-2}$ and 0.4 $mg \cdot cm^{-2}$, respectively.

[0051] The performances of the intrinsic GaN materials in different forms for the photocatalytic methane conversion reaction were tested at 5°C under UV irradiation from a 300-W xenon lamp. To quantitatively evaluate the photocatalytic activities under solar UV illumination (290-380 nm), a set of UV filters was carefully mounted in the system to completely block wavelengths shorter than 290 nm and longer than 380 nm from the xenon lamp. After reactions, the GaN NWs were found to show the highest photo-activity for the methane dehydroaromatization reactions among all the GaN samples tested. The catalytic reaction led to the formation of benzene with nearly 9 times molar amounts of H_2, as confirmed by gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) (see Table 1, entry 1, below).

[0052] The results presented in Table 1 below were obtained from reactions carried out at a temperature of 5°C; using 150 μmol of methane as reactants; and irrading at a wavelenght of 290-380 nm using an UV irradiation at an intensity of 7.5 $mWcm^{-2}$ for 12 h. The reaction was preferably conducted under high vacuum such that when pentane or hexane is used as reactants, these alkanes are as well gaseous. After the reaction, the amounts of hydrogen or carbon oxides (if any) were directly measured by gas chromatography with a thermal conductivity detector (TCD). The organic products were thermally desorbed by heating the catalyst gradually up to 250°C (and this temperature was kept for 60 min) under evacuation, collected with a liquid N_2 trap, and analyzed by gas chromatography and gas chromatography-mass spectrometry.

Table 1

Results of various samples for photocatalytic methane conversion

Entry	Substrates	Amount (mg)	Converted Methane ($\mu mol \times 10^{-2}$)	Yield ($\mu mol \times 10^{-2}$)				
				Benzene	toluene	Ethane	Ethylene	Hydrogen
1	i-GaN NWs	0.35 (3.5 cm^2)	59.37	9.53	n.d.[a]	1.04	0.01	88.60
2	i-GaN powders	0.35 (3.5 cm^2)	12.14	1.97	n.d.	0.05	n.d.	18.09
3	i-GaN thin-films	4.0 (10.0 cm^2)	0	n.d.	n.d.	n.d.	n.d.	n.d.
4	i-GaN NWs-400	0.17 (3.5 cm^2)	25.13	4.15	n.d.	0.07	n.d.	37.61
5	n-GaN NWs	0.35 (3.5 cm^2)	147.34	23.36	0.21	1.37	0.21	220.09
6	p-GaN NWs	0.35 (3.5 cm^2)	11.78	1.90	n.d.	0.11	0.04	17.55
7	n-GaN NWs[b]	0.35 (3.5 cm^2)	410.12	63.70	0.87	7.34	2.65	615.12
8	Si substrate	250 (3.5 cm^2)	trace	n.d.	n.d.	n.d.	n.d.	trace

[a] Not detectable

[b] Irradiation time: 36 h.

[0053] The selectivity for benzene over alternative hydrocarbon products (toluene, ethane and ethylene) was measured to be 96.5%. Carbon mass balances during the conversion were close to 100% and no carbon oxides were detected by GC. Using a series of UV long-pass cut-out filters from 320 to 375 nm the minimum light energy required to drive this reaction over GaN samples was determined to correspond to a wavelength of 360 nm. No activity was detected under darkness. Besides GaN NWs, GaN powders (Table 1, entry 2) also showed a substantial activity but GaN thin-films (Table 1, entry 3) did not show any photo-activity for methane conversion at all. It is counterintuitive, as the strong piezoelectric field in GaN thin-films can induce effective photo-excited carrier separation, and thus the quantum efficiency of typical

photocatalytic reactions like water splitting was enhanced by GaN thin-films compared to the powdered sample as reported by the inventors (Wang, D. F. *et al.*, Nano Lett. 11, 2353-2357 (2011)).

[0054] Specific to alkane conversion, the exposure of active facets of catalysts for C-H bond activation plays a crucial role in determining the overall catalytic activities (Zhong, D. Y. et al. Science 334, 213-216 (2011)). In this regard, the structural effect of GaN materials on the photocatalytic performances was comprehensively investigated. The specific surface area of GaN NWs can be calculated to be 5.7 m^2/g by measuring their densities, diameters and lengths. The proportions of the top c-plane and lateral m-plane are 3% and 97%, respectively. The Brunauer–Emmett–Teller (BET) specific surface area of GaN powders is 3.2 m^2/g and the TEM image (Fig. 5A) reveals that the amount of exposed c-planes is in the same level as that of exposed m-planes on the surface of powdered samples. In the case of GaN thin-films, the exposed surface is entirely c-plane as confirmed by XRD. Obviously, the surface area of the planar samples is independent of its thickness and mass, but only depends on the dimension of the slice used (10.0 cm^2 in the test reported herein). For further comparison, a slice of short GaN NW sample with the length of 400 nm and an average diameter of 80 nm was prepared (designated as GaN nanowires-400) by simply reducing the growth times (Table 1, entry 4). Fig. 2A presents the total surface area of each catalyst used in the test and their corresponding photoactivities for the methane conversion reaction. It is noted that the performance of GaN materials depends strongly on their exposed m-plane but is not correlated with c-plane. GaN thin-films have negligible m-plane exposed and hence are unable to convert methane. In contrast, when the photocatalytic dehydroaromatization reaction was attempted using pure ethylene instead of methane as the reactant, both c-plane and m-plane showed remarkable activities (Fig. 2B). These observations unambiguously indicate that the exposed m-plane is the catalytically active facet for the photo-driven methane dehydroaromatization reactions. In Figs. 2A and 2B, 0.35 mg of GaN nanowires, 0.17 mg of GaN nanowires-400, 0.35 mg of GaN powders and 4.0 mg of GaN thin-films were respectively irradiated in the reaction process at 290-380 nm and at an intensity of 7.5 $mWcm^{-2}$ for 12 hours.

[0055] As shown in Fig. 6, the m-plane of ideal wurtzite GaN is composed of binary gallium and nitrogen atoms tetrahedrally coordinated with each other, whereas the c-plane contains only one type of atom (gallium or nitrogen). In the exposed GaN m-plane, Ga^{3+} and N^{3-} can interact with the methyl group and H atom of the adsorbed methane molecule, respectively. The GaN lattice is consisted of alternating positively-charged Ga and negatively-charged N atomic planes, which can produce strong electrostatic polarization along the c-direction and thus, stretch the methane molecules absorbed on m-plane. Note that the length of the Ga-N bond in m-plane is 1.95Å, which is significantly longer than methane C-H bond (1.09 Å), as evidence by the inset of Fig. 6 which illustrates high-resolution TEM images of the top c-plane and lateral m-

plane of GaN and hence, such length is highly beneficial to stretching the C-H bond. The polarized methane C-H bond is significantly weakened, promoting its cleavage under UV irradiation. However, c-plane is made up of only Ga (or N) atoms. The absence of dipoles in the exposed c-plane leave the C-H bond of the absorbed methane molecule intact, which cannot be broken by photons with energy <4.3 eV (290 nm). More importantly, an induction period was observed when the UV illumination started immediately upon the exposure of GaN NWs to methane (Fig. 7). For comparison, if GaN NWs were exposed to methane in darkness for 24-hour prior to the UV illumination, the GaN NWs would show a constant conversion rate since the UV irradiation, and no induction period was observed. This observation clearly indicates that the process of methane adsorption and polarization on the surface of GaN has a large influence on the photocatalytic process.

[0056] The incorporation of silicon or magnesium dopants (for example) into GaN NWs can alter its surface band bending and carrier transport properties (Zhang, Z. & Yates, Jr. J. T., Chem. Rev. 112, 5520-5551 (2012)). To evaluate the effect of doping on the activity of GaN NWs, Si-doped n-type and Mg-doped p-type GaN NWs (Figs. 8A and 8B) were synthetized. As shown in Fig. 9, the n-type GaN NWs (Table 1, entry 5) exhibited significantly enhanced photoactivity for methane dehydroaromatization compared to the intrinsic ones. On the other hand, the activity of p-type GaN NWs (Table 1, entry 6) was severely reduced. These results are consistent with the mechanism of photoinduced methane C-H bond activation proposed earlier by Li et al., (2011 and 2012, *supra*). Upon UV irradiation, the photogenerated electrons in the conduction band migrate to the surface of GaN NWs, and then jump to the empty C-H σ*-antibonding orbitals of the polarized methane, followed by the cleavage of methane C-H bond. Consequently, the more free electrons can reach the interface, the more facile the conversion of methane becomes. Obviously, the concentration of free electron on the surface of n-type (majority carrier) nanowires is much higher than those of intrinsic and p-type (minority carrier) ones. The surface electron concentration of n-type will be further increased under illumination due to the reduction of surface band bending, the energy barrier of electron transfer (Kronik, L. & Shapira, Y., Surf. Interface Anal. 31, 954-965 (2001)). Therefore, the photocatalytic performance of n-type GaN is remarkably enhanced.

[0057] An average methane conversion rate of 325 $\mu molh^{-1}g^{-1}$ was achieved after 36 hour-UV irradiation by using 0.35 mg of n-type GaN NWs (Table 1, entry 7). Besides methane, the n-type GaN NWs also show a high photoactivity for the dehydroaromatization of ethane into benzene. For comparison, the univalent zinc material reported previously exhibits a methane conversion rate of 9.8 $\mu molh^{-1}$ g^{-1} and no activity for ethane (Li *et al.*, 2011, *supra*). None of other previously reported materials shows any photoactivity under these conditions (they can only work under UVC light shorter than 270 nm)(Yuliati *et al.*, *supra*). During the reactions, butane, hexane and cyclohexane were not detected; whereas small amounts of ethane and

ethylene were observed. On the basis of these experimental results, a plausible mechanism was proposed as shown in Fig. 10. The dehydroaromatization reaction starts with the polarization of methane on the exposed m-plane (dark reaction), followed by breaking the methane C-H bond under UV irradiation and subsequent C-C coupling reaction, forming ethane and hydrogen. The ethylene produced from the ethane dehydrogenation reaction can further lose its hydrogen to form acetylene. Finally, benzene is formed from the cyclization of acetylene. The reaction rate of each step over n-type GaN NWs can be estimated by using pure methane, ethane, ethylene and acetylene as the reactants, respectively (Fig. 11). It is indicated that the cleavage of methane C-H bond and subsequent C-C coupling reaction is the rate-determining step in the overall dehydroaromatization reaction. The extremely high conversion rate of acetylene cyclization to benzene can explain why no acetylene produced during the reaction could be detected. To pinpoint the detailed mechanism, the catalytic performances of n-type GaN NWs under varying light intensity (Fig. 12) were tested. The experimental results revealed that the methane conversion rate is proportional to the square of light intensity, and hence the quantum yield increases linearly as a function of light intensity. This observation indicates that the process of methane C-H bond cleavage, which is the rate-determining step, requires two photons to break two independent C-H bonds simultaneously and form ethane and hydrogen (Kim, J. D., *et al.*, Proc. Natl. Acad. Sci. U.S.A. 110, 10073-10077 (2013)).

[0058] The performance of GaN NWs was repeatedly tested and has shown that it can be used repeatedly without noticeable deactivation after several cycles. The reactions were conducted at a temperature of 5°C, with 150 μmol of methane as reactant, irradiating with a source between 290-380 nm UV irradiation at an intensity of 7.5 $mWcm^{-2}$, for 12 h (of irradiating time) for each cycle. If desired, the hydrocarbon products adsorbed on the surface of GaN NWs can be completely stripped by an oxygen plasma treatment whereas the crystal structure remained intact (Fig. 13). More importantly, the lattice Ga^{3+} remained unchanged during the methane conversion reaction. Neither of the binding energy peaks with maxima at 19.1 (typical for Ga^{+}) and 17.7 eV (typical for Ga^{0}) was detected after a long time reaction (Serykh, A. I. & Amiridis, M. D. Surf. Sci. 603, 2037-2041 (2009)). Therefore, GaN materials have proven to be highly stable for the methane conversion reaction.

[0059] In another embodiment, the invention relates to a process using type IIIA metal catalyst, such as gallium-based catalyst for the conversion of light alkanes into aromatic hydrocarbons upon heating. GaN is an active and stable catalyst for the dehydroaromatization of light alkanes (from C1 to C6 alkanes and cyclohexane) with high benzene selectivity at elevated temperature. Using density functional theory calculations, a detailed mechanism explains the cleavage of the first C-H bond of methane occurring on the surface of GaN, which is the crucial step in the overall conversion of methane.

[0060] As to light alkane dehydroaromatization reactions in the absence of any oxidant [Equation (2)], considerable conversions can only be expected at high temperature (see Fig. 14). GaN, with Wurtzite crystal structure, which is mechanically and chemically stable, is appropriate for use in harsh industrial environments. Herein, an example of non-oxidative conversion of light alkanes (from C1 to C6 alkanes) to benzene is described using GaN catalyst. Compared with Ga_2O_3, GaN exhibits higher aromatization activity and aromatic selectivity under the identical conditions.

[0061] $$6\ C_nH_{2n+2} \rightarrow n\ C_6H_6 + 3(n+2)\ H_2 \qquad (2)$$

[0062] The catalytic performances of GaN catalyst for the aromatization of light alkanes were carried out at 400°C in an airtight quartz reactor for 24 hours. Specifically, 20 mg of GaN powders was spread evenly on the bottom of the reactor in vacuum, which was then evacuated at 550°C for 2 h to remove water and other molecules adsorbed in the powders. Afterwards, the reactor was cooled to 400°C under vacuum, followed by reacting with 100 μmol of corresponding light alkane. The organic products were analyzed by gas chromatography and gas chromatography-mass spectrometry.

[0063] As shown in Fig. 15A, GaN powders showed aromatization ability for all examined alkanes from methane to n-hexane. The catalytic reaction led to the formation of benzene as the major aromatic product as well as other unsaturated hydrocarbons such as cyclohexene and toluene. Among all the light alkanes tested, propane and n-hexane gave the highest benzene selectivity (87%) and the highest conversion (10.9%), respectively. Figure 15B shows the time courses of benzene evolution from n-hexane over 20 mg of GaN powders. According to the data, GaN powders showed a constant conversion rate within 48 hours, and no induction period was observed, indicating that GaN is the active species in the activation of methane. Furthermore, after long time reaction (> 48 hours) in the presence of n-hexane at 400°C, the XPS spectrum for the GaN material was essentially the same as that for the parent GaN; neither of the binding energy peaks with maxima at 19.1 (typical for Ga^+) and 17.7 eV (typical for Ga^0) was detected, and the only gallium signal in the XPS spectrum corresponds to Ga3+ species. These results further confirm that the Ga^{3+} cations in GaN are not reduced to become additional active centers during the aromatization reaction.

[0064] To further demonstrate the activity of GaN, pure Ga_2O_3 powders was used as a reference in the methane (Fig. 16A) and propane (Fig. 16B) aromatization reactions in parallel to GaN powders under the same conditions and only small proportion of aromatic products was detected. The performance of GaN can be used repeatedly without noticeable deactivation after the calcination treatment in oxygen at 550°C, whereas the crystal structure remained intact.

[0065] In summary, a new process has now been unveiled for using a gallium-based catalyst for the conversion of light alkanes into aromatic hydrocarbons. Compared with gallium oxide, GaN exhibit higher activity for C-H activation of light alkanes and higher selectivity towards the formation of benzene.

[0066] The compounds of the present disclosure can be prepared according to the procedures denoted in the following Examples or modifications thereof using readily available starting materials, reagents, and conventional procedures or variations thereof well-known to a practitioner of ordinary skill in the art of inorganic chemistry.

Example 1

Growth of GaN Nanowires

[0067] The catalyst-free GaN nanowires are grown on a Si (111) substrate using a radio frequency plasma-assisted molecular beam epitaxy (MBE) in nitrogen rich conditions. Prior to loading into the MBE system, the Si substrates were cleaned by hydrofluoric acid and standard solvent solutions. Growth conditions include the following: a temperature of ~750°C, nitrogen flow rate of 1-2 sccm, and a forward plasma power of ~400 W. The synthesized nanowires can be doped with tetravalent (Si4+) and divalent (Mg2+) ions to make it n and p type, respectively. The doping density is controlled by tuning the effusion cell temperatures of Si and Mg. Usually, the higher the effusion cell temperature is, the higher the doping density is. For n-type doping the Si effusion cell temperature is 1350°C. For P-doping, the Mg effusion cell temperature is 265°C. As a result, Si-doped n-type and Mg-doped p-type GaN NWs have been synthesized with net carrier concentrations (300 K) of n = 5 × 1018 cm^{-3} and p = 1 × 1018 cm^{-3}, respectively. The other growth parameters were kept constant including the growth duration (4 hrs).

Example 2

Photo-Driven Light Alkane Dehydroaromatization Reaction

[0068] A slice of freshly prepared GaN NWs with areas of 3.5 cm^2 (corresponding to 0.35 mg of GaN NWs) or a slice of GaN thin-films with areas of 10.0 cm^2 (corresponding to 4.0 mg of GaN NWs) was placed on the bottom of an air-tight quartz reactor in vacuum, followed by introduction of 150 μmol pure methane (99.999% purity). In the case of powdered GaN samples, 0.35 mg of GaN powder was spread evenly on the bottom of reactor in vacuum, which was then evacuated at 250 °C for 2 h to remove water and other molecules adsorbed in the powders. Afterwards, the reactor was cooled slowly to 5 °C under vacuum, followed by reaction with 150 μmol of pure methane under UV irradiation. The light intensity measured at wavelengths between 290 and 380 nm was ca. 7.5 $mWcm^{-2}$. The hydrocarbon products were analyzed by GC with a flame ionization detector and GC-MS. The amounts of hydrogen or carbon oxides (if any)

were measured by GC with a thermal conductivity detector. The GC and GC-MS traces in the 8 entries in Table 1 above were looked at.

Example 2

General Characterization

[0069] The powder X-ray diffraction (XRD) patterns were recorded on a Bruker D8 Advanced Diffractometer with Cu Kα radiation (λ = 1.5418 Å). High resolution bright field transmission electron microscope (TEM) images were obtained using FEI Tecnai G2 F20 S/TEM at accelerating voltage of 200 kV. Scanning electron microscopy (SEM) images were recorded using LASEM Hitachi S-4700. The UV-vis absorption spectra of the GaN thin-films and UV filters were measured with a Shimadzu UV-2450 spectrophotometer. The X-ray photoelectron spectroscopy (XPS) was performed on an ESCALAB 250 X-ray photoelectron spectrometer with a monochromated X-ray source (Al Kα hυ = 1486.6 eV). The energy scale of the spectrometer was calibrated using $Au_4f_{7/2}$, $Cu2p_{3/2}$, and $Ag3d_{5/2}$ peak positions. The standard deviation for the binding energy (BE) values was 0.1 eV. The Brunauer-Emmett-Teller (BET) surface areas of the samples were measured from the adsorption of N_2 at 77 K by using a Micromeritics ASAP 2020M system. The Raman spectra were obtained with a Senterra confocal Raman spectrometer and the 532 nm radiation from a solid state laser was used as the exciting source, the power of the laser being 350 mW.

Carbon Balance

[0070] The calculation of the carbon balance during the photocatalytic methane dehydroaromatization reaction was carefully performed based on the ratio of carbon output (ethane, ethylene, benzene and toluene) to carbon input (methane), see equation (3):

$$\text{Carbon balance} = \frac{\text{Moles of products in terms of carbon}}{\text{Moles of the converted methane in terms of carbon}} \times 100\ \% \quad (3)$$

[0071] As an example (Table 1, Entry 1), after the reaction, converted methane (0.5937 μmol), produced benzene (0.0953 μmol), ethane (0.0104 μmol) and ethylene (0.0001 μmol) were detected by GC and GC-MS, and none of the carbon oxides (CO_2 and CO) could be detected by GC with a thermal conductivity detector (TCD) from the system. Thus, according to equation (3), the value of the carbon balance under this condition is calculated to be 99.8%:

Carbon balance = (0.0953 × 6 + 0.0104 × 2 + 0.0001 × 2) μmol × 100 % / 0.5937 μmol = 99.8%

Calculation of Conversion and Selectivity

[0072] The conversion of methane is defined as the ratio of moles of methane consumed in the reaction to the total moles of methane initially added (4). The selectivity to benzene is

defined as the ratio of moles of benzene produced to the total moles of all hydrocarbon products in terms of carbon (5).

$$\text{Conversion of methane} = \frac{\text{Moles of methane consumed}}{\text{Moles of methane initially added}} \times 100\,\% \qquad (4)$$

$$\text{Selectivity of ethane} = \frac{\text{Moles of benzene produced in terms of carbon}}{\text{Moles of all hydrocarbon products in terms of carbon}} \times 100\,\% \qquad (5)$$

[0073] While the invention has been described in connection with specific embodiments thereof, it is understood that it is capable of further modifications and that this application is intended to cover any variation, use, or adaptation of the invention following, in general, the principles of the invention and including such departures from the present disclosure that come within known, or customary practice within the art to which the invention pertains and as may be applied to the essential features hereinbefore set forth.

Claims

1. A photocatalytic process for the conversion of a light alkane into an aromatic compound and molecular hydrogen, said process comprising the steps of:
   a) combining a gaseous light alkane with a catalyst comprising at least a group IIIA metal nitride as a reaction mixture, and
   b) adding to the reaction mixture, photoenergy absorbable by said catalyst to yield an aromatic compound and molecular hydrogen.

2. The photocatalytic process according to claim 1, wherein the catalyst is gallium nitride.

3. The photocatalytic process according to claim 1 or 2, wherein the catalyst is Si-doped n-type gallium nitride.

4. The photocatalytic process according to claim 1, 2 or 3, wherein the catalyst is a nano or microstructured material.

5. The photocatalytic process according to claim 4, wherein the catalyst is a nanowire.

6. The photocatalytic process according to any one of claims 1-4, wherein the catalyst is film.

7. The photocatalytic process according to any one of claims 1-4, wherein the catalyst is a powder.

8. The photocatalytic process according to any one of claims 1-7, wherein the photoenergy is solar illumination.

9. The photocatalytic process according to any one of claims 1-8, wherein the photoenergy is UV illumination between 290-380 nm.

10. The photocatalytic process according to claim 9, wherein the photoenergy is UV illumination between 360-380 nm.

11. The photocatalytic process according to any one of claims 1-10, wherein the light alkane is methane, ethane, propane, butane, pentane, hexane, cyclohexane or a mixture thereof.

12. The photocatalytic process according to any one of claims 1-10, wherein the light alkane is methane, ethane, propane, butane, or a mixture thereof.

13. The photocatalytic process according to any one of claims 1-10, wherein the light alkane is methane, ethane, or a mixture thereof.

14. The photocatalytic process according to any one of claims 1-10, wherein the light alkane is ethane.

15. The photocatalytic process according to any one of claims 1-10, wherein the light alkane is methane.

16. The photocatalytic process according to any one of claims 1 to 15, wherein the aromatic compound is benzene.

17. A process for the conversion of a light alkane into an aromatic compound, said process comprising the steps of:

a) combining a light alkane with a catalyst comprising at least a group IIIA metal nitride as a reaction mixture, and

b) heating the reaction mixture to a temperature above 250°C to yield an aromatic compound.

18. A process according to claim 17, wherein the reaction mixture is heated at a temperature above 300°C.

19. A process according to claim 17 or 18, wherein the reaction mixture is heated at a temperature above 350°C.

20. A process according to any one of claims 17 to 19, wherein the reaction mixture is heated at a temperature between 375 to 425°C.

21. A process according to any one of claims 17-20, wherein the reaction mixture is heated at a temperature between 395 to 405°C.

22. A process according to any one of claims 17 to 21, wherein the catalyst is dried before the reaction.

23. The process according to any one of claims 17-22, wherein the catalyst is gallium nitride.

24. The process according to any one of claims 17-22, wherein the catalyst is Si-doped n-type gallium nitride.

25. The process according to any one of claims 17-24, wherein the catalyst is a nano or microstructured material.

26. The process according to claim 25, wherein the catalyst is a nanowire.

27. The process according to any one of claims 17-25, wherein the catalyst is film.

28. The process according to any one of claims 17-25, wherein the catalyst is a powder.

29. The process according to any one of claims 17-28, wherein the light alkane is methane, ethane, propane, butane, pentane, hexane, cyclohexane or a mixture thereof.

30. The process according to any one of claims 17-28, wherein the light alkane is methane, ethane, propane, butane, or a mixture thereof.

31. The process according to any one of claims 17-28, wherein the light alkane is methane, ethane, or a mixture thereof.

32. The process according to any one of claims 17-28, wherein the light alkane is ethane.

33. The process according to any one of claims 17-28, wherein the light alkane is methane.

34. The process according to any one of claims 17-33, wherein the aromatic compound is benzene.

35. Use of the process of any one of claims 1-34 for producing molecular hydrogen.

36. Use of the process of any one of claims 1-34 for producing an aromatic compound.

37. The use of claim 36, wherein the aromatic compound is at least on of benzene, toluene and xylene.

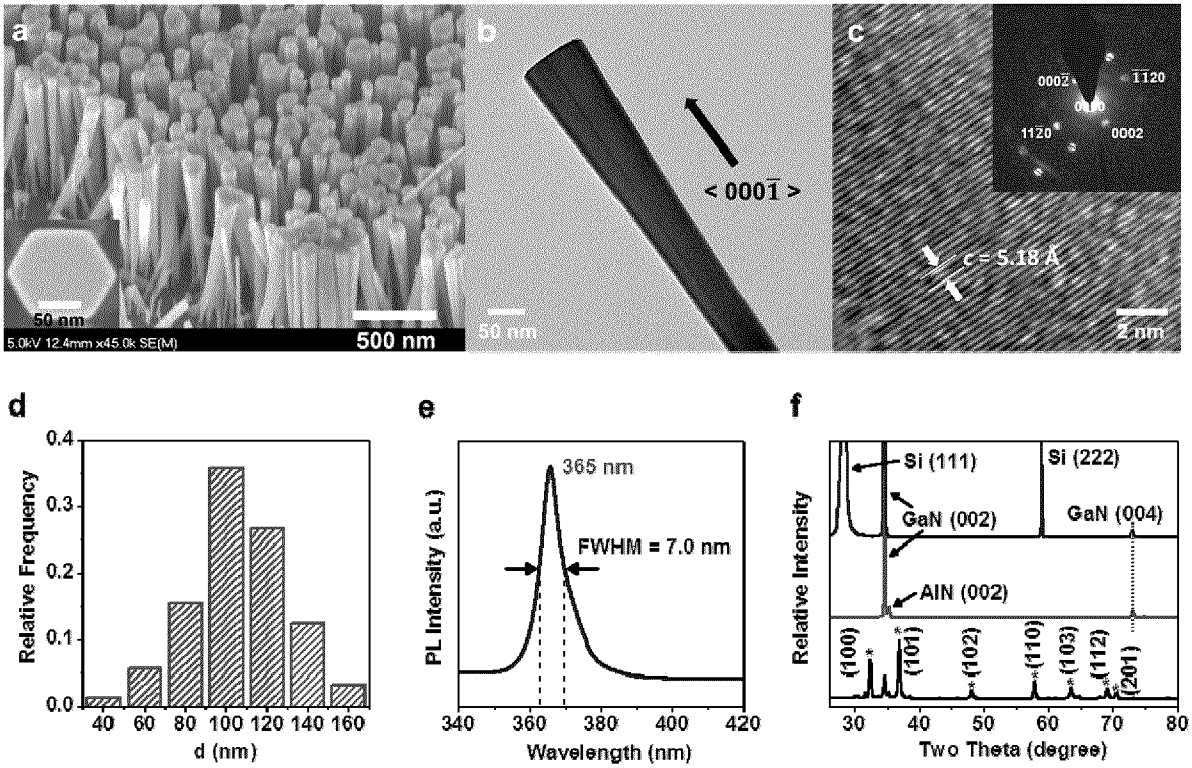

Figure 1

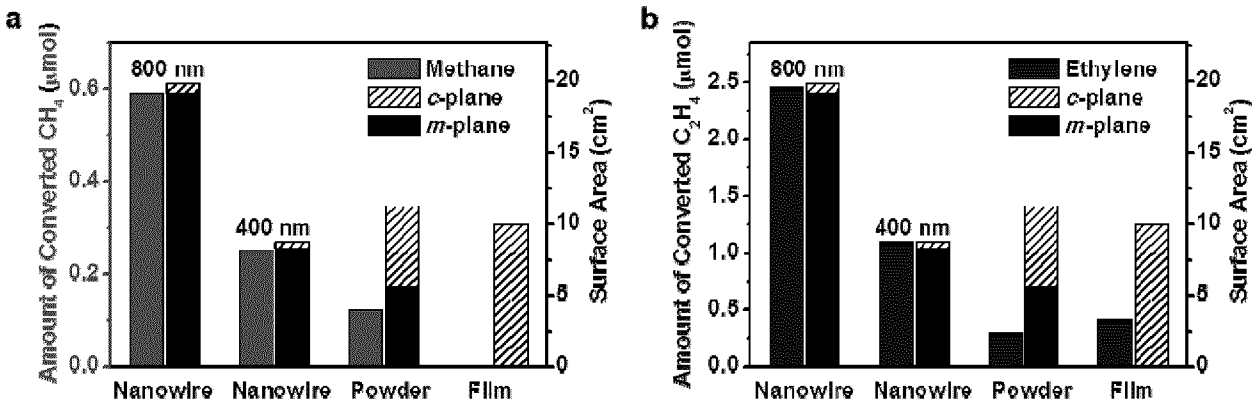

Figure 2

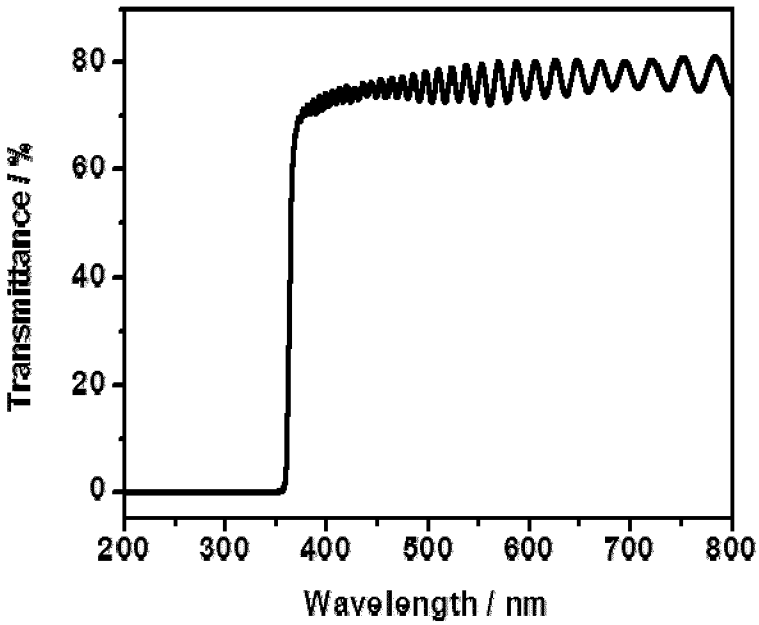

Figure 3

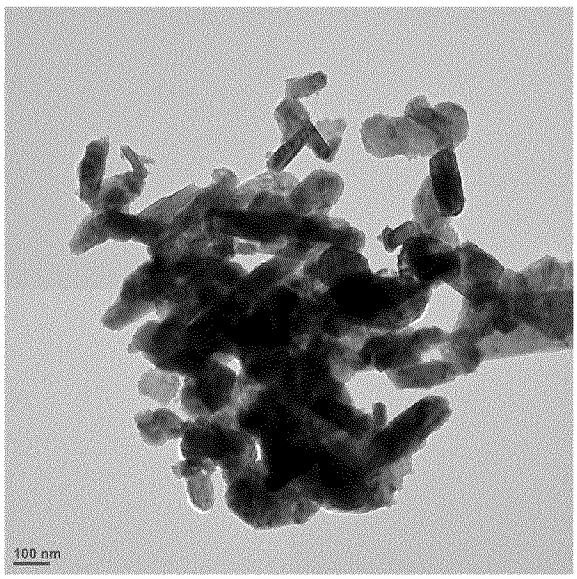

Figure 4

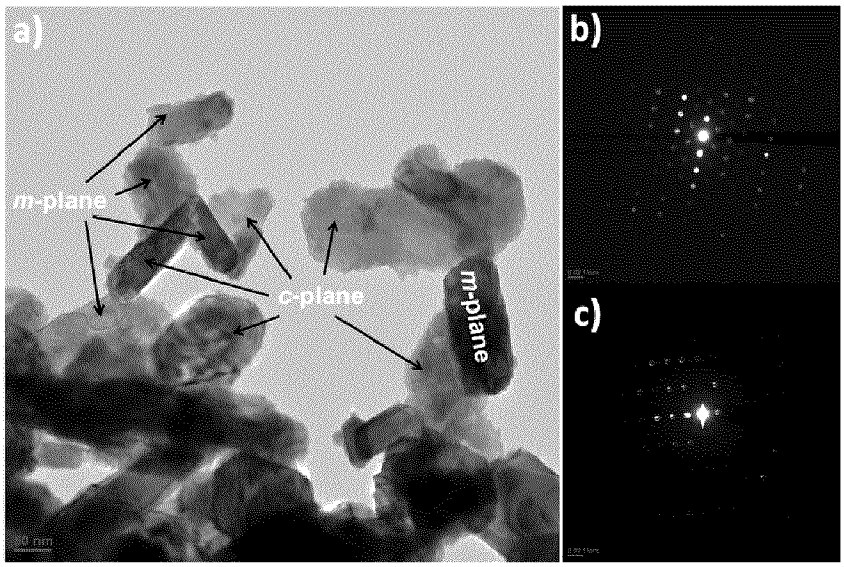

Figure 5

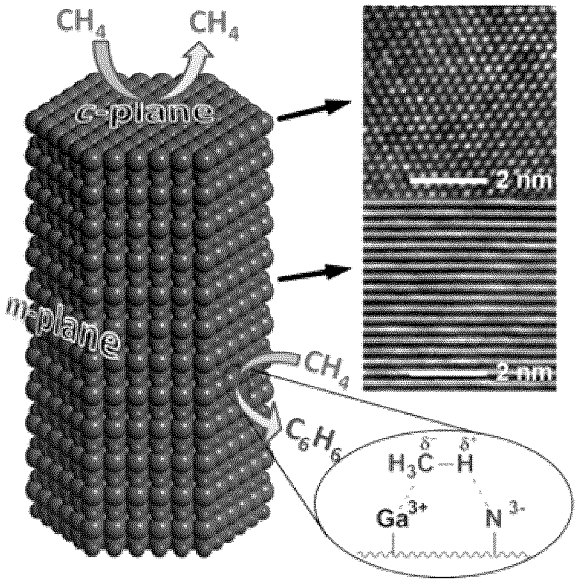

Figure 6

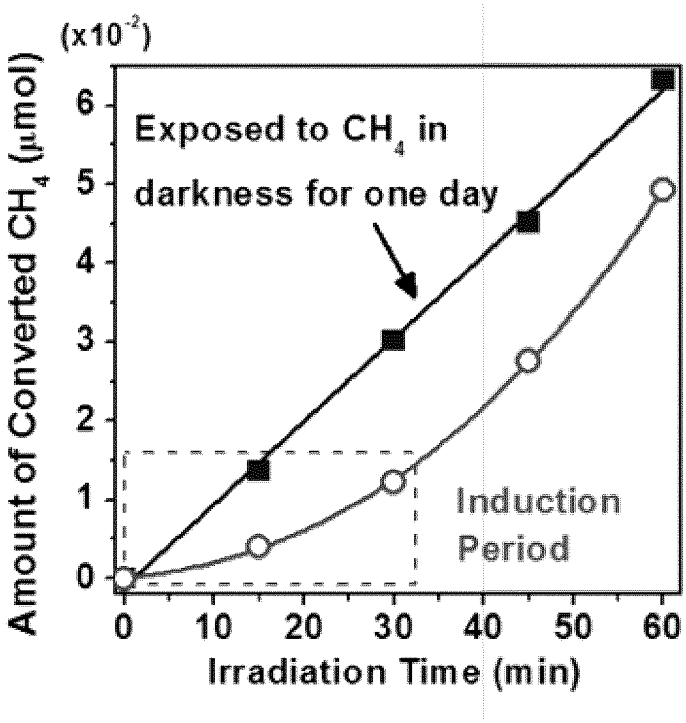

Figure 7

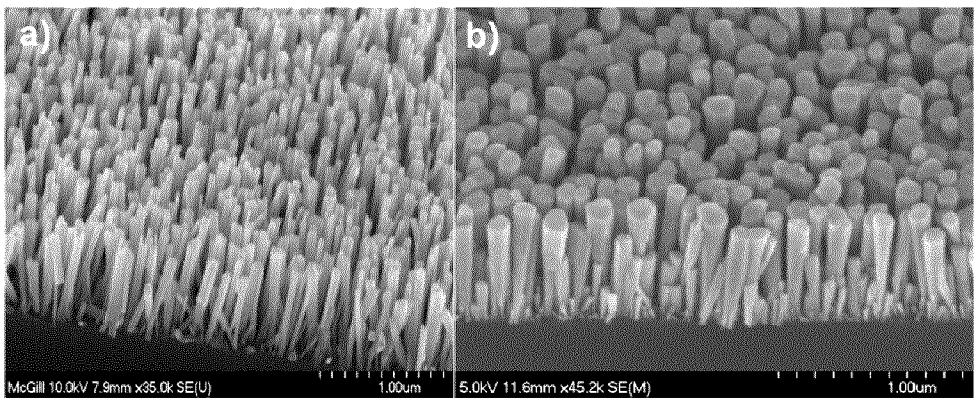

Figure 8

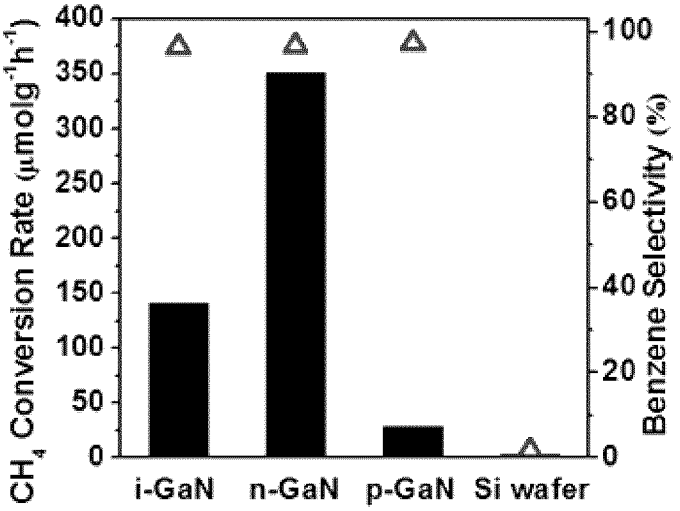

Figure 9

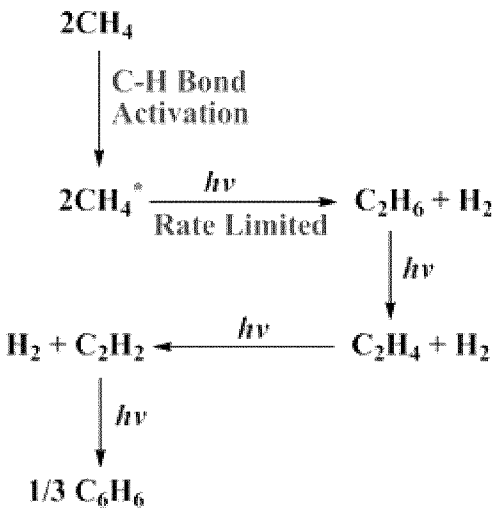

Figure 10

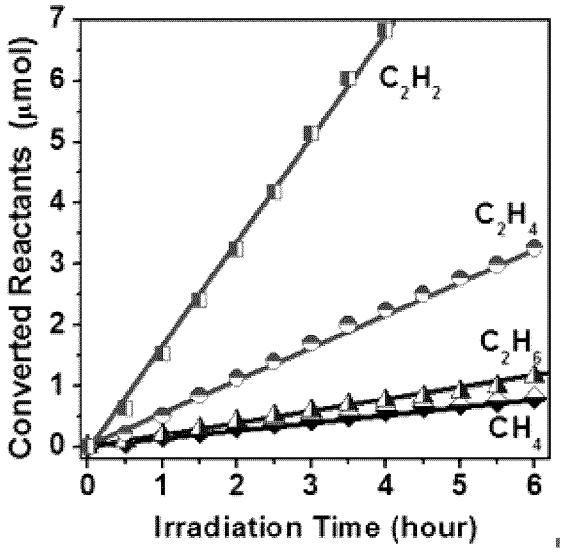

Figure 11

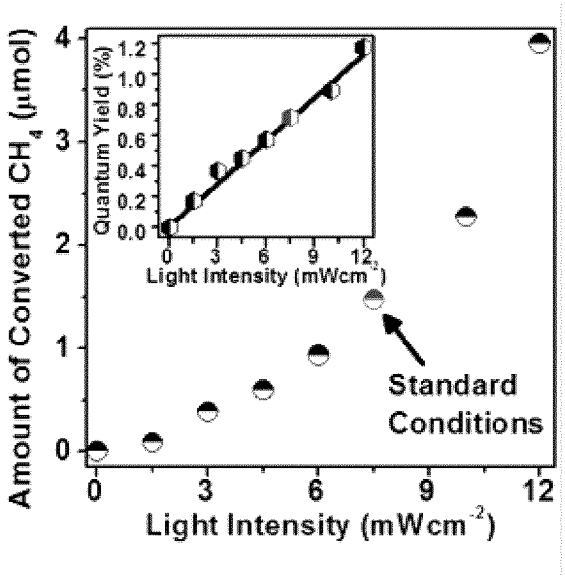

Figure 12

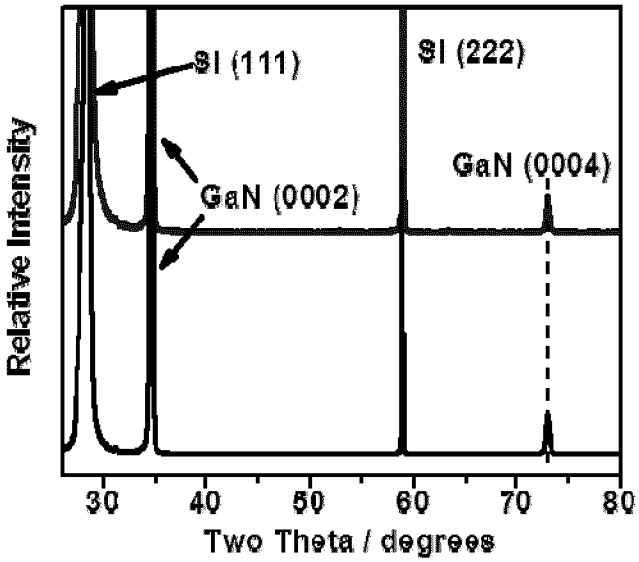

Figure 13

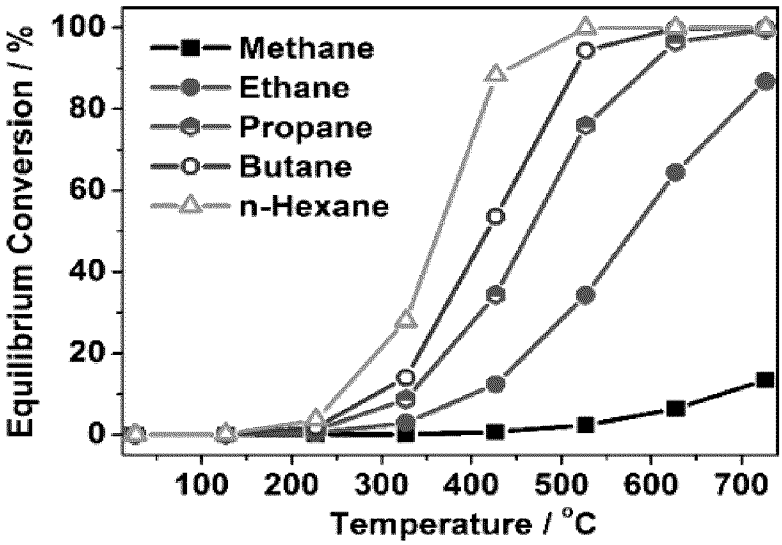

Figure 14

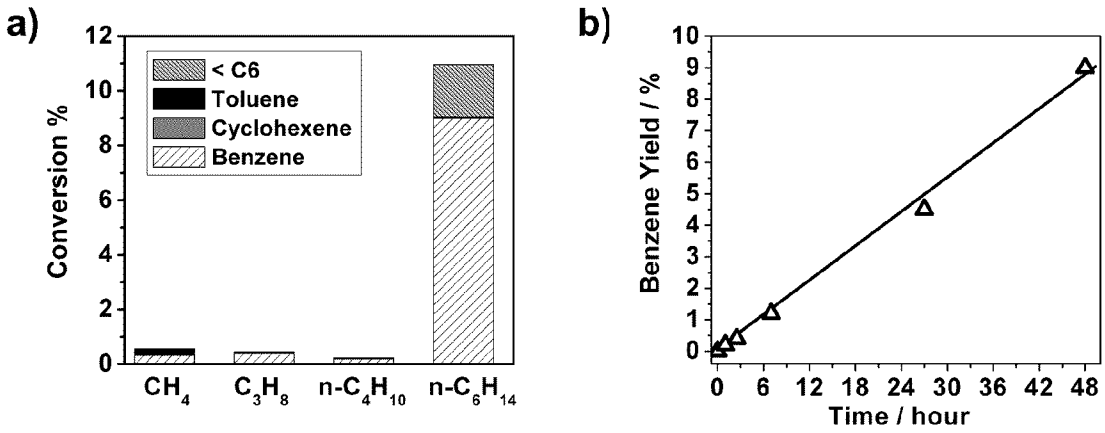

Figure 15

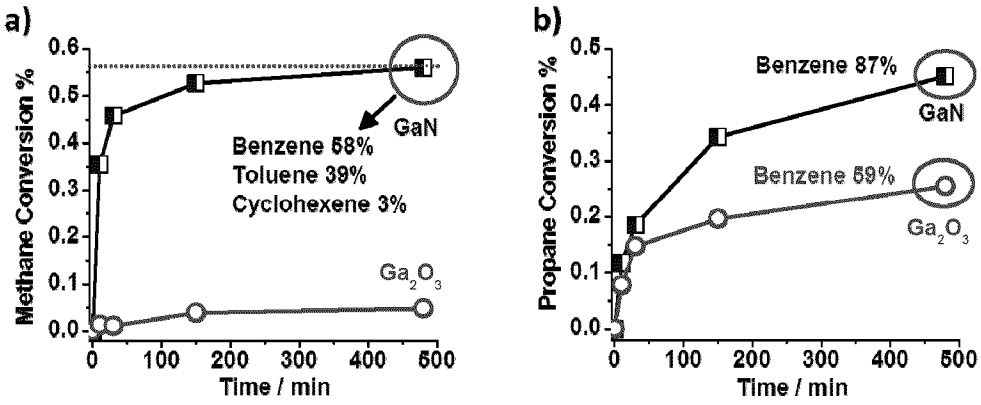

Figure 16

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CA2014/050864

A. CLASSIFICATION OF SUBJECT MATTER
IPC: ***C07C 2/76*** (2006.01), ***B01J 27/24*** (2006.01), ***B01J 37/34*** (2006.01), ***C01B 3/26*** (2006.01).

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)
C07C 2/76 (2006.01), ***B01J 27/24*** (2006.01), ***B01J 37/34*** (2006.01), ***C01B 3/26*** (2006.01).

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

Electronic database(s) consulted during the international search (name of database(s) and, where practicable, search terms used)
QUESTEL(FamPat)/Scopus: aluminium/gallium/indium/thallium, nitride, AlN/GaN/InN/TlN, aromatic/benzene/toluene/xylene/BTX /dehydroaromatization, hydrogen/H2

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	LI *et al.*, "Synergistic Effect on the Photoactivation of the Methane C-H Bond over Ga^{3+}-Modified ETS-10", Angew. Chem. Intl. Ed., 7 May 2012 (07-05-2012), Vol. 51(19), pp. 4702–4706. [ISSN 1433-7851 (print); 1521-3773 (online)] [DOI: 10.1002/anie.201200045] http://onlinelibrary.wiley.com/doi/10.1002/anie.201200045/abstract **D1**: See entire article.	1-16
X	US2012/0036889 A1 IACCINO *et* al. 16 February 2012 (16-02-2012)	17-24, 27-37
A	Methane conversion process. **D2**: See paragraphs 0058-0060, 0063-0066, 0068-0069, 0073.	25-26

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"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 14 November 2014 (14-11-2014)	Date of mailing of the international search report 01 December 2014 (01-12-2014)
Name and mailing address of the ISA/CA Canadian Intellectual Property Office Place du Portage I, C114 - 1st Floor, Box PCT 50 Victoria Street Gatineau, Quebec K1A 0C9 Facsimile No.: 001-819-953-2476	Authorized officer C. Bourque (819) 934-3596

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