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Thalappil et al.

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(54) **METHOD FOR CREATING NANOPORES IN MOS_2 NANOSHEETS BY CHEMICAL DRILLING FOR DISINFECTION OF WATER UNDER VISIBLE LIGHT**

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CPC ***B01D 67/006*** (2013.01); ***B01D 61/027*** (2013.01); ***B01D 67/0069*** (2013.01);
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(58) **Field of Classification Search**
None
See application file for complete search history.

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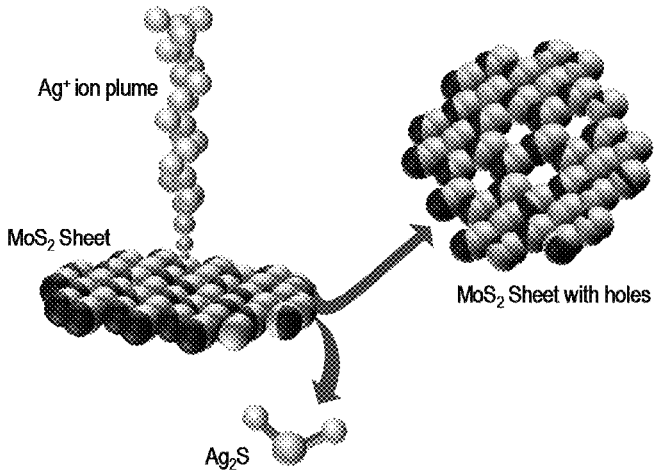
(57) **ABSTRACT**

The present invention relates to a new method for creating nanopores in single layer molybdenum disulfide (MoS_2) nanosheets (NSs) by the electrospray deposition (ESD) of silver ions on a water suspension of the former. Electrospray deposited silver ions react with the MoS_2 NSs at the liquid-air interface resulting in Ag_2S nanoparticles (NPs) which goes into the solution leaving the NSs with holes of 3-5 nm diameter. Specific reaction with the S of MoS_2 NSs leads to Mo-rich edges. Such Mo-rich defects are highly efficient for the generation of active oxygen species such as H_2O_2, under visible light, which causes efficient disinfection of water. The holey MoS_2 NSs shows 10^5 times higher efficiency in
(Continued)



disinfection compared to normal MoS_2 NSs. Developed a conceptual prototype and tested with multiple bacterial strains and a viral strain, demonstrating the utility of the method for practical applications.

15 Claims, 11 Drawing Sheets

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B01D 71/02	(2006.01)
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B01J 35/00	(2006.01)
B01J 35/10	(2006.01)
B01J 37/34	(2006.01)
C01G 39/06	(2006.01)
C02F 1/30	(2006.01)
C02F 1/44	(2006.01)

(52) **U.S. Cl.**

CPC ***B01D 69/10*** (2013.01); ***B01D 69/145*** (2013.01); ***B01D 71/022*** (2013.01); ***B01J 27/051*** (2013.01); ***B01J 35/004*** (2013.01); ***B01J 35/0013*** (2013.01); ***B01J 35/1061*** (2013.01); ***B01J 37/348*** (2013.01); ***C01G 39/06*** (2013.01); ***C02F 1/30*** (2013.01); ***C02F 1/442*** (2013.01); *B01D 2323/26* (2013.01); *C01P 2004/24* (2013.01); *C02F 2303/04* (2013.01); *C02F 2305/023* (2013.01); *C02F 2305/10* (2013.01)

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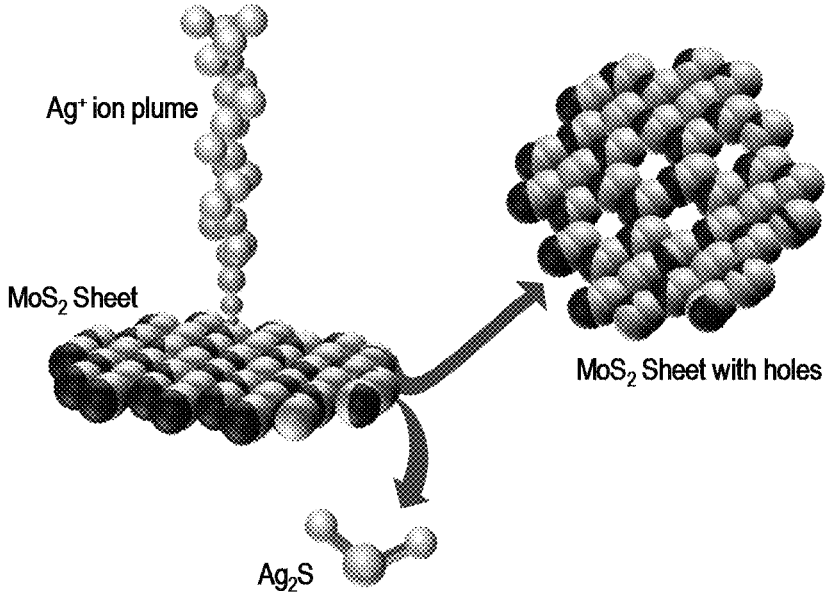


FIGURE 1

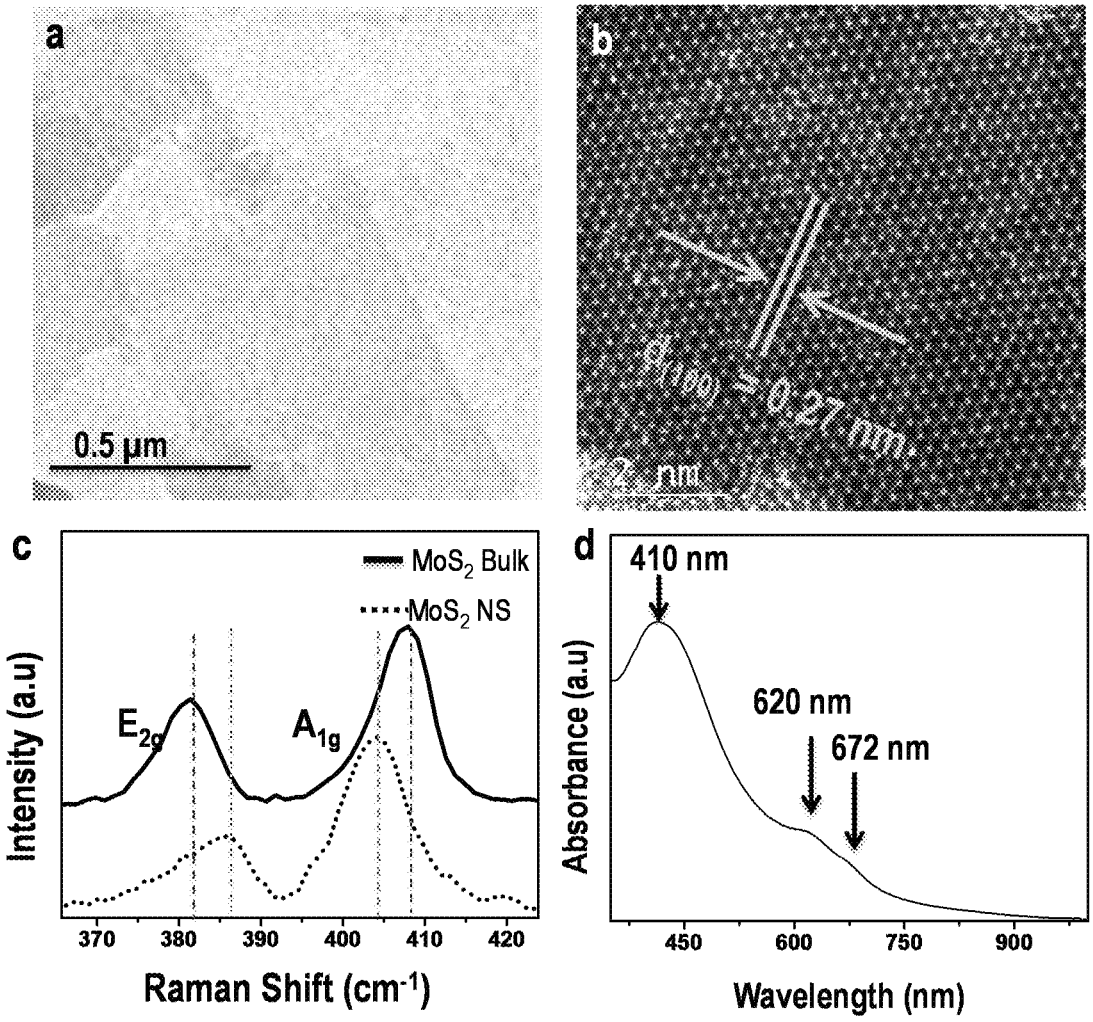

a
0.5 μm
b
$d_{(100)} \approx 0.27$ nm
2 nm
c
MoS_2 Bulk
MoS_2 NS
E_{2g}
A_{1g}
Intensity (a.u)
370
380
390
400
410
420
Raman Shift (cm^{-1})
d
410 nm
620 nm
672 nm
Absorbance (a.u)
450
600
750
900
Wavelength (nm)

FIGURE 2

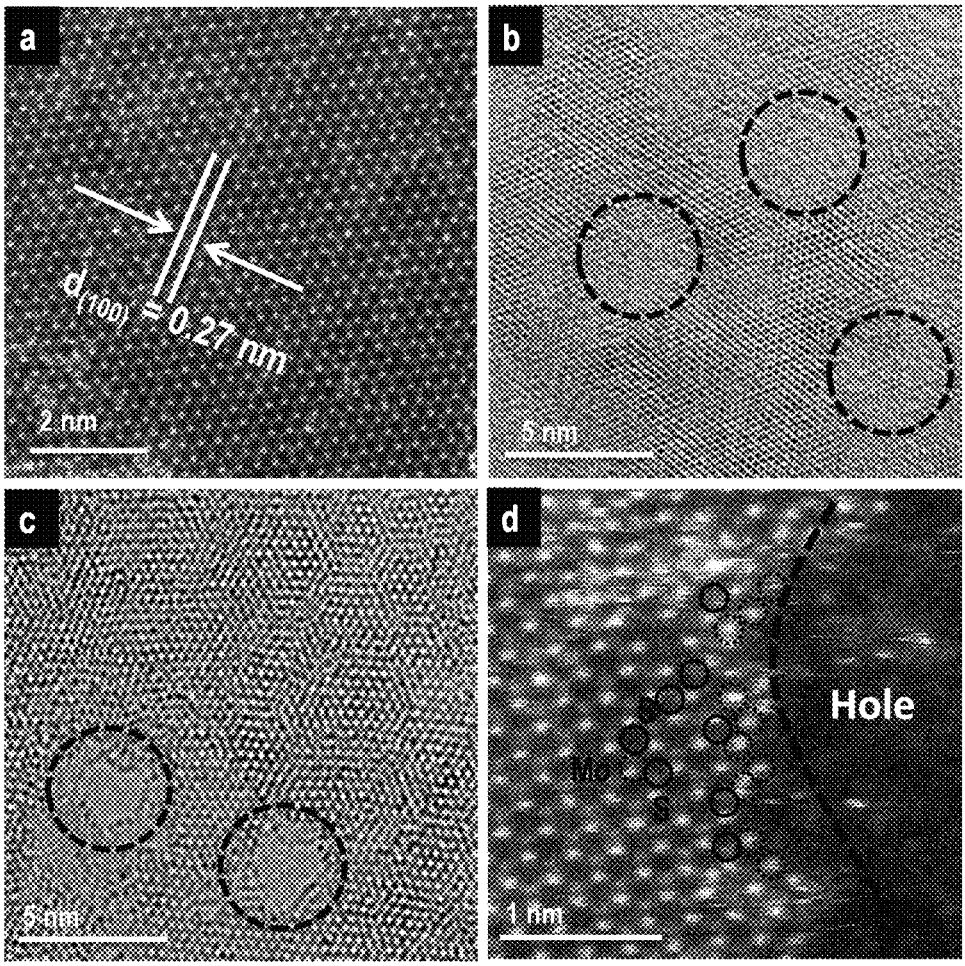


FIGURE 3

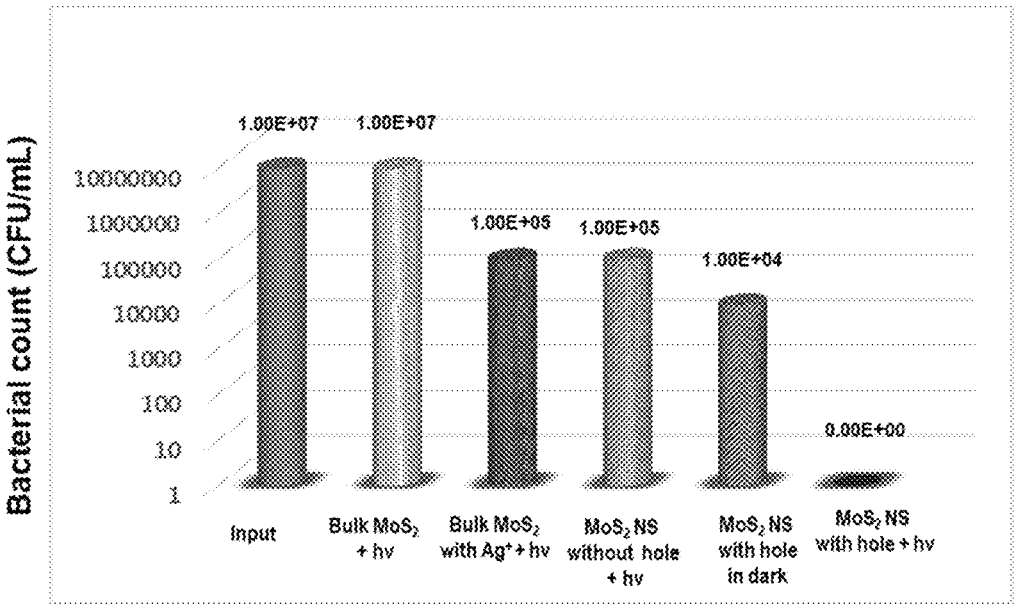

Bacterial count (CFU/mL)
10000000
1000000
100000
10000
1000
100
10
1
1.00E+07
1.00E+07
1.00E+05
1.00E+05
1.00E+04
0.00E+00
Input
Bulk MoS_2 + hv
Bulk MoS_2 with Ag^+ + hv
MoS_2 NS without hole + hv
MoS_2 NS with hole in dark
MoS_2 NS with hole + hv

FIGURE 4

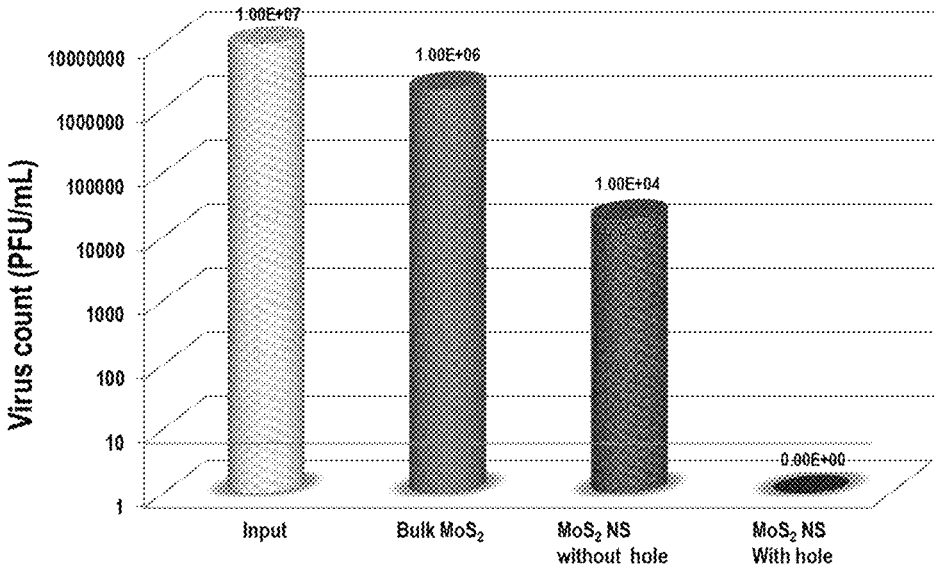

Virus count (PFU/mL)
10000000
1000000
100000
10000
1000
100
10
1
1.00E+07
1.00E+06
1.00E+04
0.00E+00
Input
Bulk MoS2
MoS2 NS without hole
MoS2 NS With hole

FIGURE 5

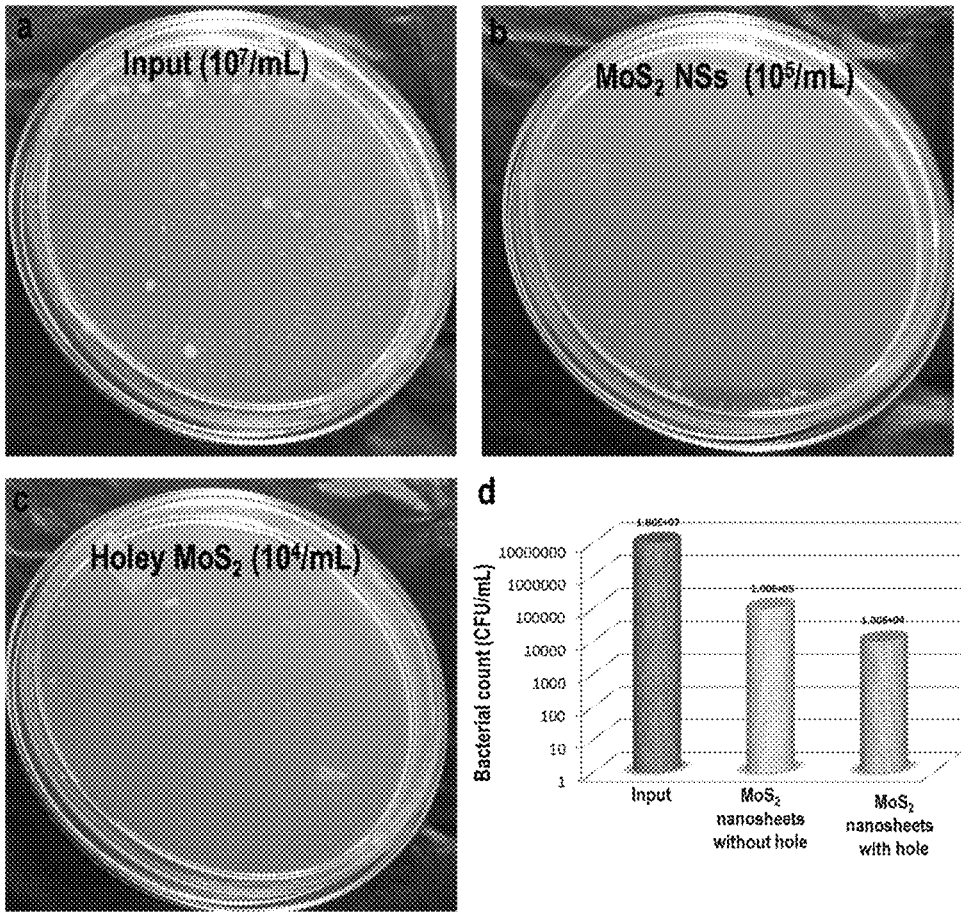

a
Input (10^7/mL)
b
MoS_2 NSs (10^5/mL)
c
Holey MoS_2 (10^4/mL)
d
Bacterial count (CFU/mL)
10000000
1000000
100000
10000
1000
100
10
1
Input
MoS_2 nanosheets without hole
MoS_2 nanosheets with hole

FIGURE 6

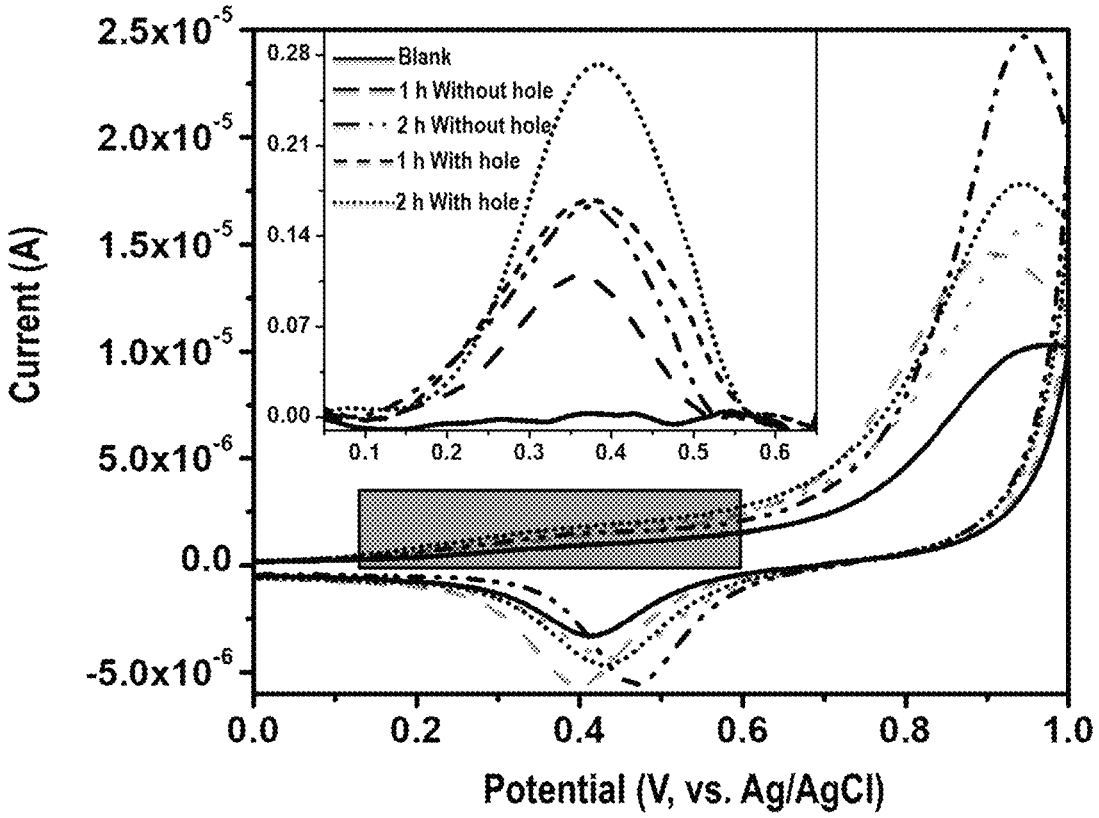

Current (A)
2.5x10-5
2.0x10-5
1.5x10-5
1.0x10-5
5.0x10-6
0.0
-5.0x10-6
0.0
0.2
0.4
0.6
0.8
1.0
Potential (V, vs. Ag/AgCl)
Blank
1 h Without hole
2 h Without hole
1 h With hole
2 h With hole
0.28
0.21
0.14
0.07
0.00
0.1
0.2
0.3
0.4
0.5
0.6

FIGURE 7

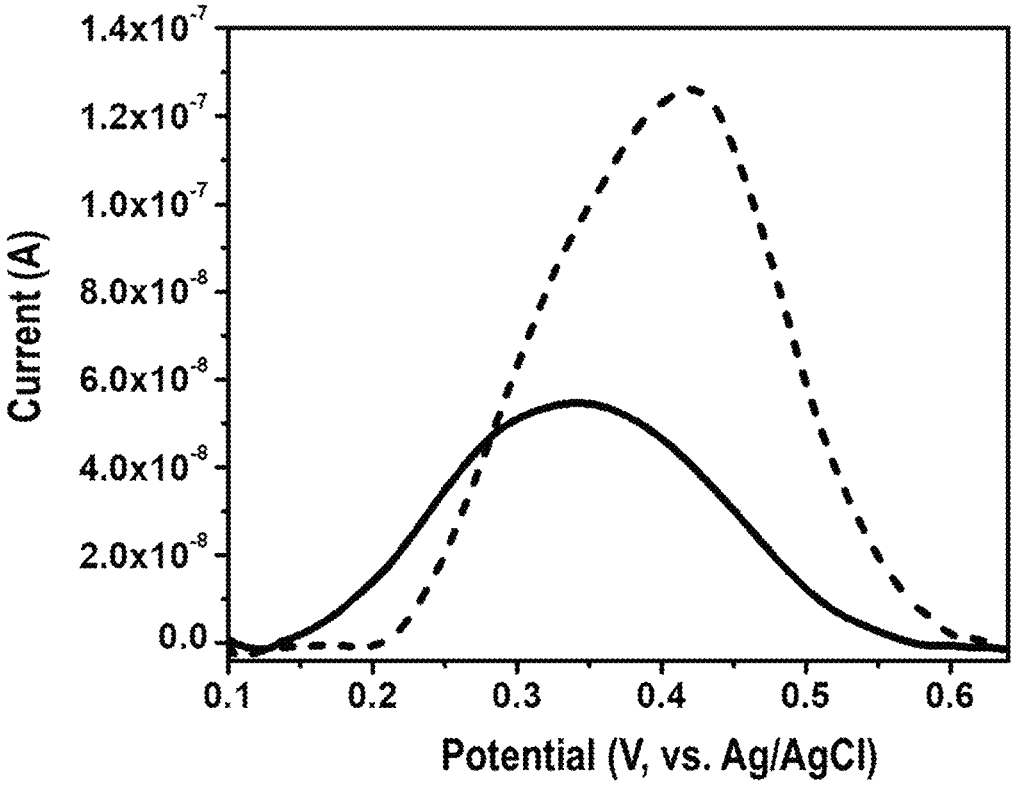

1.4x10-7
1.2x10-7
1.0x10-7
8.0x10-8
6.0x10-8
4.0x10-8
2.0x10-8
0.0
Current (A)
0.1
0.2
0.3
0.4
0.5
0.6
Potential (V, vs. Ag/AgCl)

FIGURE 8

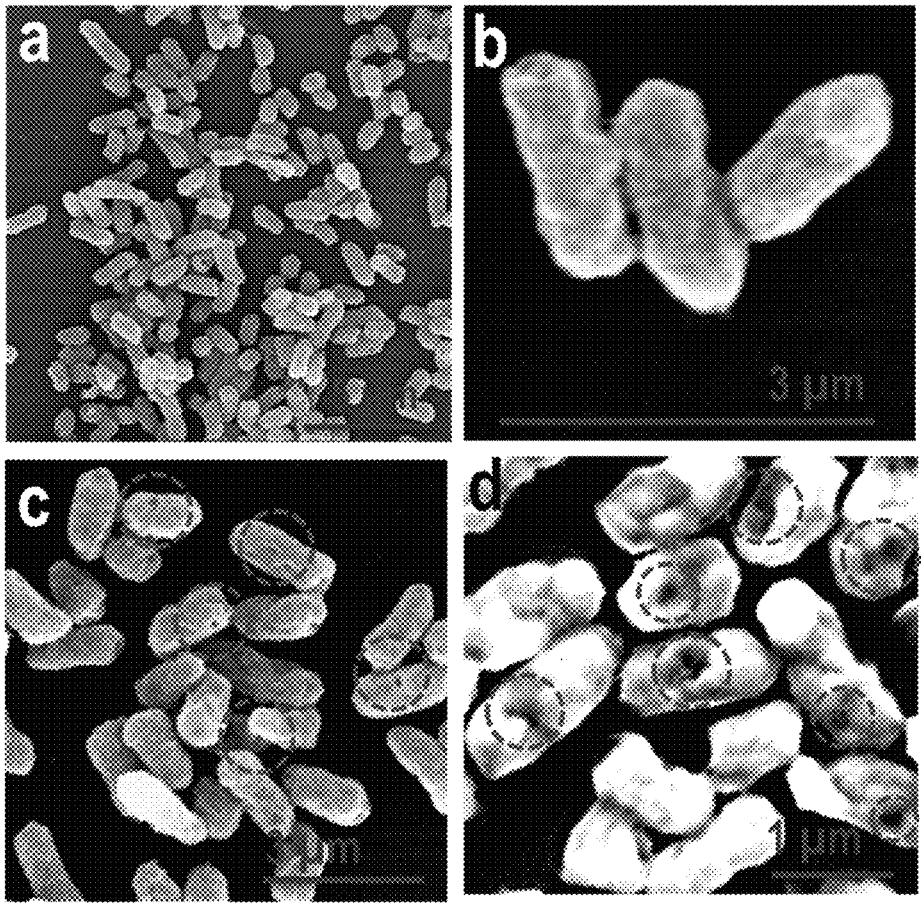


FIGURE 9

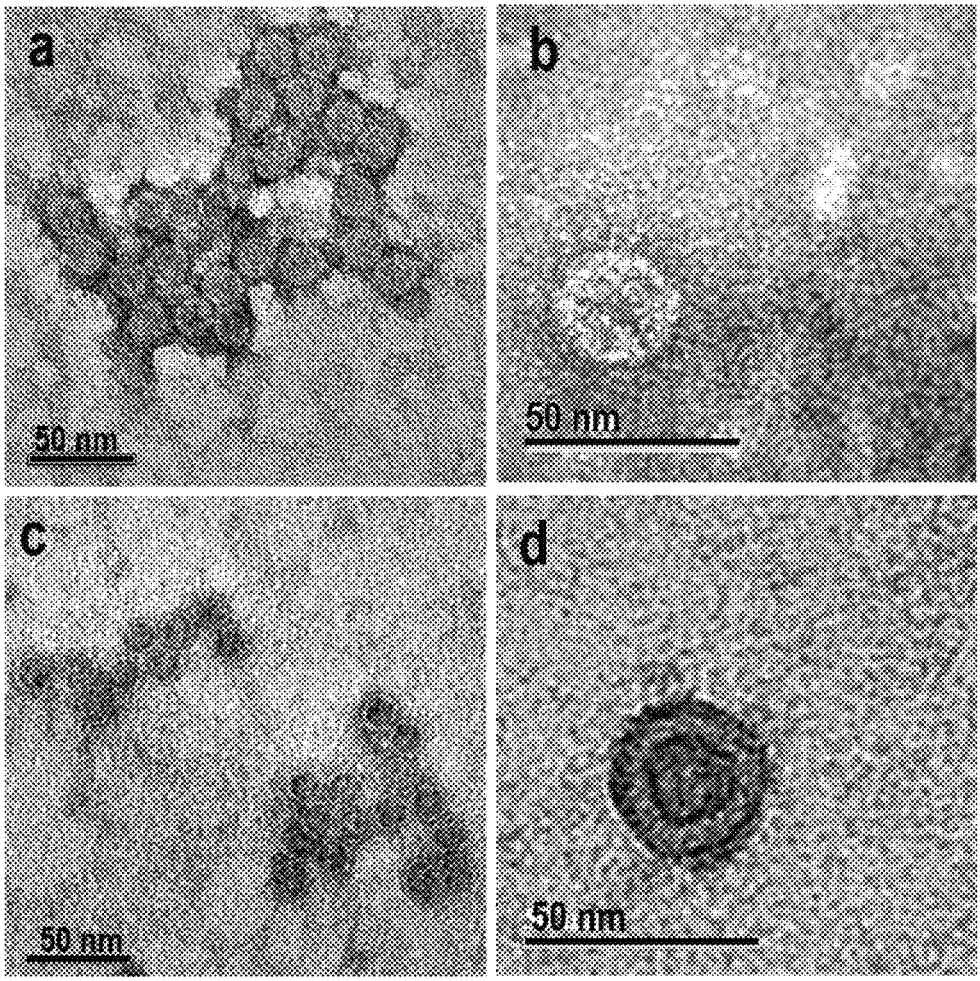


FIGURE 10

Figure 11A

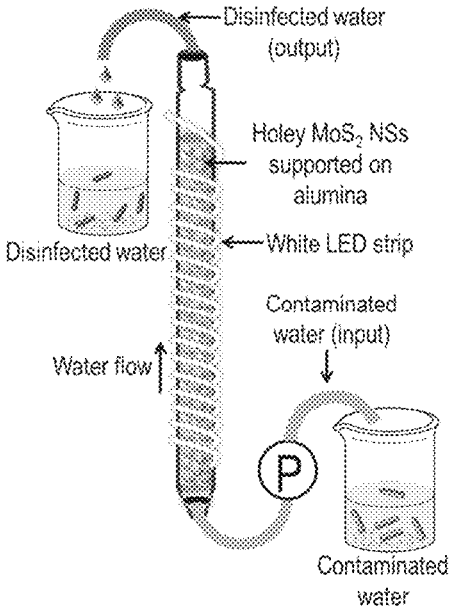
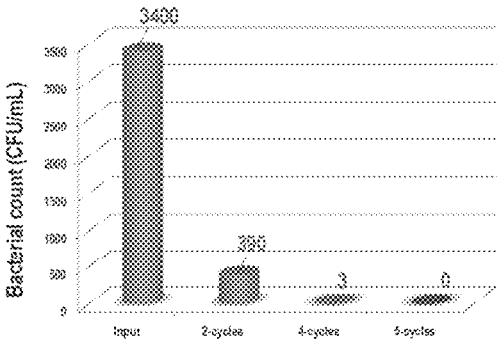


Figure 11B



METHOD FOR CREATING NANOPORES IN MOS_2 NANOSHEETS BY CHEMICAL DRILLING FOR DISINFECTION OF WATER UNDER VISIBLE LIGHT

RELATED APPLICATIONS

The present application is a National Phase of International Application No. PCT/IN2018/050677, filed Oct. 18, 2018, and claims priority based on Indian Patent Application No. 201741037148, filed Oct. 20, 2017.

FIELD OF THE INVENTION

The present invention relates to a new method for creating nanopores in single layer MoS_2 nanosheets (NSs). More specifically it relates to creating nanoscale holes in chemically synthesized MoS_2 nanosheets (NSs) by electrospraying Ag ions. These nanoporous MoS_2 NSs are highly effective in both water desalination and disinfection.

BACKGROUND OF THE INVENTION

In the recent past, graphene a two-dimensional allotrope of carbon received huge interest of researchers globally due to its interesting properties [Guo S et al., Chem. Soc. Rev. 2011, 40 (5), 2644-2672]. Graphene, the basic building block of graphite has very interesting properties like Quantum Hall Effect [Zhang, Y et al., Nature (London, U.K.) 2005, 438 (7065), 201-204; Taychatanapat T et al., Nat. Phys. 2011, 7 (8), 621-625], ballistic electron transport [Yazyev O. V et al., Nat. Mater. 2010, 9 (10), 806-809; Chen F et al., Acc. Chem. Res. 2009, 42 (3), 429-438], high conductivity [Heersche, H. B et al., Nature (London, U.K.) 2007, 446 (7131), 56-59; Miao F et al., Science (Washington, D.C., U.S.) 2007, 317 (5844), 1530-1533; Zhou, S. Y et al., Nat. Phys. 2006, 2 (9), 595-599], unusual chemical reactivity [Sen Gupta, S et al., ACS Sustainable Chem. Eng. 2015, 3 (6), 1155-1163], photosensitivity [Chitara, B et al., Adv. Mater. (Weinheim, Ger.) 2011, 23 (45), 5419-5424], bio-sensing [Jung, J. H et al., Angew. Chem., Int. Ed. 2010, 49 (33), 5708-5711, S5708/1-S5708/4], battery applications [Su, Y et al., ACS Nano 2012, 6 (9), 8349-8356; Fang, Y et al., J. Am. Chem. Soc. 2013, 135 (4), 1524-1530], etc. Other 2D materials of similar layered structure, for example, molybdenum disulfide (MoS_2) is one of the examples of the large family of 2D metal chalcogenides. These metal chalcogenides can be represented by a general formula of MX2, where M is the metal and X represents the chalcogen (S, Se, Te). These 2D metal chalcogenides also have interesting properties like graphene [Seo, J.-W et al., Angew. Chem., Int. Ed. 2007, 46 (46), 8828-8831; Lee, H. S et al., Nano Lett. 2012, 12 (7), 3695-3700; Yin, Z et al., ACS Nano 2012, 6 (1), 74-80; Zhou, W et al., Small 2013, 9 (1), 140-147]. For example, they have properties such as catalysis [Xie, J et al., Adv. Mater. (Weinheim, Ger.) 2013, 25 (40), 5807-5813], light harvesting, hydrogen evolution reaction [Xie, J et al., Adv. Mater. (Weinheim, Ger.) 2013, 25 (40), 5807-5813; Lukowski, M. A et al., J. Am. Chem. Soc. 2013, 135 (28), 10274-10277], biomolecules detection [Zhu, C et al., J. Am. Chem. Soc. 2013, 135 (16), 5998-6001], lithium ion storage [Jiang, H et al., Adv. Mater. (Weinheim, Ger.) 2015, 27 (24), 3687-3695; Xu, X et al., Nanoscale 2014, 6 (10), 5245-5250], etc.

Both theoretical [Hinnemann, B et al., J. Am. Chem. Soc. 2005, 127 (15), 5308-5309] and experimental [Jaramillo, T. F et al., Science (Washington, D.C., U.S.) 2007, 317 (5834),

100-102] studies have shown that the edges of these 2D sheets are more active catalytically than the basal surface. Hence, defect-rich MoS_2 nanosheets (NSs) are of more interest to researchers due to their increased effective surface area [Xie, J et al., Adv. Mater. (Weinheim, Ger.) 2013, 25 (40), 5807-5813]. Creating such defects to a single layer MoS_2 sheet still remains a challenge. Such defects can be created by atom bombardment, which requires sophisticated instrumentation. Whereas, in recent past, we have developed a methodology for creating functional nanomaterials under ambient conditions which require no sophisticated instrumentation. Dimensionality of the materials can be controlled easily in this method. Using the same method, defect rich 2D nanosheets can be created for an advanced application like disinfection of water.

Water scarcity is one of the main problems of the modern world. Rapid, energy efficient desalination and disinfection processes are required to address the problem [Shannon, M. A et al., Nature (London, U.K.) 2008, 452 (7185), 301-310; Schwarzenbach, R. P et al., Science (Washington, D.C., U.S.) 2006, 313 (5790), 1072-1077; Liu, C et al., Nano Lett. 2013, 13 (9), 4288-4293; Logan, B. E et al., Nature (London, U.K.) 2012, 488 (7411), 313-319]. 2D nanomaterials like graphene has shown to be an efficient material for water purification. There are several reports where graphene-based materials were used for the removal of arsenic [Chandra, V et al., ACS Nano 2010, 4 (7), 3979-3986], ions [Cohen-Tanugi, D et al., Nano Lett. 2012, 12 (7), 3602-3608; Han, Y et al., Adv. Funct. Mater. 2013, 23 (29), 3693-3700; Pugazhenthiran, N et al., ACS Appl. Mater. Interfaces 2015, 7 (36), 20156-20163], dyes [Ramesha, G. K et al., J. Colloid Interface Sci. 2011, 361 (1), 270-277; Li, B et al., J. Mater. Chem. 2011, 21 (10), 3346-3349; Ai L.-H et al., J. Hazard. Mater. 2011, 192 (3), 1515-1524], antibiotics [Gao, Y et al., J. Colloid Interface Sci. 2012, 368 (1), 540-546], pesticides, etc. Recent reports also show that MoS_2 NSs has potential utility in water purification [Li, Q et al., Langmuir 2014, 30 (29), 8965-8972; Li, W et al., ACS Nano 2016, 10 (2), 1829-1835]. These NSs are also potential candidates for desalination as well as disinfection of water. A recent computational study shows that MoS_2 NSs with nanopores can effectively do desalination of water. They have also shown that water flux is higher (70% higher than the graphenenanopores) for a hole with Mo rich edges [Heiranian, M et al., Nat. Commun. 2015, 6, 8616]. In another very recent report, MoS_2 NSs were shown to be effective for the disinfection of water under visible light. They have shown that the reactive edges of the NSs are responsible for the generation of active oxygen species like H_2O_2 which, in turn, is the cause of disinfection [Liu, C et al., Nat. Nanotechnol. 2016]. These reports prove the tremendous potential of defect rich MoS_2 NSs.

For the first time, this invention provides an easy, cost-effective, ambient, solution-based method to create nanopores in single layer MoS_2 nanosheets. In this process, Ag ions are electrosprayed on a water suspension of chemically synthesized MoS_2 NSs. In the course of deposition, Ag ions react with the NSs and form Ag_2S, leaving them with defects. The size of the holes can be controlled by varying the deposition time. These nanoporous MoS_2 NSs is highly reactive due to the increase in effective surface area and are effective in both water desalination and disinfection.

SUMMARY OF THE INVENTION

The present invention relates to a new method for creating nanopores in single layer MoS_2 nanosheets (NSs). More

specifically relates to the creation of nanoscale holes in chemically synthesized MoS_2 nanosheets (NSs) by electrospraying Ag ions.

In one embodiment, the present invention provides an easy, cost-effective, ambient, solution-based method to create nanopores in single layer MoS_2 nanosheets. The nanoholes are created by electrospraying of Ag ions on a water suspension of chemically synthesized MoS_2 NSs, wherein the Ag ions react with the nanosheets and forms Ag_2S, leaving the nanosheets with defects. This reaction process will make the MoS_2 NSs porous, with Mo-rich edges.

In another embodiment, the present invention illustrates electrospray deposition of reactive ions on a substrate which can make interesting new materials. For example, an electrospray deposition of Ag ions on MoS_2 nanosheets creates nanoscale holes by reacting it with charged droplets of silver acetate. Wherein, the Ag ions are from various salts of silver including silver acetate, silver nitrate and silver perchlorate.

In other embodiment, the present invention provides a new material used for effective disinfection and desalination of water. Electrospray deposition of silver acetate on chemically synthesized MoS_2 nanosheets reacts and forms Ag_2S which creates holes in the nanosheets. This reaction process will make the MoS_2 NSs porous, with Mo-rich edges. These nanoporous MoS_2 NSs will be highly effective in both water desalination and disinfection. High reactivity of the porous nanosheets is due to the increase in the effective surface area. Mo enriched pores will lead to the larger flux of water, much larger than graphene. The edges of MoS_2 NSs are responsible for their unusual reactivity. These NSs, with tiny holes in it, will have more reactive edges to show enhanced reactivity. Moreover, chemical drilling with metal ions like Ag^+ make the MoS_2 nanosheets photocatalytically more active which increases the ROS generation and disinfection efficiency. A working prototype is developed using immobilized nanosheets on oxide supports for water disinfection using low power LEDs.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. **1** shows drilling of MoS_2 NSs by ambient ions. Schematic representation of chemical drilling of MoS_2 NSs using electrospray deposited Ag^+ ions.

FIG. **2** shows characterization of MoS_2 NSs. (a) TEM image of as-synthesized MoS_2 nanosheet. (b) HAADF TEM image of (a) MoS_2 nanosheet showing that there are no defects in it. (c) Raman spectrum collected from the MoS_2 nanosheet and bulk MoS_2. The peak difference (~18 cm^{-1}) of E_{2g} and A_{1g} for MoS_2 NSs suggests that the sheets are one layer thick. (d) UV-Vis spectrum collected from a suspension of MoS_2 NSs.

FIG. **3** shows characterization of holey MoS_2 NSs. (a) STEM image of the as-synthesized MoS_2 NSs showing no defects in it. (b) HRTEM image of a MoS_2 NS, floating on water after the deposition process, with holes. (c) STEM image of the same showing clear holes on a single NS. (d) HAADF STEM image of a holey MoS_2 NS taken from the subphase showing a Mo enriched edge. Black circles in image (d) denote Mo and the dotted circles represent S.

FIG. **4** shows anti-bacterial performance of holey MoS_2 NSs. The antibacterial activity of the porous MoS_2 NSs, with Mo-rich edges is compared with bulk MoS_2, bulk MoS_2 with the same amount of Ag used for drilling, MoS_2 NSs without holes and holey MoS_2 NSs in dark. In all the experiments, parameters like, light intensity, irradiation time (2 h), sample concentrations, etc., were maintained constant. The entire visible spectrum was exposed to the sample although one frequency (v) is mentioned. The test organism used was *E. coli.*

FIG. **5** shows the comparison of the antiviral activity of the porous MoS_2 NSs, with Mo-rich edges. The activity is compared with bulk MoS_2 and MoS_2 NSs without holes. The test organisms used was F-specific bacteriophage MS2 grown on *E. coli* (ATCC 15597-B1). In all the experiments, parameters like, light intensity, irradiation time (2 h), sample concentrations, etc., were maintained constant. The entire visible spectrum was exposed to the sample although one frequency (v) is mentioned.

FIG. **6** shows antibacterial performance of holey MoS_2. (a-c) Photograph of the antibacterial activity (with *Bacillus subtilis* bacteria) of MoS_2 NSs shown in (b) and with holey MoS_2 shown in (c). (a) Input bacterial concentration and (d) comparison of antibacterial activity of MoS_2 NSs and holey MoS_2.

FIG. **7** shows quantitative detection of H_2O_2 using CV. Cyclic voltammetry (CV) traces of 5 mL of MoS_2 solution, in phosphate buffered saline (PBS), using a gold electrode. Inset shows background corrected CV traces of holey MoS_2 and MoS_2 NSs without hole.

FIG. **8** shows linear sweep voltammetry (LSV) profile of MoS_2 NS suspensions with different time of spraying of Ag^+. LSV spectrum MoS_2 NSs suspension after 10 and 20 min of Ag^+ deposition and 1 h of visible light irradiation.

FIG. **9** (a-b) show SEM images of *E. coli* cells before disinfection and (c-d) after disinfection. Circles in c and d show the damage in the cells due to reaction with H_2O_2.

FIG. **10** (a, c) show TEM images of virus before (live virus) and after (dead virus) the treatment with the sample (holey MoS_2), respectively. Magnified TEM images of live (b) and dead (d) viruses show the clear contrast difference between the two.

FIG. **11**A is a prototype with holey MoS_2 for water disinfection using low power LED strips.

FIG. **11**B is a plot of bacterial count after 2-5 cycles of operation.

Referring to the drawings, the embodiments of the present invention are further described. The figures are not necessarily drawn to scale, and in some instances the drawings have been exaggerated or simplified for illustrative purposes only. One of ordinary skill in the art may appreciate the many possible applications and variations of the present invention based on the following examples of possible embodiments of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The following description is presented to enable any person skilled in the art to make and use the embodiments, and is provided in the context of a particular application and its requirements. Various modifications to the disclosed embodiments will be readily apparent to those skilled in the art, and the general principles defined herein may be applied to other embodiments and applications without departing from the spirit and scope of the present disclosure. Thus, the present invention is not limited to the embodiments shown, but is to be accorded the widest scope consistent with the principles and features disclosed herein.

The present invention relates to a new method for creating nanopores in single layer MoS_2 NSs. More specifically relates to creating nanoscale holes in chemically synthesized MoS_2 NSs by electrospraying Ag ions.

The present invention provides an easy, cost-effective, ambient, solution-based method to create nanopores in single layer MoS_2 nanosheets. The nanoholes are created by electrospraying Ag ions on a water suspension of chemically synthesized MoS_2 NSs, wherein the Ag ions react with the nanosheets and forms Ag_2S, leaving them with defects. This reaction process will make the MoS_2 NSs porous, with Mo-rich edges.

The present invention illustrates electrospray deposition of reactive ions on a substrate which can make interesting new materials. For example, an electrospray deposition of Ag ions on MoS_2 NSs creates nanoscale holes by reacting it with charged droplets of silver acetate. Wherein, the Ag ions are from various salts of silver including silver acetate, silver nitrate and silver perchlorate.

The present invention provides a new material used for effective disinfection and desalination of water. Electrospray deposition of silver acetate on chemically synthesized MoS_2 nanosheets reacts and forms Ag_2S which creates holes in the nanosheets. This reaction process will make the MoS_2 NSs porous, with Mo-rich edges. These nanoporous MoS_2 NSs will be highly effective in both water desalination and disinfection. The high reactivity of the porous NSs is due to the increase in effective surface area. The edges of MoS_2 NSs are responsible for their unusual reactivity. Mo enriched pores may lead to larger flux of filtered water, much larger than graphene. These NSs, with tiny holes in it, will have more reactive edges to show enhanced reactivity. Moreover chemical drilling with metal ions like Ag^+ make the MoS_2 nanosheets photo catalytically more active which increase the ROS generation and disinfection efficiency.

The following description details the method and application of the new material and explains the experimental parts for creating a hole in a chemically synthesized substrate by chemical drilling.

All the commercially available chemicals were used as is, without any further purification. Silver acetate (AgOAc), molybdenum disulfide (MoS_2), 1.6 M n-butyllithium in hexane and solvent hexane were purchased from Sigma Aldrich, India.

Synthesis of MoS_2 NS:

Chemical exfoliation method was used to synthesize MoS_2 NSs, from MoS_2 powder. 300 mg of MoS_2 powder was taken under an argon atmosphere and 3 mL of 1.6 M n-butyllithium was added to it. The resulting solution was stirred for 2 days under the same atmosphere. Then the resulting lithium intercalated product was washed repeatedly with hexane to remove unreacted reactants followed by addition of 80 mL of distilled water. The resulting solution was sonicated in a bath sonicator for 1 h. Then the aqueous dispersion of MoS_2 NSs was centrifuged at a speed of 10000 rpm to remove bulk, un-exfoliated MoS_2. The quality of the synthesized MoS_2 NSs was checked using electron microscopy, UV-Vis and Raman spectroscopy. The concentration of MoS_2 dispersion was determined using inductively coupled plasma mass spectrometry (ICP MS).

Electrospray deposition on MoS_2 NSs:

For electrospray deposition, a home built nanoelectrospray ionization (nESI) source was made. The nESI tip was made by pulling a borosilicate glass capillary into two, using a micropipette puller (Sutter Instruments, U.S.A.). Each tip, after pulling, was checked using a microscope to ensure the size and quality of the cut. Tips with an opening of 10-15 μm were used for all deposition experiment. 10 mM aqueous solution of AgOAc was filled in the nESI tips using a microinjector pipette tip and it was connected to a platinum electrode, for high voltage connection. For deposition on MoS_2 NSs, an aqueous suspension of 3.7 mM (in terms of Mo) MoS_2 NS was taken in a properly shaped Eppendorf vial and deposition was performed. The water suspension of MoS_2 was connected to ground through a picoammeter. The deposition current was varied from 20-100 nA for different experiments.

FIG. **1** schematically shows the chemical drilling process of MoS_2 NSs. When a potential of 2-2.5 kV was applied to the nESI source, filled with aqueous solution of AgOAc, through a Pt wire electrode, a spray plume of solvated Ag^+ ions was seen. FIG. **1** shows the Ag^+ ion plume schematically. Then the plume was directed towards a grounded aqueous suspension of MoS_2 NSs. Ag ions react with the NSs and form Ag_2S nanoparticles (NPs). With time, Ag_2S NPs go into water resulting in nanoporous MoS_2 NSs. The reaction of Ag^+ ions with MoS_2 NSs in bulk solution phase converting MoS_2 NSs completely to Ag_2S was reported recently from our group [Mondal B, et al., Nanoscale 2016, 8 (19), 10282-10290].

To prove that the deposition of ions followed by the reaction is the only reason for the defects in MoS_2 NSs, a detailed characterization of synthesized NSs were done. FIG. **2** shows the characterization of as synthesized MoS_2 NSs using various spectroscopic and microscopic techniques. FIGS. **2***a* and **2***b* show TEM images of the MoS_2 NSs at different magnifications. From the TEM images, it is clearly seen that with our synthesis, we have obtained thin single layer sheets of MoS_2 in the nanometer dimension.

From the high-resolution TEM (HRTEM) image (FIG. **2***b*) it is clear that the sheets are single crystalline in nature. Raman spectroscopic measurement of the synthesized NSs also shows the 2c nature of them. FIG. **2***c* shows Raman spectra collected from MoS_2 NSs (dotted line) and MoS_2 bulk (solid line), respectively. Peaks at 387 cm^{-1} (E_{2g}) and 409 cm^{-1} (A_{1g}) prove the 2D nature of the NSs. The increase in FWHM for NSs and the softening of A_{1g} and E_{2g} bands indicate the successful exfoliation of bulk MoS_2 to 2D nano scale form. UV-Vis spectrum is taken from the aqueous suspension also proves the 2D nature of the NSs. This characterization and imaging of the as-synthesized NSs proved that they are defectless single crystalline sheets made of MoS_2. FIG. **2***d* shows the UV-Vis spectrum of as-synthesized MoS_2 NSs.

With these MoS_2 NSs, the electrospray deposition experiments were done. The deposition time and rate were optimized by trial and error based method. In a typical experiment, Ag^+ ions were electrosprayed on MoS_2 NSs suspension (3.7 mM with respect to Mo) for 30 min at a deposition current of 60 nA. After the deposition, a portion of the NSs was seen floating on the water surface and rest of it was still in the bulk. Both of these categories of NSs were taken on a carbon coated TEM grid for imaging. FIG. **3***a* shows a STEM image of the as-synthesized MoS_2 NS. The HRTEM image (collected from the floating layer of NSs) in FIG. **3***b* shows the presence of holes (indicated with dotted circles) in a MoS_2 NS. The HRTEM image was taken from a single layer MoS_2 NS to prove the clear discontinuity of the lattice planes. FIG. **3***c* shows a STEM image of MoS_2 NSs after the creation of holes. The image clearly shows part of a hole in a single crystalline NS present in bulk water. The dimensions of the holes were in the range of 3-5 nm. We speculate dynamics of the suspended NSs on the liquid surface during deposition leading to the creation of holes in all the NSs. This motion can be due to the transfer of charged droplets on the water surface in presence of a tangential electric field. From the independent experiments, we know that hydroxyl ions (due to their high mobility), generated

due to hydrolysis of water, are the charge carriers from the center of the spray to the ground electrode kept at the rim of the liquid reservoir, causing a hydrodynamic flow in the liquid. This flow may be the reason for the presence of nanoporous sheets both on the surface of the water and in the bulk. To see the fate of the NSs with longer deposition time, an experiment was performed where the deposition time was kept at 2 h. In this case, the whole NS was reacted and got converted to Ag_2S NPs. The process of the selective reaction of incoming Ag^+ ions makes the holey MoS_2 NSs porous with Mo-rich edges. HAADF STEM image shown in FIG. **3***d* clearly shows the Mo enriched edges of the holes in a single layer MoS_2 NS. From FIG. **2***d*, the distance between the two Mo atoms is 0.26 nm. Considering the holes as a circle of 3 nm diameter, the number of Mo atoms per hole is ~35. Thus, due to hole formation, a 1 μm×1 μm NS exposes ~2.7×10^5 additional Mo atoms. Note that the STEM image of FIG. **3***c* suggests >7800 holes per 1 μm^2. This process of creating nanoscale holes on 2D sheets by ambient ion reactions is referred to as chemical drilling. Low deposition time has maintained in order to control the size of the holes. For this reason, in all our experiments of creating nm sized holes in the MoS_2 NSs (except the control experiment showing longer deposition leading to complete reaction of the NSs to form Ag_2S NPs), the concentration of the Ag_2S NPs formed was negligible in comparison to the amount of MoS_2 in solution. From an earlier report, it's evident that such small holes with enriched Mo have the highest efficiency in water purification [Heiranian M et al., Nat. Commun. 2015, 6, 8616]. Hence, these 2D sheets of MoS_2 are potential candidates for efficient desalination. On the other hand, with increased active surface area, due to the presence of a large number of edges, they can act as more reactive entities for other applications like disinfection of water.

Disinfection of Water:

The photocatalytic disinfection performance of nanoporous MoS_2 sheets was then checked under visible light and the disinfection efficiency was then compared with the controls; namely as synthesized MoS_2 NSs under visible light at the same concentration of Ag^+ used for chemical drilling and an equal mass of bulk MoS_2 under same experimental conditions.

A Xenon lamp equipped with UV filter was used as a light source. In an aspect, 10 mL of synthetic water (typically containing Escherichia coli ATCC 25922 in a concentration of 1×10^7 CFU/mL, unless otherwise mentioned) was used. A high concentration of the bacterial input was maintained considering the activity of the proposed material in the treatment of water from challenging environments. 1 mL of the diluted samples was plated along with nutrient agar on a sterile petridish using the pour plate method after 2 h reaction time. After 48 h of incubation at 37° C., the colonies were counted and recorded.

Disinfection of bacteria: To check the efficiency of disinfection of holey MoS_2 NSs, a series of experiments are performed along with several control experiments. The disinfection efficiency of the MoS_2 NSs are tested using bacteria and virus-contaminated water. FIG. **4** shows that when the contaminated water exposed to porous MoS_2 NSs and visible light showed 10,000,000 times reduction in bacteria, from 10^7 CFU/mL to 10° CFU/mL for *E. coli* (or 7 log reduction), in 2 h whereas the as-synthesized MoS_2 NSs and bulk MoS_2 with equivalent concentration of Ag, used for the drilling process, showed only 1% of disinfection efficiency (or 2 log reduction) (FIG. **4**). But holey MoS_2 NSs in dark showed only 3 log reduction (FIG. **4**) in the bacteria count. It is noted that Ag^+ at a concentration above 50 ppb can be an excellent disinfectant. Under the same experimental conditions, bulk MoS_2 showed negligible disinfection efficiency for the mentioned bacterial input. This suggests that chemical drilling makes the MoS_2 nanosheets photocatalytically more active. The Mo-rich defects in the NSs provide enhanced active surface area for the generation of reactive oxygen species (ROS). The disinfection efficiency of the material is tested with gram-positive bacteria also (*Bacillus subtilis*). It is noticed that *Bacillus subtilis* are more resistive towards H_2O_2 than *E. coli* under the same experimental conditions (FIG. **6**).

The following description shows that the holey MoS_2 NSs are more efficient in generating at least one ROS species, namely H_2O_2. The disinfection efficiency of Ag^+ alone was also examined under the same experimental conditions taking the same amount of Ag^+ ions used for chemical drilling. Ag^+ ions showed a negligible effect on *E. coli* inactivation because the concentration of Ag^+ was 0.2 μM, much lower than the concentration needed for disinfection at a bacterial load of 10^7 CFU/mL.

Disinfection of viruses: Considering the fact that the major water purification techniques used for virus removal are the addition of chlorine which produces harmful disinfection byproducts, however the proposed holey MoS_2 NSs could serve as an efficient method to reduce pathogenic viruses by a safer method. The bulk MoS_2 with and without Ag^+ and MoS_2 NSs without holes are unable to affect the phage significantly, the porous MoS_2 NSs are found to achieve a 7 log reduction by photocatalytic disinfection (FIG. **5**). Moreover, this experiment proves that this method can disinfect virus at comparatively higher concentrations.

From earlier reports, it is known that MoS_2 in presence of visible light can generate active oxygen species like H_2O_2. Chong Liu et. al. has shown that the edges of MoS_2 NSs are more active in this reaction. Thus the generation of H_2O_2, in presence of visible light is one of the reasons for the disinfection of water. To prove that the holey MoS_2 is more efficient for the production of H_2O_2, a set of cyclic voltammetry (CV) experiments are performed. For all the CV experiments, a pre-cleaned gold electrode is used as the working electrode, Ag/AgCl is used as the reference electrode and Pt is used as the counter electrode. Prior to CV measurements of each sample, 5 mL of as-synthesized MoS_2 suspension was dried at 55° C. in a glass bottle. Subsequently, CV experiments are performed by adding 5 mL of 1 M phosphate buffered saline (PBS, pH~7.3) to the bottle having previously dried MoS_2 and electrochemical experiment is performed after exposing the dispersion to visible light (for 1 or 2 h, depending on the experiment). CV of each sample was performed from 0 to +1 V with a fixed scan rate of 100 mV/s. CV profiles of Au, performed in blank solution (only PBS), as well as in PBS along with as synthesized MoS_2 NSs and holey MoS_2 NSs irradiated with visible light for 1 h and 2 h, respectively are shown in FIG. **7**. Each CV profile has two major peaks, one observed around +0.95 V corresponds to the formation of $AuCl_4^-$ during the forward potential scan (0 to +1V) and another around +0.43 V due to the reduction of gold chloride in the reverse potential scan (+1V to 0). Along with these, a small hump is observed in the CV scan, around +0.45 V (marked portion in the spectrum was multiplied 3 times for better visualization) which corresponds to the oxidation of H_2O_2. In the course of the reaction, M-OH or M═O might be formed as intermediates which ultimately get converted to ROS. Although the reaction mixture with as synthesized MoS_2 NSs shows some amount of H_2O_2, the holey MoS_2 NSs are more efficient in the generation of H_2O_2 because of the presence of enhanced

reactive surface area. To prove the fact that defects in the MoS_2 sheets have a significant role in H_2O_2 generation, a control experiment is carried out. In this experiment, two sets of holey MoS_2 samples are synthesized by varying the deposition time of Ag^+ (10 and 20 min at a deposition rate of 100 nA). More deposition time will enable the creation of more holes in NSs. All the other parameters are kept constant and the CV is measured successively. FIG. **8** shows the feature corresponding to H_2O_2 in the voltammogram. The H_2O_2 concentration is higher in the second sample, i.e. the MoS_2 NSs with more holes (Ag deposition for 20 min). The disinfection process involves other ROS species also, yet the focus of the invention is to detect H_2O_2.

Imaging of Bacteria and Virus Before and After the Treatment with the Sample:

SEM imaging establishes the damage of bacterial cells. FIG. **9***a-b* show the SEM images of the bacterial cells before disinfection (healthy cells of *E. coli*). On the other hand, FIGS. **9***c-d* show the SEM images of dead *E. coli* cells at different magnifications. It is seen clearly from these images that the bacterial cells are damaged (black circles) due to reaction with H_2O_2. TEM images of the virus before (FIG. **10***a-b*) and after (FIG. **10***c-d*) irradiation show a clear contrast difference. This is because the uranyl acetate stain enters defective viral capsids and causes a distinct difference in contrast between untreated and treated viruses. Dense dark centered capsids (defective capsids) which had taken up the uranyl acetate stain were seen as dark whereas untreated viruses were rigid and did not show the stain within. All the above disinfection processes were performed under a Xenon arc lamp.

The present invention provides a working prototype design for the disinfection of water developed using a commercially available low power LED strip. FIGS. **11**A and **11**B show the schematic representation of a prototype, wherein the prototype comprises holey MoS_2 NSs supported on alumina, packed in a borosilicate glass tube (column size and radius was 10 inches and 3 mm inner diameter, respectively) and a LED (4.8 W/m) strip was wrapped around the borosilicate glass tube. Contaminated water was pushed from below using a syringe pump and pure water was collected from the top. Antigravity flow of the contaminated water was chosen for longer contact of it with the holey MoS_2 NSs. Contaminated water with bacterial load of 10^3 CFU/mL was passed through the column multiple times and after each cycle, the sample was taken for plating. The result showed 100% disinfection after 5 cycles (FIG. **11**B).

Thus the present invention provides a cheap ambient method for making nanometer size holes in a single crystalline NS. Electrospray deposition of reactive ions on a substrate can make interesting new materials. Resulting porous MoS_2 NSs can act as a better membrane for desalination of water. In addition, Mo enriched pores will lead to the larger flux of water, predicted to be much larger than that of graphene [Heiranian, M. et al., Nature Communications 6, 8616 (2015)]. The edges of MoS_2 NSs are responsible for their unusual reactivity. These NSs, with tiny holes in it, will have more reactive edges to show enhanced reactivity.

It may be appreciated by those skilled in the art that the drawings, examples and detailed description herein are to be regarded in an illustrative rather than a restrictive manner.

We claim:

1. A method of making nanoscale holes in two dimensional MoS_2 nanosheets, the method comprising:

electrospraying deposition of reactive Ag^+ ions onto the two dimensional MoS_2 nanosheet, wherein the Ag^+ ions react with the MoS_2 nanosheet forming Ag_2S and a defect-rich MoS_2 nanosheet;

generating H_2O_2 under visible light using the nanoscale holes in the MoS_2 nanosheet; and

exposing contaminated water to the H_2O_2 for disinfection.

2. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, wherein the Ag^+ ions are selected from various salts of Ag comprising silver acetate, silver nitrate, and silver perchlorate.

3. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, wherein the nanoscale holes have dimensions below 20 nm.

4. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, wherein the reaction between electrosprayed AG+ ions and MoS_2 nanosheets makes nanoporous MoS_2 nanosheets with Mo-rich edges.

5. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, further comprising metal ions including monovalent ions Ag^+, Cu^+, and divalent ions, Hg^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+}.

6. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **5**, further comprising electrospraying the metal ions in water, acetonitrile, methanol, ethanol, dimethyl formamide, tetrahydrofuran, and combination thereof at different proportions.

7. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, the two dimensional materials comprising MoS_2, $MoSe_2$, WS_2, WSe_2.

8. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, wherein the two dimensional nanosheets are supported on substrates including water, ITO-coated glass, copper, silicon using an adsorption process.

9. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **5**, wherein the metal ions are deposited on the nanosheet substrate using nanoelectrospray ionization.

10. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, wherein the chemical reaction of MoS_2 nanosheets with the metal ions is photocatalytically more active which increases the generation of reactive oxygen species and disinfection efficiency.

11. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, wherein the nanoporous MoS_2 nanosheets supported on silica or alumina are used as a device for filtration.

12. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **5**, wherein the metal ions for chemical etching are supplied as droplets in the gas phase onto the two dimensional nanosheet supported on a substrate.

13. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **5**, wherein the metal ions for chemical etching are supplied in solution containing the two dimensional nanosheets.

14. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, wherein the nanoporous MoS_2 nanosheets act as a membrane for desalination of water.

15. The method of making nanoscale holes in two dimensional MoS_2 nanosheets as claimed in claim **1**, further comprising using molecular ions to extract sulphur.

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