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प्रमाणित किया जाता है कि पेटेंटी को उपरोक्त आवेदन में यथाप्रकटित METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTERS नामक आविष्कार के लिए, पेटेंट अधिनियम, १९७० के उपबंधों के अनुसार आज तारीख 28th day of December 2015 से बीस वर्ष की अवधि के लिए पेटेंट अनुदत्त किया गया है।

It is hereby certified that a patent has been granted to the patentee for an invention entitled METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTERS as disclosed in the above mentioned application for the term of 20 years from the 28th day of December 2015 in accordance with the provisions of the Patents Act, 1970.



अनुदान की तारीख : 03/07/2020 Date of Grant : पेटेंट नियंत्रक Controller of Patent

टिप्पणी - इस पेटेंट के नवीकरण के लिए फीस, यदि इसे बनाए रखा जाना है, 28th day of December 2017को और उसके पश्चात प्रत्येक वर्ष्य मे उसी दिन देय होगी। Note. - The fees for renewal of this patent, if it is to be maintained will fall / has fallen due on 28th day of December 2017 and on the same day in every year thereafter.





FORM 2

THE PATENTS ACT, 1970

(**39 OF 1970**)

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The Patents Rules, 2003

COMPLETE SPECIFICATÍON

(Refer section 10 and rule 13)

TITLE OF THE INVENTION:

METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTERS

2. APPLICANT:

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3. Preamble to the Description

COMPLETE SPECIFICATION

The following specification particularly describes the invention and the manner in which is to be performed.

COMPLETE SPECIFICATION

TITLE OF THE INVENTION

5 METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTERS

FIELD OF THE INVENTION

10 The present invention pertains to a nanoscale assembly, in particular, crossed bilayer assemblies of nanowires (NWs) with an atomically precise cluster. The invention relates to an ordered assembly of crossed NWs and is of interest to applications in nanoscale optics and electronics.

15 BACKGROUND OF THE INVENTION

Self-organization of micro and nanostructures leading to superlattices enabling the creation of photonic crystals, [Y. A. Vlasov. et al, Nature 2001, 414, 289; B. Gates. et al, Adv. Mater. 2000, 12, 653; G. A. Ozin. et al, Adv. Funct. Mater. 2001, 11, 95; R. C. Schroden. et al, Chem. Mater. 2002, 14, 3305; H.Yamada. et al, Adv. Mater. 2009, 21, 4134], sensors [T. Cassagneau. et al, Adv. Mater. 2002, 14, 1837; X. Xu. et al, J. Am. Chem. Soc. 2008, 130, 3113; A. C. Sharma. et al, J. Am. Chem. Soc. 2004, 126, 2971], materials for biomimetics [M. Kolle. et al, Nat. Nanotechnol. 2010, 5, 511], energy harvesting [Y. G. Seo. et al Adv. Funct. Mater. 2011, 21, 3094; J. P. Bosco. et al, Chem. Mater. 2010, 22, 966], and high density storage [S. Sun.et al, Science 2000, 287, 1989; H. Zeng.et al, Nature 2002, 420, 395; A. Ethirajan. et al, Adv. Mater. 2007, 19, 406] etc. is known for some time. Such self-assemblies in 2D and 3D are formed in homogeneous liquids and at liquid-vapor/gas or liquid-liquid interfaces with single or multiple phases [G. M. Whitesides. et al, Science 2002, 295, 2418; F. X. Redl. et al, Nature 2003, 423, 968; J. Zhang. et al, Self-Assembled Nanostructures, Kluwer Academic, 2003; G. M. Whitesides.

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et al, Springer, 2005, pp. 217].

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Synthetic methodologies used for generating such structures are typically complex and molecular driving forces enabling such interactions are understood poorly. 1D structures such as nanowires (NWs) [D. Whang.et al, Nano Lett. 2003, 3, 1255; A. Tao.et al, Nano Lett. 2003, 3, 1229; D. Wang.et al, J. Am. Chem. Soc. 2005, 127, 11871; S. Acharya.et al, Adv. Mater. 2006, 18, 210; I. Patla. et al, Nano Lett. 2007, 7, 1459; L. Mai.et al, Nano Lett. 2009, 9, 826] and

nanotubes (NTs) [X. Li. et al, J. Am. Chem. Soc. 2007, 129, 4890] spontaneously organize parallel to their long axis, similar to 'logs-on-a-river' [P. Yang, Nature 2003, 425, 243.]. Similar assemblies leading to the formation of monolayers at interfaces [J.W. Liu. el al, J. Am. Chem. Soc. 2010, 132, 8945; G. D. Moon. et al, ACS Nano 2011, 5, 8600] are known for tellurium NWs (Te NWs). Organized bilayer structures are seen rarely and are obtained through successive transfer of monolayers [D. Whang. et al, Nano Lett. 2003, 3, 1255; J.W. Liu. el al, J. Am. Chem. Soc. 2010, 132, 8945]. One-step formation of such integrated architectures directly from solution, however, is not known so far.

As is known in the art, nanowires are typically fabricated from a metal or a semiconductor material. Recently, advances in materials processing techniques have resulted in 10 the fabrication of novel nanostructures, such as metallic nanowires, as well as multilayered nanowires. For example WO 2011/146142 A1 discloses a method for fabricating nanostructures, which includes the steps of forming a multi-segmented nanowire. This method utilizes template directed electrodeposition to fabricate nanowires with alternating layers of sacrificial/noble metal, enabling a new level of control over particle spacing, aspect ratio, and composition.Co/Au 15 and Ni/Au multisegmented nanowires were created in this method and those NWs were then used to create Te/Au nanopeapods by galvanic displacement of Co/Ni by Te, producing Te nanotubes and nanowires with embedded Au particles, respectively. Similarly, PCT application WO2013/128458 A1 describes a process for preparation of a conductive film comprising metal nanowires by a surfactant/template assisted method which involves the use of a precursor 20 solution based on surfactant (such as CTAB), metal precursor (such as HAuC14 and AgNO3) and reducing agent (such as metal borohydride or sodium ascorbate). US Publication 2013/0022995 A1 discloses a method for preparing a metal nanowire including gold nanoclusters on a surface, wherein the gold nanoclusters provides a gold thin layer on a metal substrate by binding to the target material of the metal nanowire. However, formation of bilayer assembly of nanowire 25 directly from a solution using precise noble metal clusters is not known so far.

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Atomically precise noble metal quantum clusters (QCs) protected with ligands is a new class of materials [M. Zhu, et al, J. Am. Chem. Soc. 2008, 130, 5883; T. U. B. Rao. et al, Angew. Chem., Int. Ed. 2010, 49, 3925; T. U. B. Rao. et al, J. Am. Chem. Soc. 2010, 132, 16304; Y. Yu J. Am. Chem. Soc. 2014, 136, 1246; I. Chakraborty. et al, J. Phys. Chem. Lett. 2013, 4, 3351]. 30 Their small size, of the order of a nm and the variety and density of functionalities present on 3 CHENNAI 28122015 17:49 190

them can be used to create new composite structures with 1D nanostructures such as NWs, as such structures are often tens of nm in diameter and hundreds of nm long. Such composite structures can have new properties distinctly different from clusters and NWs.

Thus the present invention relates to the formation of crossed bilayer assemblies of nanowires using atomically precise noble metal quantum clusters (QCs) protected with ligands using direct, one-step and solution based procedure.

SUMMARY OF THE INVENTION

The present invention relates to the formation of new composite structures with 1D nanostructures such as nanowires (NWs) using atomically precise noble metal quantum clusters 10 (QCs) protected with ligands.

Wherein the atomically precise noble metal quantum clusters (QCs) protected with ligands are used for the formation of crossed bilayer precision assemblies of 1D tellurium nanowires (Te NWs).

In one embodiment, the invention relates to molecular interactions between the ligands of atomically precise noble metal quantum clusters anchored on Te NWs which can spontaneously create bilayers of the latter, with precise geometry.

Wherein the atomically precise noble metal quantum clusters protected with ligands are Ag44(p-MBA)30 [where p-MBA or para-mercaptobenzoic acid is the ligand protecting the cluster core] anchored on Te NWs to create bilayers. In order to validate the role of cluster sandwiching for NW assembly formation, another well-known cluster with the same monolayer protection, $Au_{102}(p-MBA)_{44}$ was used.

In other embodiment of the invention depicts that two layers of Te NWs assemble at 81° with respect to each other dictated by the molecular assembly of a cluster, Ag44(p-MBA)30 [where p-MBA or para-mercaptobenzoic acid is the ligand protecting the cluster core], anchored on the former. The observed assembly, reminiscent of weaving, is formed at the air-water

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interface, and such films of cm² area are transferrable onto solid substrates. In yet another embodiment, the invention shows precisely oriented bilayer assembly of the NWs was obtained by slowly dropping a dispersion of Ag44@Te NWs in 1-butanol on a static water surface. Thus butanol plays a crucial role in the assembly formation. 30 4 . IPO CHENNAI 28132015 17:49

In yet other embodiment the present invention relates to a direct, one-step, solution based procedure for creating crossed bilayer structure of NWs with precise angle between the layers was developed by coating MBA protected QCs over NW surfaces. Clusters bound to the surface of a NW form hydrogen bonds with clusters sitting on the neighbouring NWs of the same and different layers.

In other aspect of the invention shows formation of such sandwiched cluster pairs, between the NWs which leads to the generation of highly ordered NW assemblies; this was rationalized from computational studies. Precise angular control was brought in by monolayer protected clusters. The diversity of clusters available and their functionalities may be used to access other arrangements. This kind of ordered assembly of crossed NWs is of interest for applications, especially in nanoscale optics and electronics.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1: (A) Structure of Ag₄₄(p-MBA)₃₀ modeled based on the crystal structure. (B) TEM image of a single Te NW. Diameter and length distributions for the Te NWs are shown in the 15 insets, (i) and (ii), respectively. The area from where the HRTEM image was collected is marked. (C) HRTEM image of the marked region of the Te NW, showing its c-axis directed growth. Lattice planes are marked. Inset shows corresponding fast Fourier transform (FFT). (D) Schematic illustration of the aligned NW-assembly. Processes involved during the assembly formation are shown. (E) TEM image of the monolayer assembly formed at air-water interface in 20 case of pristine Te NWs. A schematic of the oriented monolayer of Te NWs is shown in the inset. (F) TEM image of the crossed-assembly formed with Ag44@Te NWs for the same NW concentration as the pristine Te NWs. Schematic illustration of the crossed bilayer structure of the assembly, seen as a weaved NW pattern in the TEM image, is shown in the inset. (G) Expanded view of the marked region in F, showing uniform inter-NW distances (~3.4 nm) for 25 both the layers. Scale bar is 400 nm in B.

Figure 2: (A, B) TEM images of the Ag44@Te NWs (C3) at different magnifications. Ag44 aggregates on the NW surface upon exposure to the electron beam and are seen as nodules in B. C) Optical image of single Ag_{44} (a) Te NW. Raman spectrum shows features of both Te and Ag_{44} . D) and E) represent images constructed by mapping the most prominent Raman features of Te 30 NW and Ag₄₄ (marked as d and e in C), respectively. 5 CHENNAI 28122015 17:49 1 P O

Figure 3: (A) H-bonding between neighboring clusters in the $Ag_{44}(MBA)_{30}$ superlattice structure. Clusters remain H-bonded with the neighboring ones between L₂ (inset a) and L₃ type of ligand bundles. (B) a, b and c represent the schematic representation of the 81° orthogonal bilayer assembly, a model of the marked region of the schematic in a) and zoomed view of the marked region in b), respectively. C and D represent other possible arrangements which are not energetically better. Clusters are assembled on Te surfaces kept at 3.4 nm, in three different planes labeled as C₁ to C₃.

Figure 4: UV-visible absorption spectra of Ag44, Te NWs and Ag44@Te NWs; A) UV-visible absorption spectra of a) Ag44(p-MBA)30 and b). Te NWs. B) ESI mass spectrum of Ag44(p-MBA)30. Expanded view of molecular ion peak (4 -ve charge) is shown in the inset along with the theoretical spectrum of the same ion. Minor features are due to fragments or association products during ionization. C) UV-vis absorption spectra of Ag44@Te NWs with increasing cluster concentration (C1-C5, marked with 1 to 5). The NWs after cluster attachment were precipitated out through centrifugation and re-dispersed prior to the measurement of the spectra.
Images of the procedure are shown in the inset. D) Shift of the 550 nm peak of Ag44 is plotted with increasing cluster concentration at a fixed Te NW concentration. Peak shift decreases with increasing concentration, indicating multilayer adsorption of clusters on Te NW surface at higher concentration. Gradual changes in positions of different peaks of Ag44 are shown in the insets.

Figure 5: Electron beam induced nodule formation on Ag₄₄@Te NWs with increasing irradiation
 time; TEM images showing time evolution of nodules upon electron beam irradiation of Ag₄₄@Te NWs (C₃). Image A was acquired immediately. Subsequent images were acquired following a 30 s electron beam irradiation. The scale bar is 50 nm for all the images.

Figure 6: Extent of nodule formation on electron beam irradiation with increasing Ag₄₄ concentration; TEM images of Ag₄₄@Te NWs at different loadings of Ag₄₄, showing the size and the extent of nodule/island coverage of the NWs; (A) C_1 , (B) C_2 , (C) C_4 and (D) C_5 . Scale

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bar is 20 nm in all the images. Figure 7: Raman spectra of Te NW and Ag₄₄; (A) Raman spectra of Te NWs. The most intense Raman peak at 124 cm⁻¹ is due to the Raman active singlet A₁ mode of Te lattice vibrations, while the less intense peak at 143 cm⁻¹ is one of the E doublets. (B) Raman spectrum of Ag₄₄. 30 The cluster is Raman active due to the Raman active nature of its protecting ligand (p-MBA). 6 IPO CHENNAI 28122015 17:49 Two strong bands observed at 1077 and 1584 cm⁻¹ arise from v_{12} and v_{8a} aromatic ring vibrations of p-MBA, respectively.

Figure 8: Structures formed from Ag_{44} @Te NW upon butanol drying, zeta potential values for Te and Ag_{44} @Te NWs; (A) Organized structure formed from butanolic dispersion of Ag_{44} @Te NWs (C₃) after solvent evaporation. (B) Increase in the value of zeta potential with increasing cluster loading. Scale bar in A is 200 nm.

Figure 9: Assembly of Ag_{44} @Te NWs with increasing Ag_{44} loading; TEM images of the kind of Ag_{44} @Te NWs assemblies formed at different loading of Ag_{44} ; (A) C₁, (B) C₂ (C) C₃, (E) C₄, (F) C₅. An area having perfect order from C₃ is expanded and shown in (D). Scale bar in D is 20 nm and is 200 nm for the other images.

Figure 10: Side and top views of modeled assembly of Ag_{44} clusters between two parallel Te layers; (A) Side view of Ag_{44} clusters sandwiched between two parallel Te surfaces. (B) Top view of the same showing H-bonded network of Ag_{44} clusters. Each cluster is surrounded by four clusters from the same plane and by two clusters from the second plane forming 13 H-bonds.

Figure 11: Additional H-bonds formed between Ag₄₄ clusters in 81° orthogonal arrangement;
 Zoomed in view of the Ag₄₄ clusters in 81° orthogonal arrangement showing the formation of
 additional H-bonds, (A) L₃ H-bonds between C₃ and C₁ and (B) L₂ H-bonds between C₂ and C₁.

Figure 12: Relaxation of steric interactions in 81° orthogonal arrangement over a 90° arrangement; (A) Steric interactions between the neighboring clusters (marked) in 90° orthogonal arrangement. (B) Those interactions diminish in 81° orthogonal arrangement.

Figure 13: UV-visible absorption spectrum of Au_{102} in water.

Figure 14: Orthogonal bilayer assembly of Au_{102} (a) TEM image of the orthogonal assembly formed form Au_{102} (a) Te NWs. A schematic representation of the assembly formation by inter-cluster H-bonding is shown in the inset. (B) Expanded view of the same assembly

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25 showing an inter NW distance of 3.7 nm and an interlayer NW angle of 77°. Scale bar is 100 nm in A and is 20 nm in B.

Figure 15: Assembly of Au_{102} @Te NWs by direct drop-casting; TEM images of orthogonal assembly formed after a dilute dispersion of Au_{102} @Te NWs was allowed to dry on the TEM grid. The system preferentially forms bilayers. Scale bar is 5 µm in both the images.

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Figure 16. Response of the Ag₄₄@Te NW device to the application of bending strain. Change in electrical conductivity of a device composed of a bilayer assembly of Ag₄₄@Te NWs deposited on a flexible PET (polyethylene terephthalate) substrate upon the application of strain is presented. Experimental details are presented below.

5 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

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DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to the formation of crossed bilayer assemblies of 1D tellurium nanowires (Te NWs) using atomically precise noble metal quantum clusters (QCs) protected with ligands.

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In one embodiment, the invention demonstrates that molecular interactions between the ligands of QCs anchored on Te NWs can spontaneously create bilayers of the latter, with precise geometry. The Te NWs of the two layers assemble at 81° with respect to each other dictated by the molecular assembly of a cluster, Ag₄₄(p-MBA)₃₀ [where p-MBA or para-mercaptobenzoic acid is the ligand protecting the cluster core], anchored on the former. The observed assembly, reminiscent of weaving, is formed at the air-water interface, and such films of cm² area are transferrable onto solid substrates.

The surface of Te NWs was modified with an atomically precise cluster, Na₄Ag₄₄(p-MBA)₃₀ before forming the nanowire assembly. The cluster Ag44(p-MBA)30 is of 4⁻ charge and Na⁺ act as counter ions. The structure of this cluster, [A. Desireddy. el al, Nature 2013, 501, 399;
H. Yang. el al, Nat commun 2013, 4, 2422] abbreviated as Ag₄₄, shown in Figure 1A, was generated based on previously reported X-ray crystallographic co-ordinates [A. Desireddy. el al, Nature 2013, 501, 399]. Ag₄₄, prepared via a reported procedure, exhibited characteristic molecular features having five intense bands at 879, 681, 574, 516 and 440 nm along with three broad bands centered around 970, 635 and 395 nm in its extinction spectrum (trace a, Figure 30 4A). Identity of the cluster was confirmed from the high resolution electrospray mass spectrum as well (Figure 4B). Te NWs, having an average length of 2.5 µm and diameter of 28 nm (Figure 8

1B) were prepared by the reduction of a Te (IV) precursor with hydrazine hydrate. The Te NWs were single crystalline with trigonal crystal structure (Figure 1C); the growth occurs along the (001) plane with 0.59 nm interplanar spacing. The NWs showed two distinctive bands in the UVvisible spectrum at 288 and 765 nm due to electronic transitions from the p-bonding and p-lone pair states, respectively, in the valence band (VB) to the p-antibonding states in the conduction band (CB) (trace b, Figure 4A) [Z.H. Lin. et al, Cryst. Growth Des. 2008, 8, 351]. Surface modification of Te NWs with Ag44 was achieved by mixing both the precursors in dimethylformamide (DMF) solution.

Increasing amounts of Ag_{44} (C₁ to C₅) were used for a fixed concentration of Te NWs to achieve larger loading of the cluster onto the Te NWs. This was followed by centrifugal 10 precipitation of the 'Ag44-modified-Te NWs' (Ag44@Te NWs) to remove the unattached Ag44. The UV-visible extinction spectra of re-dispersed Ag44@Te NWs showed the above mentioned features of both Ag44 and Te NWs. The cluster-features in the UV-visible spectrum became more prominent with increasing Ag44 concentration (Figure 4C), an indication of adsorption of more and more cluster molecules on the Te NW surface. The observed shift in the positions of the 15 cluster-features in Ag44@Te NWs relative to free Ag44 was another indication of the attachment of Ag44 to the NW surface. The peak-shift of the 550 nm feature of Ag44 steadily decreased with increasing concentration of Ag₄₄ initially and converged later to a value of ~ 5 nm (Figure 4D). This trend was observed for other peaks also (Figure 4D), and can be explained to be due to adsorption. At low cluster concentrations, the NW surface is accessible to all the QCs, which 20 attach uniformly to it (on equivalent highest energy sites) leading to a large change in peak positions. But as the cluster concentration increases, adsorption over the available lower energy sites as well as multilayers becomes possible, resulting in a reduced peak-shift. Finally, as saturation adsorption is reached, the peak-shift converges.

Solvent evaporation at the air-liquid interface is the basis of the Langmuir-Blodgett (LB) 25 process, which has been used for generating monolayer assemblies of nanomaterials of various shapes and sizes [A. R. Tao. et al, Acc. Chem. Res. 2008, 41, 1662]. Similar monolayer assemblies of hydrophilic-nanostructures can be obtained through fast-spreading of a suspension over a water surface, assisted by solvent drying [G. D. Moon. et al, ACS Nano 2011, 5, 8600]. This process is considerably faster (completed within a few minutes) than the Langmiur-Blodgett 30 technique, which normally requires hours. Following the same strategy, a dispersion of Ag44@Te 9 CHENNAI 28122015 17:49 100

NWs in 1-butanol was spread over water, taken in a petridish. As butanol evaporated, a freestanding assembly was formed on water, which was transferred onto transmission electron microscopy (TEM) grids and examined. The experimental process is schematically outlined in Figure 1D, and the mechanistic details of the assembly are discussed later in the manuscript. A TEM image of the assembly (Figure 1E) formed when pristine Te NWs were subjected to the above procedure gives a monolayer in which the NWs are parallel to each other. In comparison, the structure of the assembly obtained using Ag₄₄@Te NWs is a crossed bilayer, as illustrated by the TEM image in Figure 1F. A schematic of the same, shown in the inset of the figure, resembles the 'Woodpile' structure. Here, NWs from the same layer lie parallel to each other, but are at an unusual angle of ~81° to NWs from the second layer, giving the assembly a woven fabric-like appearance. The inter-NW distance in both the layers was measured to be 3.4 ± 0.3 nm (Figure 1G). The different states of aggregation of Ag₄₄@Te NWs in comparison to Te NWs drive the formation of the orthogonal bilayer assembly.

Cluster-attachment to the NWs is confirmed by electron microscopy studies of the Ag44@Te NWs. For small clusters like Ag44, distinct identification of individual QCs is difficult 15 through standard electron microscopy, and when attached on a thick Te NW surface, they did not produce enough contrast to be identified (Figure 2A). However, these clusters tend to aggregate to form nanoparticles (NPs) upon high energy electron beam (200 kV) irradiation and close inspection revealed the presence of small nodules on the NWs (Figure 2B). At this point, it is important to clarify that the nodules seen on the NWs are due to electron beam irradiation of 20 QCs and not due to their solution phase aggregation on the Te NW surface, as proven in a previous study from our group. This was substantiated further by following the time evolution (over a period of 2 min) of the nodules on NWs (Figure 5), which demonstrated the systematic growth of silver particles upon electron beam exposure. The TEM data discussed so far is for C₃ as at this cluster concentration, nodule formation and their evolution were observed most 25 prominently. At cluster concentrations lower than C_3 ($C_1 \& C_2$) smaller and fewer nodules were formed, making them indistinguishable. At higher concentrations (C4 & C5), continuous darker islands were observed, almost instantaneously, upon electron beam irradiation (Figure 6). Though electron microscopy confirms cluster binding to the NWs, a more direct confirmation was available from non-destructive Raman spectroscopy. For Te NWs, an intense 30 Raman peak appeared at 124 cm⁻¹ due to the Raman active singlet A₁ mode (breathing in the ab 10 JPO CHENNAI 28122015 17:49

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plane) of lattice vibrations (Figure 7A), while $Ag_{44}MBA_{30}$ exhibited several peaks (Figure 7B) with two strong bands at 1077 and 1584 cm⁻¹ arising from v₁₂ (ring breathing) and v_{8a} (ring inplane stretching) aromatic ring vibrations, respectively [H. Park. et al, J. Phys. Chem. 1990, 94, 7576]. It is to be noted that for Raman spectral imaging, thicker and longer Te NWs were synthesized. The Raman spectrum collected from Ag_{44} @Te NWs showed the prominent features of both Te NWs and Ag_{44} (Figure 2C). Optical image of the NW used for Raman imaging is shown in Figure 2C. Raman intensity maps constructed by taking the most intense peaks of Te NW and Ag_{44} (marked as d and e in Figure 2C, respectively) are presented in Figures 2D and 2E, respectively. The cluster map matches exactly with that of Te confirming its uniform coverage on the NW surface.

Precisely oriented bilayer assembly of the NWs was obtained by slowly dropping a dispersion of Ag_{44} @Te NWs in 1-butanol on a static water surface. Butanol plays a crucial role in the assembly formation. Although butanol is thermodynamically miscible with water (solubility of 73 g/L), the rate of mixing is slow due to its alkyl chain. Thus, when it is dropped on water, it quickly spreads to form a thin layer. A part of it evaporates while the other part slowly mixes with water. As the butanolic dispersion of Ag_{44} @Te NWs is dropped on water, the NWs are dragged along with butanol and they remain in the thin butanol layer. However, the speed of spreading decreases with distance, and the NWs cannot be dragged along beyond a point and they accumulate in a small region. The NW concentration increases further in the butanol layer as it evaporates and mixes with water. Once a certain critical concentration of NWs is reached, controlled aggregation of the NWs may happen within the solvent layer (Figure 1D). TEM images taken by directly drop-casting the Ag_{44} @Te NW dispersion in 1-butanol (at C₃, where the Woodpile structure forms) (Figure 8A) showed the possibility of formation of preorganized NW aggregates during solvent evaporation.

According to the Derjaguin-Landau-Verwey-Overbeek (DLVO) theory, the repulsive force between two particles is directly proportional to the magnitude of zeta potential. The zeta

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potential for the Te NWs was -6.7 mV whereas it was -2.6 mV for Ag_{44} (@Te NWs (C_3) for the same NW concentration. A systematic increase in the value of zeta potential was found (Figure 8B) with increased loading of Ag_{44} (C_1 to C_5) onto Te NWs. This indicates increased tendency of aggregate formation, in Ag_{44} (@Te NWs than in Te NWs, presumably induced by the attached Ag_{44} . Changing the Ag_{44} concentration from C_1 - C_5 led to the synthesis of assemblies of

11 JPO CHENNAI 28132015 17:49 Ag₄₄@Te NWs with different geometries (Figure 9). For instance, a monolayer assembly was observed for C₁, while for C₅, bundled NWs were seen. C₃ was the optimum concentration for ordered bilayer assembly while C₂ and C₄ showed the onset of bilayers and bundles, respectively. Thus, cluster loading determines the nature of the assembly. As hydrogen bonding (H-bonding) determines the nucleation of Ag₄₄ in its crystal growth, [B. Yoon. et al, Nat. Mater. 2014, 13, 807] the preformed aggregates directed through H-bonding may exist at the air-liquid interface. Thickness of the liquid layer and concentration of Ag₄₄@Te NWs restrict growth beyond bilayer.

The origin of such unique assembled structures can be rationalized from the structure of Ag44, which forms a crystalline lattice in which individual Ag44 clusters are connected to the neighboring ones via hydrogen bonding between the p-MBA ligands present in its shell structure 10 [B. Yoon. et al, Nat. Mater. 2014, 13, 807]. Figure 3A displays a view of two types of H-bonding between neighboring clusters in the Ag44(MBA)30 super lattice structure. In each cluster, the MBA ligands are present in bundles of two (L₂) or three (L₃) units. H-bonding is known to occur between either two L₂ pairs (Figure 3A) or two L₃ pairs (Figure 3A) of ligands in the Ag₄₄ crystal. In Ag44@Te NWs, Ag44 clusters anchor themselves onto the NW surfaces through the 15 carboxylate (-COO-) groups of p-MBA. While a few of the p-MBA ligands of an Ag44 cluster are engaged in its attachment to the NW, others are free. As Ag44@Te NWs within the alcohol layer come in close proximity due to the evaporation of butanol, the free p-MBA ligands of two neighboring Ag44 clusters attached to adjacent NWs may form H-bonds. As cluster coverage of the NWs plays an important role in determining the final structure of the NW assembly, 20 formation of these H-bonds may be the driving force for the assembly.

To understand the role played by H-bonding in deciding the angle between the layers, the invention have computationally modeled how Ag₄₄ clusters could arrange in between (i) a pair of parallel Te surfaces separated by 3.4 nm and (ii) a pair of parallel Te surfaces separated by 3.4 nm and a third Te surface at a distance of 3.4 nm in a second layer at an angle of 81° to first two. It can be seen that in order to fit into the 3.4 nm inter-NW distance, the clusters are so arranged that they belong to two different planes (P₁ and P₂), labeled as C₁ and C₂, respectively (Figure 10A). In such a scenario, in any plane, each cluster is surrounded by four clusters from the same plane and by two clusters from the second plane, as can be seen from the top view of the same arrangement (Figure 10B). Consequently, each cluster is involved in three L₃ H-bonds (9 in all) and two L₂ H-bonds (4 in all) i.e., a total of 13 H-bonds. This will be the case whether the Te

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surfaces are from the same or two different layers (Figure 3Bb). This model is representative of the 81° crossed bilayer assembly (Figure 3Ba), the experimentally observed structure. In this case, however, additional H-bonding can occur between clusters belonging to three different planes (C1, C2 and C3) in the intersecting region. As illustrated in the close-up views in Figures 11 A and B, each cluster in P₃ plane (labelled C₃) can be involved in (a) one L₃ H-bonding with a 5 neighboring cluster in P_1 (C_1) and (b) one L_2 H-bonding each with two neighboring clusters in P_2 (C₂), making a total of seven additional H-bonds. A further zoomed in view of the L₃ H-bonding between C_3 and C_1 is shown in Figure 3Bc. We further modeled two extreme cases of NW assembly in the following manner; (i) a pair of parallel Te surfaces separated by 3.4 nm and an additional third Te surface in a second layer at an angle of 90° at a distance of 3.4 nm (Figure 10 3Cb) and (ii) two pairs of parallel Te surfaces which are in a parallel arrangement, such that each is separated by 3.4 nm (Figure 3Db). Former represents orthogonal (90°) bilayer assembly of Te NWs (Figure 3Ca), while latter represents parallel (0°) assembly of the same (Figure 3Da). While formation of L_2 H-bonds between C_3 and C_2 remains feasible in both the arrangements, formation of L₃ H-bonds between C_3 and C_1 get greatly affected. The model for 90° orthogonal 15 assembly (Figure 3Db), although appears similar to the 81° crossed bilayer one, closer inspection (Figure 3Dc) reveals that ligand bundles involved in L₃ H-bonding in the earlier case moves away from each other; making L₃ bonding impossible. Formation of a L₁ H-bond, involving a pair of MBA ligands, however, is still possible in this case (Figure 3Dc). In case of parallel assembly, those ligand groups move further away from each other as can be seen from both the 20 model (Figure 3Db) and close-up view (Figure 3Dc); thereby further diminishing the possibly of H-bonded interaction between C₃ and C₁. Therefore, conclude that greater number of H-bonds will be formed in an 81° crossed bilayer assembly and so greater will be the stability of the structure. Assuming that all the Ag44 clusters absorb on equivalent sites, 81° orthogonal arrangement of the NWs leads to the most symmetrical arrangement of the sandwiched H-25 bonded network of clusters. Furthermore, ligands from the neighbouring clusters tend to bump

into each other in case of 90° orthogonal assembly whereas this steric factor becomes relaxed in

81° orthogonal assembly (Figure 12), making this structure further stable.

The invention found the concentration of the NWs in the butanol dispersion to play an

important role in the bilayer assembly. An amount of 1 mL of the as-synthesized Te NWs per 30

mL of butanol was optimal for the above assembly to occur. At concentrations higher than this,

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the NWs did not disperse well in butanol, while at lower concentrations more randomly oriented NWs were observed. This indicates that while crossed assembly formation is stabilized through H-bonding, concentration of NWs controls the kinetics and structure of the assembly. However, environmental factors like room temperature (increase by 8°C) and humidity (10% increase) did not have much effect on the ease of assembly formation.

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In order to validate the role of cluster sandwiching for NW assembly formation, another well-known cluster with the same monolayer protection, $Au_{102}(p-MBA)_{44}$ (referred hereafter as Au102), was used instead. Like Ag₄₄, Au₁₀₂ was synthesized by a reported procedure and was characterized by UV-visible spectroscopy (Figure 13). A large area TEM image of the assembly of Au₁₀₂@Te NWs displays an interlaced array of Te NWs (Figure 14A). A zoomed in view of the same reveals that inter-NW distances are longer (3.7 ± 0.2 nm) than in the case of Ag₄₄ (Figure 14B). The difference of ~0.3 nm can be accounted in terms of the larger diameter of Au₁₀₂ (1.3 nm) vs. Ag₄₄ (1.1 nm) cores. The angle between the Au NWs of the two layers changed slightly to ~77° for Au₁₀₂ from 81° for Ag₄₄. This is understandable as the geometrical arrangements of the ligands in the two clusters are different. Our conjecture of inter-cluster H-bond formation between QC@Te NWs from an evaporating dispersion leads to the formation of crossed assembly was further tested by directly drop casting a dilute dispersion of Au₁₀₂@Te NWs (in water). The grid contained several patches of large area crossed assembly of the NWs with very few isolated NWs (Figure 15). MBA functionalized Te NWs formed only monolayer assemblies in the relevant concentration window.

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These bilayer structure of NWs, formed through cluster sandwiching, are stable for weeks in air when trasferred onto suitable substrates. In order to demonstrate a potential application of the bilayer assembly, we constructed an electronic device by transferring the assembly on a PET substrate. The device showed changes in the electrical conductivity upon bending (Figure 16) and may be used in strain sensing (as in electronic skin).

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Experimental Section

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The synthesis methods incorporated in the experimental section of this application illustrate the method which is employed for the synthesis of preferred embodiments of the invention.

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Synthesis of Te NWs: Te NWs were synthesized from TeO₂ by a polyol method [B. Mayers. et al, Mater. Chem. 2002, 12, 1875]. 480 mg of TeO₂ was dissolved into 50 mL of ethylene glycol (EG) containing 140 mg of dissolved NaOH and 1.5 g of PVP at 120 °C on a magnetic stirrer-cum-hotplate. Then, the temperature of the solution was elevated to 160 °C and 300 μ L of hydrazine monohydrate was quickly injected into this hot solution. The solution turned brown immediately and then slowly turned into dark blue after some time indicating the formation of Te NWs. The reaction mixture was removed from the hotplate after 30 min and was left to cool naturally.

Thicker and longer Te NWs, used for Raman imaging experiment were also synthesized by a polyol method, with slight modification. PVP (0.6 g) and TeO2 (0.72 g) were dissolved in 10 40 mL of EG by heating the mixture at 170°C on a magnetic stirrer-cum-hotplate. Nearly 0.3 g of NaOH was dissolved in 10 mL EG by heating and the resulting solution was added to the reaction mixture at 170°C. The solution turned dark grey immediately. The reaction was continued for 45 min and then cooled down to room temperature to produce Te NWs of ~6-8 μ m length and ~100-120 nm diameter. 15

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Synthesis of Ag44: Ag44 cluster was synthesized using a reported procedure [A. Desireddy. et al, Nature 2013, 501, 399]. Initially 128 mg of AgNO3 was taken in a beaker containing DMSO and water (4:7 volume ratio) mixture under constant stirring. 173 mg of MBA was added to the mixture and stirring was continued. 50% CsOH was added drop-wise till the cloudy nature of thiolates became clear and a greenish yellow color appeared. Then 283 mg of NaBH₄ in 9 mL water was added drop-wise to obtain a brown colored solution. Color of this solution changed to deep red after 1 h, which confirmed the cluster formation. This crude cluster was purified using DMF, which precipitated the cluster, and the solution was centrifuged. After removing the centrifugate, the cluster was extracted in citric acid containing DMF solution. This is to acidify all the protons of carboxylic acid, which makes the cluster soluble in DMF. The extracted cluster

was again precipitated using toluene and the solution was centrifuged. The acidification step was

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repeated one more time. After this, the precipitate was re-dissolved in 25 mL DMF to get the purified cluster. It is important to mention here that when all carboxylates are protonated, there is

no need of citric acid and DMF can extract the cluster. Protonation is the key step for this

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purification. 30

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Synthesis of Au_{102} : The Au_{102} (MBA)₄₄ cluster was synthesized using the method developed by Kalisman et al. About 28 mM HAuCl₄, 95 mM p-MBA and 300 mM NaOH were mixed in a water-methanol mixture (47% (v/v) methanol) in such a way that the final concentrations of HAuCl₄ and p-MBA were 3 mM and 9 mM, respectively. The solution was kept under stirring condition. Then freshly prepared NaBH4 solution (150 mM in water) was added to the HAuCl₄/p-MBA mixture. The NaBH4 and Au mole ratio was 2:1. The stirring was continued overnight. After the NaBH₄ addition, the mixture turned black slowly, which indicated the gold cluster formation. The crude cluster was precipitated by ammonium acetate (80 mM) and centrifuged at 13000 rpm for 10 min. The pellet was allowed to dry in air overnight, redissolved in 200 µL of water, and purified by fractional precipitation, using methanol. The final cluster was extracted in water.

Surface modification of Te NWs with Ag_{44} : 5 mL of the EG dispersion of Te NWs was diluted with DMF and was centrifuged at 12000 rpm for 10 min to precipitate the NWs. The precipitated NWs were re-dispersed-precipitated three more times from DMF to get clean NWs. These were finally dispersed in 20 mL of DMF. To this solution taken separately (4 mL each), 100, 200, 300, 500 and 750 µL stock solutions of Ag_{44} (C₁ to C₅, respectively) were added under constant magnetic stirring. Stirring was continued for 1 h and NWs were then centrifuged out from the unreacted cluster. The same method was followed in the case of Au_{102} .

Assembly formation: The centrifuged QC@Te NWs were dispersed in 1 mL of 1-butanol by gentle sonication. Millipore water was filled to the brim of a petridish and the dispersion was dropped slowly on the surface of water from a pipette. NW assembly forms within a couple of minutes and floats on the surface of water. At this point, the assembly appears like a shiny mirror. The assembly was then transferred onto the TEM grids for examination with an electron microscope.

Instrumentation: UV-visible absorption/extinction spectra were recorded using a Perkin-Elmer Lambda 25 spectrophotometer in the range 200-1100 nm using absorption cells having a

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Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) were performed at an accelerating voltage of 200 kV on a JEOL 3010, 30 300 kV instrument equipped with a UHR polepiece. A Gatan 794 multiscan CCD camera was used for image acquisition. NW assemblies floating on water were transferred on 300-mesh 16 IPO CHENNAI 28122015 17:49

path length of 1 cm.

carbon coated copper grid (spi Supplies, 3530C-MB) and dried in ambient condition, before TEM analysis. NW dispersions were dropcasted on grids and dried prior to analysis. Raman spectra were recorded on a Witec alpha300 S confocal Raman spectrometer with a 633 nm (He-Ne) laser using a Zeiss 20x objective. Single nanowire Raman imaging was performed using a Nikon 100x objective. Data was processed by the Witec Project Plus software package. Zeta potential measurements were performed on a Malvern Zetasizer Nano ZS-90.

Chemicals used: All the chemicals were commercially available and were used without further purification. Silver nitrate (AgNO₃, 99%), gold (III) chloride trihydrate (HAuCl₄, $3H_2O$, 99%), 4-mercaptobenzoic acid (MBA, 97%) and sodium borohydride (NaBH₄, 99.99%) were purchased from Aldrich. Tellurium dioxide (TeO₂, 99.9%) powder, hydrazine monohydrate (N₂H₄.H2O, 99-100%) and PVP (Polyvinylpyrrolidone, K25) were supplied by Alfa Aesar, Fischer Scientific and SD Fine Chemicals, respectively. Ethylene glycol (LR), dimethylformamide (DMF, AR grade), dimethysulfoxide (DMSO, AR grade), toluene (AR grade), methanol (AR grade), ammonium acetate, citric acid and sodium hydroxide (NaOH) pellets were procured from RANKEM, India

Computational modelling: The structure for Ag₄₄(MBA)₃₀ was generated using the X-ray crystallographic coordinates deposited at the Cambridge Crystallographic Data Centre (CCDC) under the deposition name CCDC 949240. To model the Te NW bilayer assembly (parallel and orthogonal), the Ag₄₄ clusters were sandwiched between Te(001) surfaces. All the structures were built using ase-gui, which is the graphical interface available with Atomic Simulation Environment (ASE)1, and VESTA2 visualization software program

Conductivity measurements: Bilayer assembly of Ag₄₄@Te NWs was transferred onto flexible PET substrates and was dried under ambient condition. Then electrical contacts were put on them with conductive silver-paste and carbon tape. A constant potential of 1 V was applied across these two contacts using a Keithley source meter and conductance of the assembly was monitored at its resting state as well as while bending the substrate.

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We Claim:

1. A direct, one-step, solution based method for creating crossed bilayer assemblies of nanowires (NWs) with precise angle between the layers, the said method comprises

anchoring the ligand protected atomically precise noble metal quantum cluster molecules over nanowire surfaces and

forming hydrogen bonds between the protecting ligand shells of atomically precise noble metal quantum clusters over the one dimensional NWs,

wherein, the hydrogen bonds are formed between the atomically precise noble metal quantum clusters bond to the surface of a NW with clusters sitting on the neighboring NWs of the same and different layers and the formation of such sandwiched cluster pairs between the NWs leads to the generation of highly ordered NW assemblies..

- 2. The method as claimed in claim 1, wherein the nanowire is tellurium nanowire modified with an atomically precise cluster.
- The method as claimed in claim 1, wherein the atomically precise clusters are Ag₄₄(p-MBA)₃₀ and Au₁₀₂(p-MBA)₄₄, wherein p-MBA is para-mercaptobenzoic acid.
- 4. The method as claimed in claim 1, wherein the molecular interactions between the ligands of atomically precise cluster molecules anchored on tellurium nanowires spontaneously create bilayers.
- 5. The method as claimed in claim 1, wherein the angle between the Ag and Au nanowires of the two layers are 81° for Ag₄₄(MBA)₃₀) and ~77^{\circ} for Au₁₀₂(MBA)₄₄.
- 6. The method as claimed in claim 1, wherein the bilayer assemblies of tellurium nanowire is formed at the air-water interface and are transferrable onto solid substrates.
- The method as claimed in claim 1, wherein the greater number of hydrogen bonds is formed in an 81° crossed bilayer assembly, thereby providing greater stability to the structure.
- 8. The method as claimed in claim 1, wherein the oriented bilayer assembly of the nanowires was obtained by slowly dropping a dispersion of quantum clusters at tellurium nanowires in 1-butanol on a static water surface.
- 9. The method as claimed in claim 1, wherein inter-cluster hydrogen bond is formed by evaporating a dispersion of the protected NWs in 1-butanol with the respective clusters.
- 10. The method as claimed in claim 1, wherein the angle between the layers is in the range of $0-90^{\circ}$.

- 11. The method as claimed in claim 1, wherein the said bilayer assemblies used for making devices such as artificial skin with a measureable change in resistance upon bending and elongation.
- 12. The method as claimed in claim 1, wherein the said assembly used for the devices involving change in the properties of the bilayer assemblies.

Dated at Chennai this June 29, 2019

Signature: Any Ingen

D. Moses Jeyakaran Advocate & Patent Agent IN/PA — 369

METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTERS

ABSTRACT

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The present invention relates to highly organized crossed bilayer assemblies of ID tellurium nanowires (NWs) are made directly from the solution state using directed hydrogen bonding between the protecting ligand shells of atomically precise quantum clusters (QCs). The said atomically precise clusters are Ag₄₄(p-MBA)₃₀ and Au₁₀₂(p-MBA)₄₄. Layers of QCs remain sandwiched between two neighbouring NWs and keep them apart at a distance, dictated by the core-size of the cluster, while orientation of ligands in space dictates interlayer geometry. This kind of ordered assembly of crossed NWs is of interest for applications, especially in nanoscale optics and electronics.

METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES 5 USING AN ATOMICALLY PRECISE CLUSTER



Figure 1

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Figure 2

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5 METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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Figure 3

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Figure 4

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5 METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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Electron beam irradiation time

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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES 10 USING AN ATOMICALLY PRECISE CLUSTER



Figure 7

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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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5 METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER



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Figure 9

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Figure 10

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5 METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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Figure 11

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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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Figure 12

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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER



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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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Figure 14

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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES USING AN ATOMICALLY PRECISE CLUSTER

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Figure 15

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METHOD FOR PREPARING CROSSED BILAYER ASSEMBLY OF 1D NANOWIRES 5 USING AN ATOMICALLY PRECISE CLUSTER

40 Ag44@TeNWs 35 Current (µA) 30· 25 100 200 300 0 Time (S)



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