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Self-organization of micro and nanostructures leading to superlattices enabling the creation of photonic crystals,^[1–5] sensors,^[6–8] materials for biomimetics,^[9] energy harvesting,^[10,11] and high-density storage,^[12-14] 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.^[15–18] 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)^[19-24] and nanotubes (NTs)^[25,26] spontaneously organize parallel to their long axis, similar to "logs-on-a-river."[27] Similar assemblies leading to the formation of monolayers at interfaces^[28,29] are known for tellurium NWs (Te NWs). Organized bilayer structures are seen rarely and are obtained through successive transfer of monolayers.^[19,28] One-step formation of such integrated architectures directly from solution, however, is not known so far.

Atomically precise noble metal quantum clusters (QCs) protected with ligands is a new class of materials.^[30-40] Their small size, of the order of a nanometer and the variety and density of functionalities present on them can be used to create new composite structures with 1D nanostructures such as NWs, as such structures are often tens of nanometers in diameter and hundreds of nanometers long. Such composite structures can have new properties distinctly different from clusters and NWs. Here, we demonstrate 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, $Ag_{44}(p-MBA)_{30}$ (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 transferable onto solid substrates.

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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 has four negative charges while Na⁺ act as counterions. The structure of this cluster,^[38,41] abbreviated as Ag44, shown in Figure 1A, was generated based on previously reported X-ray crystallographic co-ordinates (see the Supporting Information).^[38] Ag₄₄, prepared via a reported procedure,^[38] 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 S1A, Supporting Information). The identity of the cluster was confirmed from the highresolution electrospray mass spectrum as well (Figure S1B, Supporting Information). Te NWs, having an average length of 2.5 µm and a diameter of 28 nm (Figure 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 UV-visible spectrum at 288 and 765 nm due to electronic transitions from the p-bonding and p-lone pair states, respectively, in the valence band to the p-antibonding states in the conduction band (trace b, Figure S1A, Supporting Information).^[42] Surface modification of Te NWs with Ag₄₄ was achieved by mixing both the precursors in dimethylformamide (DMF) solution. Increasing amounts of Ag₄₄ ([C₁] to [C₅], see the Experimental Section) 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 precipitation of the "Ag44modified-Te NWs" (Ag44@Te NWs) to remove the unattached Ag₄₄. The UV–visible extinction spectra of redispersed 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 S1C, Supporting Information), an indication of adsorption of more and more cluster molecules on the Te NW surface. The observed shift in the positions of the 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 Ag_{44} steadily decreased with increasing concentration of Ag44 initially and converged later to a value of ≈5 nm (Figure S1D, Supporting Information). This trend was also observed for other peaks (insets, Figure S1D, Supporting Information), and can be explained to be due to adsorption. At low cluster concentrations, the NW surface is accessible to all the QCs, which 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 avail-

able lower energy sites as well as multilayers becomes possible,

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Figure 1. A) Structure of $Ag_{44}(p-MBA)_{30}$ modeled based on the crystal structure.^[38] B) TEM image of a single Te NW. Diameter and length distributions for the Te NWs are shown in the insets, (i) and (ii), respectively. The area from where the HRTEM image was collected is marked. Scale bar is 400 nm. 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. 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 the air–water interface in 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 Ag_{44} @Te NWs for the same NW concentration as the pristine Te NWs. Schematic illustration 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 both the layers.

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) process, which has been used for generating monolayer assemblies of nanomaterials of various shapes and sizes.^[43] Similar monolayer assemblies of hydrophilic-nanostructures can be obtained through fast-spreading of a suspension over a water surface, assisted by solvent drying.^[29] This process is considerably faster (completed within a few minutes) than the Langmiur-Blodgett technique, which normally requires hours. Following the same strategy, a dispersion of Ag44@Te NWs in 1-butanol was spread over water, taken in a petri dish. 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 (shown in 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.^[44] Here, NWs from the same layer lie parallel to each other, but are at an unusual angle of $\approx 81^{\circ}$ 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). We believe that different states of aggregation of Ag₄₄@Te NWs in comparison to Te NWs drive the formation of the orthogonal bilayer assembly. We will discuss the details below.

Cluster-attachment to the NWs is confirmed by electron microscopy studies of the Ag_{44} @Te NWs. For small clusters like Ag_{44} , distinct identification of individual QCs is difficult through standard electron microscopy, and when attached on a thick Te NW surface, they did not produce enough contrast to be identified (**Figure 2**A). However, these clusters tend to

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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 Ag₄₄@Te NW. Raman spectrum shows features of both Te and Ag₄₄. D,E) Images constructed by mapping the most prominent Raman features of Te NW and Ag₄₄ (marked as (d) and (e) in (C)), respectively.

aggregate to form nanoparticles 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 QCs and not due to their solution phase aggregation on the Te NW surface, as proven in a previous study from our group.^[45] This was substantiated further by following the time evolution (over a period of 2 min) of the nodules on NWs (Figure S2, Supporting Information), which demonstrated the systematic growth of silver particles upon electron beam exposure. The TEM data discussed so far is for $[C_3]$ as at this cluster concentration, nodule formation and their evolution were observed most prominently. At cluster concentrations lower than $[C_3]$ ($[C_1]$ and $[C_2]$), smaller and fewer nodules were formed, making them indistinguishable. At higher concentrations ([C₄] and [C₅]), continuous darker islands were observed, almost instantaneously, upon electron beam irradiation (Figure S3, Supporting Information).

Though electron microscopy confirms cluster binding to the NWs, a more direct confirmation was available from nondestructive Raman spectroscopy. For Te NWs, an intense Raman peak appeared at 124 $\rm cm^{-1}$ due to the Raman active singlet A_1 mode (breathing in the *ab* plane) of lattice vibrations (Figure S4A, Supporting Information),^[46] while Ag₄₄(p-MBA)₃₀ exhibited several peaks (Figure S4B, Supporting Information) with two strong bands at 1077 and 1584 cm⁻¹ arising from v_{12} (ring breathing) and v_{8a} (ring in-plane stretching) aromatic ring vibrations, respectively.^[47] It is to be noted that for Raman spectral imaging, thicker and longer Te NWs were synthesized (see the Supporting Information). The Raman spectrum collected from Ag₄₄@Te NWs showed the prominent features of both Te NWs and Ag₄₄ (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 Ag₄₄ (marked as (d) and (e) in Figure 2C, respectively) are presented in Figure 2D,E, respectively. The cluster map matches exactly with that of Te confirming its uniform coverage on the NW surface. The Raman image in conjunction with UV-visible extinction spectra and time-dependent evolution of the nodules upon electron beam irradiation proves that the clusters remain on the NW surface in their pristine form.

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

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assembly formation. Although butanol is thermodynamically miscible with water (solubility of 73 g L^{-1}), 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 Ag₄₄@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 (schematically shown in Figure 1D). TEM images taken by directly drop-casting the Ag44@Te NW dispersion in 1-butanol (at $[C_3]$, where the Woodpile structure forms) (Figure S5A, Supporting Information) showed the possibility of formation of preorganized NW aggregates during solvent evaporation.

According to the Derjaguin–Landau–Verwey–Overbeek theory, the repulsive force between two particles is directly proportional to the magnitude of the zeta potential. The zeta potential for the Te NWs was –6.7 mV, whereas it was –2.6 mV for Ag₄₄@Te NWs ([C₃]) for the same NW concentration. A systematic increase in the value of zeta potential was found (Figure S5B, Supporting Information) with increased loading of Ag₄₄ ([C₁] to [C₅]) onto the Te NWs. This indicates an increased tendency of aggregate formation, in Ag₄₄@Te NWs than in Te NWs, presumably induced by the attached Ag₄₄. Changing



the Ag₄₄ concentration from $[C_1]$ to $[C_5]$ led to the synthesis of assemblies of Ag₄₄@Te NWs with different geometries (see TEM images in Figure S6, Supporting Information). For instance, a monolayer assembly was observed for $[C_1]$, whereas for $[C_5]$, bundled NWs were seen. $[C_3]$ was the optimum concentration for ordered bilayer assembly while $[C_2]$ and $[C_4]$ 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,^[48] we infer that 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.^[48] Figure 3A displays a view of two types of H-bonding between neighboring clusters in the Ag44(p-MBA)30 superlattice structure. In each cluster, the *p*-MBA ligands are present in bundles of two (L_2) or three (L₃) units. H-bonding is known to occur between either two L₂ pairs (inset a, Figure 3A) or two L₃ pairs (inset b, Figure 3A) of ligands in the Ag44 crystal. In Ag44@Te NWs, Ag44 clusters anchor themselves onto the NW surfaces through the carboxylate (-COO⁻) groups of *p*-MBA. The X-ray photoelectron spectroscopy (XPS) spectrum of the Te 3d region (Figure S7, Supporting Information) showed the emergence of peaks at higher binding energies in case of Ag44@Te NWs which is indicative



Figure 3. A) H-bonding between neighboring clusters in the $Ag_{44}(p-MBA)_{30}$ superlattice structure. Clusters remain H-bonded with the neighboring ones between L_2 (inset a) and L_3 type of ligand bundles. B) (a–c) 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,D) Representation of 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 C_1-C_3 .



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of Te—O bond formation, supporting our proposition. While a few of the *p*-MBA ligands of an Ag₄₄ cluster are engaged in its attachment to the NW, others are free. As Ag_{44} @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, 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, we have computationally modeled (see the Supporting Information for the modeling details) 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 the 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 S8A, Supporting Information). 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 S8B, Supporting Information). Consequently, each cluster is involved in three L₃ H-bonds (nine in all) and two L₂ H-bonds (four in all), i.e., a total of 13 H-bonds. This will be the case whether the Te 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 Figure S9A,B (Supporting Information), each cluster in P₃ plane (labeled C₃) can be involved in (a) one L₃ H-bonding with a neighboring cluster in P_1 (C₁) and (b) one L₂ H-bonding each with two neighboring clusters in P2 (C2), making a total of seven additional H-bonds. A further zoomed in view of the L₃ H-bonding between C₃ and C1 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 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 the formation of L₂ H-bonds between C₃ and C₂ remains feasible in both the arrangements, the formation of L₃ H-bonds between C₃ and C₁ gets greatly affected. Although the model for 90° orthogonal assembly (Figure 3Db) 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 an L₁ H-bond, involving a pair of *p*-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 model (Figure 3Db) and close-up view (Figure 3Dc); thereby further diminishing the possibility of H-bonded interaction between C_3 and C_1 . We, 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-bonded network of clusters. Furthermore, ligands from the neighboring clusters tend to bump into each other in case of 90° orthogonal assembly whereas this steric factor becomes relaxed in 81° orthogonal assembly (Figure S10, Supporting Information), making this structure more stable.

We found that the concentration of the NWs in the butanol dispersion played an important role in the bilayer assembly. An amount of 1 mL of the as-synthesized Te NWs per mL of butanol was optimal for the above assembly to occur. At concentrations higher than this, 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, the 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.

In order to validate the role of cluster sandwiching for NW assembly formation, another well-known cluster with the same monolayer protection, Au₁₀₂(p-MBA)₄₄ (referred hereafter as Au₁₀₂), was used instead. Like Ag₄₄, Au₁₀₂ was synthesized by a reported procedure^[35] and was characterized by UV-visible spectroscopy (Figure S11, Supporting Information). A largearea TEM image of the assembly of Au₁₀₂@Te NWs displays an interlaced array of Te NWs (Figure S12A, Supporting Information). A zoomed-in view reveals that inter-NW distances are longer (3.7 \pm 0.2 nm) than in the case of Ag₄₄ (Figure S12B, Supporting Information). The difference of ≈0.3 nm can be accounted in terms of the larger diameter of Au₁₀₂ (1.3 nm) versus Ag44 (1.1 nm) cores. The angle between the Au NWs of the two layers changed slightly to ${\approx}77^{\circ}$ for Au_{102} from 81° for Ag₄₄. This is understandable as the geometrical arrangements of the ligands in the two clusters are different. Our conjecture of intercluster 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 S13, Supporting Information). p-MBA functionalized Te NWs formed only monolayer assemblies in the relevant concentration window.

The bilayer structures of NWs, formed through cluster sandwiching, are stable in air for weeks when transferred 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 (polyethylene terephthalate) substrate. The device showed changes in the electrical conductivity upon bending (Figure S14, Supporting Information) and may be used in strain sensing (as in electronic skin).

In summary, a direct, one-step, solution-based procedure for creating a crossed bilayer structure of NWs with a precise angle between the layers was developed by coating *p*-MBA-protected QCs over NW surfaces. Clusters bound to the surface of a NW





form hydrogen bonds with clusters sitting on the neighboring NWs of the same and different layers. Formation of such sandwiched cluster pairs between the NWs leads to the generation of highly ordered NW assemblies, which 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. Some of these applications will be investigated in the future. Creation of other NW architectures by cluster assembly is an interesting possibility.

Experimental Section

Synthesis of Te NWs: Te NWs were synthesized from TeO₂ by a polyol method.^[49] 480 mg of TeO₂ was dissolved into 50 mL of ethylene glycol (EG) containing 140 mg of dissolved NaOH and 1.5 g of Polyvinylpyrrolidone (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 the 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 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 \approx 6–8 μ m length and \approx 100–120 nm diameter.

Synthesis of Ag_{44}: Ag_{44} cluster was synthesized using a reported procedure.^[38] Initially, 128 mg of AgNO₃ was added to a beaker containing Dimethyl sulfoxide (DMSO) and water (4:7 volume ratio) mixture under constant stirring. 173 mg of p-MBA was added to the mixture and stirring was continued. 50% CsOH was added drop-wise until the cloudy nature of thiolates became clear and a greenish yellow color appeared. Subsequently, 283 mg of NaBH₄ in 9 mL water was added drop-wise to obtain a brown-colored solution. The 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. After this step, the solution was centrifuged. After removing the centrifugate, the cluster was extracted in citric acid-containing DMF solution. This was done to acidify all the protons of the carboxylic acid, which makes the cluster soluble in DMF. The extracted cluster was again precipitated using toluene and separated from the solution by centrifugation. The acidification step was repeated one more time. After this step, the precipitate was redissolved in 25 mL DMF to obtain the purified cluster. Note that when all the carboxylates are protonated, the use of citric acid is not necessary, and DMF can be used to extract the cluster. Protonation is the key step for this purification.

Synthesis of Au_{102} : The $Au_{102}(p$ -MBA)₄₄ cluster was synthesized using the method developed by Kalisman and co-workers.^[35] About 28 $\times 10^{-3}$ M HAuCl₄, 95 $\times 10^{-3}$ M p-MBA, and 300 $\times 10^{-3}$ M 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 $\times 10^{-3}$ and 9 $\times 10^{-3}$ M, respectively. The solution was kept stirring. Then, freshly prepared NaBH₄ solution (150 $\times 10^{-3}$ M in water) was added to the HAuCl₄/p-MBA mixture. The molar ratio of NaBH₄ and Au was 2:1. The stirring was continued overnight. After the NaBH₄ addition, the mixture turned black slowly, which indicated gold cluster formation.

The crude cluster was precipitated by ammonium acetate (80×10^{-3} m) and centrifuged at 13 000 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 Ag₄₄: 5 mL of the EG dispersion of Te NWs was diluted with DMF and was centrifuged at 12 000 rpm for 10 min to precipitate the NWs. The precipitated NWs were redispersed and precipitated three more times from DMF to obtain clean NWs which were finally dispersed in 20 mL DMF. 4 mL aliquots of this solution were combined with 100, 200, 300, 500, and 750 μ L stock solution of Ag₄₄ ([C₁] to [C₅] respectively) 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 Au₁₀₂.

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 petri dish and the dispersion was dropped slowly on the surface of water from a pipette. NW assembly was formed within a couple of minutes and floated on the surface of water. At this stage, the assembly appeared like a shiny mirror. The assembly was then transferred onto the TEM grids for examination by electron microscopy.

Instrumentation: UV–visible absorption/extinction spectra were recorded using a Perkin–Elmer Lambda 25 spectrophotometer in the range of 200 to 1100 nm using absorption cells with a path length of 1 cm.

TEM and high-resolution transmission electron microscopy (HRTEM) were performed at an accelerating voltage of 200 kV on a JEOL 3010 instrument equipped with a Ultra-high-resolution (UHR) polepiece. A Gatan 794 multiscan charge-coupled device (CCD) camera was used for image acquisition. NW assemblies floating on water were transferred on 300-mesh carbon coated copper grid (spi Supplies, 3530-MB) and dried in ambient condition, before TEM analysis. NW dispersions were drop-casted on grids and dried prior to analysis. Raman spectra were recorded on a Witec alpha300 S confocal Raman spectrometer equipped with a 633 nm (He-Ne) laser using a Zeiss 20× 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.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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