Controlled and Selective Growth of 1D and 3D CdTe Nanostructures through a Structurally Engineered Porous Alumina Template for Enhanced Optical Applications

Harsimran Singh Bindra,a Subish John,b Somnath C. Roy,b Om Prakash Sinha,a S. S. Islam,c and Rannay Nayak a,b,c

aAmity Institute of Nanotechnology, Amity University, Noida, India 
bDepartment of Physics, Indian Institute of Technology Madras, Chennai, India 
cCenter of Nanoscience and Nanotechnology, Jamia Millia Islamia University, Delhi, India

Current manuscript describes porous alumina (PA) template assisted electrodeposition of high aspect ratio nanowires and dense hierarchical structures of CdTe. We demonstrate here for the first time that simple structural tuning of a PA template can lead to electrochemical growth of diverse shapes of CdTe nanostructures. Facile and cost-effective modifications have been implemented for the fabrication of self-organized through-hole PA membrane and its transfer onto any rough substrate. These modifications have facilitated extended duration (30 minute to 1 hour) electrodeposition of CdTe nanostructures at high bath temperature of 60°C without delaminating the PA membrane. High aspect ratio nanowires of 60 nm diameter and 2.8 μm length were growth through the self-ordered PA membrane without any underlying metal coating i.e. without altering its optical properties. An average of 56% optical absorption (within 350 nm – 1400 nm wavelength) and a moderate photoluminescence was observed for the CdTe nanowires. Minor variation in the anodization process resulted into a non-uniform/branched PA template that enabled the formation of dense 3D hierarchical structures of CdTe using similar electrodeposition conditions as that used for CdTe nanowires. The hierarchical CdTe nanostructures exhibited very high total optical absorption of ~90% within 350 nm – 1400 nm wavelength and a strong photoluminescence was also demonstrated that was almost 10 fold more intense than the CdTe nanowires.

© The Author(s) 2017. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOE: 10.1149/2.0091804jes]

Manuscript submitted October 23, 2017; revised manuscript received November 28, 2017. Published December 15, 2017. This paper is part of the JES Focus Issue on Processes at the Semiconductor-Solution Interface.

CdTe, CdS, CdSe are well established II-VI periodic group optically active chalcogenide semiconductor materials with immense applications in optoelectronic, photonics and bio-labelling applications. Intervention of Nanoscience and Nanotechnology has enabled realization of low dimensional nanostructures of Cadmium chalcogenides (CdS, CdSe, or CdTe) with enhanced surface area to volume ratio that have attracted major appreciation with their unique and enhanced electronic and optical properties.1-3 Specifically, 1D Cadmium chalcogenide nanowires/nanorods have demonstrated high performance optoelectronic applications such as optical waveguides, lasers, photoluminescence, photodetectors (visible, NIR), solar cells, etc.4,5 It is realized that a precise control over the size and the structure of nanostructures enables vast tuning of the energy band gaps and generates unique optical properties.6 Unlike 2D structures, nanowires can accommodate large amount of mismatch related strain via radial expansion or contraction. It is known that nanowires with high aspect ratio can provide efficient absorption even with smaller depth that can increase the efficacy of photovoltaic devices.7 Especially, CdTe nanowires holds potential for low-cost photovoltaic due to its high absorption coefficient, with a capability of absorbing significant amount of sunlight in a layer thickness of only ~1 μm, as compared to ~10 μm for Si. Overall, it is apparent that there has been a major focus onto controlling the structural parameters and morphology of 1D nanostructures for enhanced properties.8,18,19

There are several methods reported for the growth of nanowires of semiconductor chalcogenides.20-23 Template assisted growth of nanowires is noted as the most efficient route because of its wide range ordering in pore diameter and facile control of high aspect ratio.22,24-27 Especially, porous alumina (PA) as a template, has gained lot of focus for template assisted growth of metal nanowires.28-30 Semiconductor nanowires1 and carbon nanotubes.32 PA template assisted electrodeposition is a simple and cost effective method that gives dense, high aspect ratio, crystalline vertically standing 1D nanostructures.33-35 It is observed that for successful electrochemical growth of nanowires/nanorods using PA template, removal of the barrier oxide is of prime importance. Two different techniques have been reported for the removal of barrier oxide layer from the bottom of the pore channels. Mallouk et al. reported removal of barrier oxide by reverse biasing the applied voltage after the anodization process.29 However, the process resulted in formation of cracks and voids along with detachment of the alumina film from some points. Wioletta et al. and Gillette et al. described another technique by decreasing the applied voltage at various ramping rates.36,37 In this process it was observed that in addition to thinning the barrier layer, various branches among the pores also develop. The above-mentioned literature protocols for barrier thinning seems to be less feasible for template assisted growth of ordered nanowires. Most reliable way appears to be the use ordered self-organized through hole PA membrane on conductive substrates to grow uniform array of semiconductor nanowires.33,35,38,39 However, PA template assisted growth of high aspect ratio semiconductor nanowires directly on transparent conductive oxides (TCO) has not been reported. Rather, a thin metal coating is electrodeposited prior, for ease and faster rate of semiconductor deposition. The reason being, poor adhesion of PA membrane often tends to delaminate the membrane off the substrates in harsh electrodeposition conditions (like high temperature, long duration current passage, acidic environment, mechanical agitation, etc.). As the PA membrane tends to peel off from the substrate, the nanowires loose their 1D geometry and starts aggregating into bulk structures.

In the present work we have demonstrated high aspect ratio electrochemical growth of CdTe nanowires directly onto FTO coated glass substrate (without any thin metal coating) through an uniform self-organized PA membrane so that the optical properties of CdTe remain unaltered. A cost-effective and facile way of transfer and an exceptionally strong adhesion of the PA membrane onto a FTO substrate have been demonstrated. Some major modifications and thus significat improvements have been incorporated in comparison to the already reported literatures on transfer and adhesion of PA membrane to enable the growth of high aspect ratio, vertically standing CdTe nanowires on FTO coated glass.33,35,39

E-mail: mnayak@amity.edu; runnayakbone@gmail.com
In addition to 1D nanostructures, 3D hyperbranched/hierarchical nanostructures have shown several advantages with enhanced optical properties. 40, 41 3D branched nanostructures possess properties like high surface area and improved direct charge transfer pathway which make them more appropriate material for energy storage applications. For instance, 3D hierarchical nanostructures of cadmium chalcogenides CdTe/CdS and CdSe/CdS has been reported with enhanced electronic and optical properties. 6, 23, 24 According to earlier reports, several techniques like sequential catalyst-assisted growth, 6, 26 solution growth on pre-formed nanowires, 6, 27 one step self-catalytic growth 6, 28 and screw dislocation in combination with VLS 6, 29, 30 have been reported for the growth of 3D hyperbranched nanostructures. It is realized that 3D structures grown by vapor phase methods gives defect free structures, but requires complex equipment; moreover, metal catalysts used in most of these growth methods can often degrade the optical properties. The one-step self-catalysed method, although does not require any metal catalyst, but the growth method requires high temperature CVD. In contrast to CVD method, the solution-phase method can be processed at lower temperature with high yield. 5, 25 A typical solution phase method involves the use of organic solvents like TOP (Trioctylphosphine), TOPO (tri-n-octylphosphine oxide) however, these solvents require high reaction temperature (>100 °C) and are relatively high cost. Moreover, the hyperbranched structures of CdTe grown using solution based method have been limited in density. 1, 24 Another literature has reported 3D periodic growth of Bi2Te3 nanostructures using pulsed electrodeposition through rutaghe shaped PA template fabricated by pulsed anodization technique. 55 These structures were shown to demonstrate unique photonic behavior. However, pulsed anodization and pulsed electrodeposition methods are known to have more complexities. Also the fabrication time for the PA template and the nanostructures, was more than 32 hours. 56 It is seen that the branched nanostructures obtained by solution method in most cases are randomly oriented, and are not free standing on substrates and may also suffer from poor crystal quality. Nevertheless, random orientation is not a major concern in energy and gas sensing applications.

In the present article, it is shown that use of a non-uniform PA template with branched porous channels (instead of uniform PA membrane) can be beneficial for the growth of high density 3D hierarchical/hyperbranched structures of CdTe. It is demonstrated here that in addition to phase transition induced branching, pore branching in the non-uniform PA template also assists in the growth of dense 3D structures of CdTe having hierarchical leaf-like architecture with a combination of microstructures and nanostructures. These leaf-like hierarchical nanostructures of CdTe with significantly enhanced surface area to volume ratio can potentially offer highly improved optical and electronic properties for diverse practical applications. As a proof-of-concept, total optical absorption and emission spectrum of the hierarchically structured CdTe has been compared with the nanowires and thin film of CdTe of same amount.

**Experimental**

**Materials.**—Aluminum (Al) foil of 99.99% purity was purchased from Alfa Aesar. Ag/AgCl electrode was purchased from CH Instruments Inc. All the chemicals used in the experiments were of AR grade obtained from Merck Millipore, namely, oxalic acid, phosphoric acid, chromic acid, perchloric acid, ethanol, mercuric chloride, hydrochloric acid, poly styrene, and chloroform.

**Pre-treatment of Al foil.**—Prior to anodization, Al foil was flattened in hot press followed by annealing at 500 °C to remove defects related to stress and strain during flattening. Thereafter, Al foil was electropolished at an input voltage of 14 V for 2 minutes using electrolyte mixture of ethanol and perchloric acid (4:1 v/v) at 2 °C temperature so as to make the foil surface smooth and free from oxide impurities.

**Preparation of non-uniform PA template for the growth of hierarchical leaf-like nanostructures of CdTe.**—PA template was fabricated by a well-established two step anodization method. 56 In brief, pre-treated Al foil was anodized for 1 hour in 0.25 M solution of oxalic acid at 50 V using platinum mesh as counter electrode. Bath temperature was maintained at 5 °C throughout the experiment. The resulting porous oxide layer was chemically etched away using mixture of 1.8 wt% chromic acid and 6 wt% phosphoric acid solutions at 60 °C for 1 hour. After chemical etching of the oxide layer, the Al foil was re-anodized for 1 hour under the same conditions as that in the 1st step anodization. After the 2nd anodization process, oxide barrier removal step was performed under which applied potential was reduced sequentially to zero followed by 10 minutes of pore widening. 56 Pore widening was performed in 5 wt% H3PO4 at room temperature.

**Preparation of uniform self-ordered PA membrane for the growth of CdTe nanostructures.**—The 1st anodization was performed for 8 hours in 0.25 M solution of oxalic acid at 50 V using platinum mesh as counter electrode at 5 °C bath temperature for an ordered pore formation. After removal of 1st step anodized porous alumina, 2nd step anodization was performed for 30 minutes under same condition as that of 1st step anodization, followed by 5 minutes of pore widening. The protocol followed for PA membrane formation and transfer onto a modified FTO coated glass substrate is an adaptation and major extension of already reported literatures. 35, 57 In brief, a thin layer of polymer (1.6 wt% poly styrene in chloroform with a plasticizer additive) solution was spin coated on the PA template and heated at 80 °C for evaporation of solvent. Thereafter, base Al substrate was chemically etched using saturated HgCl2 solution in HCl. After removal of the Al substrate, PA membrane filled with polymer filler was washed thoroughly with distilled water and then treated with solution of 5 wt%, phosphoric acid for oxide barrier removal. After the oxide barrier removal, the membrane was again washed with distilled water and carefully placed on a chemically modified FTO coated glass slide. Thereafter, polymer filler was removed from the pores of the membrane using chloroform with a uniquely modified protocol in comparison to already reported literatures. 35, 58, 59 Finally, annealing was performed at 100 °C for 30 minutes for ensuring a strong mechanical adhesion of the membrane onto a desired substrate. The substrate (FTO coated glass) was further modified by an electrochemically coated thin optically transparent polymer layer that enabled a strong adhesion of the membrane onto any rough substrate. Details of this protocol is under consideration for publication elsewhere.

**Electrochemical growth of 1D and 3D CdTe nanostructures.**—Chronoamperometric deposition of CdTe was performed in a three electrode cell using an electrochemical workstation by Palmsens, model EMSTAT 3+. Platinum mesh (1 in. × 3 in.) and Ag/AgCl were used as the auxiliary and reference electrodes respectively. PA template on Al substrate and PA membrane on modified FTO coated glass substrates were used as the work electrode for deposition of 3D leaf-like hierarchical structures and 1D nanowires of CdTe respectively. An aqueous electrolyte mixture containing 0.2 M Cs2SO4 and 0.5 mM TeO2 was used. pH of the bath was maintained at 1.8 for improving dissolution of TeO2 in aqueous medium. The growth was performed for 30 minutes to 1 hour at 60 °C at different cathodic potentials ranging from 0.6 to 0.65 V. 1D and 3D CdTe nanostructures growth was performed with fixed charge deposition of 1.5 C to keep the amount of CdTe deposition constant each time for an optimum comparison of optical properties. Same amount of charge deposition was also maintained during the growth of CdTe thin film onto FTO coated glass substrate.

**Sample characterization.**—Surface morphology analysis was performed using Scanning Electron Microscope from Zeiss (Model EVO 8.44B) and UV Vis absorption analysis was performed using Shimadzu UV- Vis-NIR spectrophotometer (UV-2600 Plus). Photoluminescence spectrum was obtained at room temperature using Shimadzu’s Photoluminescence Spectrofluorophotometer (RF-5301PC).
X-Ray diffraction graphs were obtained using Rigaku X-ray diffractometer (Model: Smart Lab).

Results

Formation of non-uniform branched PA template.—Figures 1a and 1b shows the top view and side view of scanning electron micrographs (SEM) of the non-uniform PA template with several branching in the porous channels. It is clear from Figure 1 that the porous structures thus formed have irregular aperiodic arrangement of pores and a substantial variation in pore size as well. Pore branching generally results due to shifting the anodization voltage away from the equilibrium condition established for regular pore growth. Barrier oxide thinning/removal on the branched non-uniform PA template was performed by sequentially reducing the applied voltage as reported by Wioletta et al. Figures 2a and 2b shows the transient change in the voltage and current density with a specific time interval respectively. It was observed that when voltage was reduced for oxide barrier removal, the current rapidly dropped to zero and then started increasing gradually till it reached a steady state value. The total anodizing time was 60 minutes that included 44 minutes of pore formation, at a constant current density of 3 mA/cm². Remaining 16 minutes were used for oxide barrier removal by sequential reduction in applied voltage with a time interval of 30 seconds. The decrease in voltage at different rates is shown in Table S1. The as-prepared template was further used to electrochemically grow CdTe nanostructures as discussed in the following text.

Growth of leaf-like 3D CdTe hierarchical structures.—Figure 3a shows the SEM of leaf-like CdTe hierarchical structures grown.
through the non-uniform branched PA template. Presence of thin oxide barrier can be predicted from the region which remained devoid or shows scanty growth of the hierarchical structures. The magnified view of these hierarchical structures (Figure 3b) clearly indicates that these are dense microscopic structures formed with the fusion of several nanowires, taking the shape of micro-dimension leaf-like structure. A significant enhancement in the surface roughness is also observed from the SEM image (Figure 3). Growth of hierarchical CdTe structures was also attempted at room temperature on the same branched PA template; however, effective hyperbranching was not observed at room temperature. Thus, 60 °C bath temperature was found to be optimum for the growth of dense hierarchical CdTe nanostructures. To confirm a major role of branched PA template in the growth of dense hyperbranched CdTe structures, we also attempted electrodepositing CdTe onto plain Al foil and dimpled Al foil (obtained after the removal of 1st step anodized layer). The SEM images are shown in Figure S2a and S2b. It is clearly visible from Figure S2 that only grainy crystalline thin film of CdTe grows on plain Al foil and dimpled Al foil. No traces of CdTe hyperbranching could be observed from the Al foil substrates.

**Formation of uniform self-ordered PA membrane.**—PA membrane consisting of highly ordered hexagonal arrays of straight, cylindrical nanopores were fabricated by a two-step anodic oxidation of Al substrate. Surface morphology of the same is shown in Figure 4. Top-view of the SEM (Figure 4a) indicates a uniform orderly arrangement of pores with an average pore diameter of 60 nm. The thickness of the pores as indicated in the side view of SEM in Figure 4b is approximately ~2 μm. As mentioned earlier in the text, that although there are several reports published on electrodeposition of nanodots and short nanowires of sub-100 nm diameter using thin PA membrane, but direct growth of high aspect ratio semiconductor nanowires/nanorods onto transparent conductive oxide substrates (without any underlying metal layer) is rarely reported. In the present work, a much simpler, more reliable and cost-effective transfer method of PA membrane onto a rough substrate is demonstrated to ensure a strong adhesion (protocol details are under consideration for publication elsewhere - mentioned earlier). In brief, the unique modifications are listed here. The first innovative modification done in this work was to use polystyrene filler with an optimum amount of plasticizer additive to prevent its brittleness and hence resist cracking of the PA membrane. This ensured ease of handling of the membrane; hence a simple plastic fork could easily transfer and place the membrane onto a substrate. The second modification used was the use of chloroform vapor to remove polymer filler from the pores of the membrane, instead of dipping the whole membrane. It is observed that often polymer residue remains on the surface of PA membrane even after complete dipping in conventional organic etchant that in turn leads to blocked pores on the membrane and hence can hinder the growth of uniform nanowires/nanorods through the pores. The variation introduced in the current work ensured complete and reliable removal of polymer filler without damaging the membrane. The third major modification was the use of a chemically modified FTO coated glass substrate. This chemical modification made on the FTO glass slide includes a thin optically transparent organic material coating that was deposited electrochemically on the FTO coated glass substrate. This chemical modification on the FTO coated glass slide ensured a strong adhesion of the PA membrane on the substrate without degrading its optical/electrical properties. It was found that the PA membrane adhered strongly onto the modified FTO substrate during electrodeposition of CdTe nanowires for almost one hour at 60 °C bath temperature which is not reported till date in any literature.

**Growth of 1D CdTe nanowires.**—CdTe nanowires were grown electrochemically through the self-ordered PA membrane at −0.6 V. Prior selecting the deposition voltage a cyclic voltammetry study in the range of −1 V to +1 V was conducted (Figure S3) for analysing the reaction mechanism taking place at different voltages. In order to optimize the deposition voltage for 1:1 stoichiometric composition of Cd and Te, series of depositions at different voltages between −0.55 V to −0.65 V were performed followed by their EDX analysis. The stoichiometric ratio of Cd:Te as obtained from EDX measurement at different voltages is shown in Figure 5a. It was observed that near 1:1 stoichiometric ratio was obtained when deposition was performed at −0.6 V. The EDX analysis at −0.6 V is shown in Figure 5b, where presence of Cd and Te in nanowires is approximately 1:1:2. In fact, it is reported that presence of larger content of Te gives higher probability for the formation of a stable p-type CdTe compound. Thus, the chroamoperometric deposition of CdTe nanowires and hierarchical structures was performed at −0.6 V for further analysis.

**Structural analysis.**—XRD was performed for both 1D and 3D CdTe nanostructures. The XRD graph shown in Figure 7a ensures that the electrochemically grown CdTe from PA templates acquired a crystalline cubic structure (confirmed with JCPDS #15-0770 and # 75-2086) but in addition to cubic structure, peaks corresponding
Figure 5. (a) Stoichiometric ratio of Cd:Te for electrodeposition at varying voltage range of $-0.55$ V to $-0.65$ V (b) EDX spectrum of CdTe nanowires grown on FTO/glass substrate at $-0.6$ V.

Figure 6. SEM image of free standing CdTe nanowires on modified FTO/glass substrate (a) Top View (b) Cross-sectional view.

Figure 7. X-Ray Diffraction Graph for (a) CdTe nanowires (b) CdTe hierarchical structures.

to hexagonal structure were also revealed (confirmed with JCPDS # 19-0193). The $2\theta$ values of $46.40^\circ$ and $65.65^\circ$ were matched with the cubic zinc blende structure corresponding to (311) and (420) index planes respectively. Peaks pointing at $32^\circ$ and $45^\circ$ correspond to the hexagonal structured index plane at (102) and (200) respectively. In addition, the peaks at $23.86^\circ$ and $39.48^\circ$ corresponds to dual crystalline phases i.e., (111)/(100) and (220)/(110) index planes for cubic/hexagonal structures respectively. Figure 7b shows the XRD graph of 3D hierarchically structured CdTe. The peaks at $43.76^\circ$, $76.90^\circ$, and $81.10^\circ$ corresponds to the (103), (006), (106) planes for the hexagonal crystal structure and peak at $63.93^\circ$ corresponds to (311) plane for the cubic structure. Overall, XRD graphs in Figure 7a and 7b indicates that hexagonal phase is dominant in the hierarchical CdTe structures whereas the CdTe nanowires dominantly indicates a mixed phase, suggesting a transition phase from cubic to hexagonal structure. Presence of Te is also observed in both Figure 7a and Figure 7b at $37.90^\circ$ corresponding to (102) plane and at $51.61^\circ$ corresponding to (202) plane (JCPDS # 36-1452). Excess Te is also reflected in the EDX data in Figure 5b. It is reported that higher concentration of Te helps to achieve a stable p-type CdTe, but there is a probability of residual strain as well if the stoichiometry is not balanced. The extra Te content can be removed by heat-treatment in presence of CdCl$_2$ as reported in other literatures.$^{62,63}$

Optical analysis.—Figure 8a represents the total optical absorption for planar thin film, 1D nanowire and 3D hierarchical structures of
CdTe at varying wavelengths. The total absorption spectra \( A(\%) = 100 - (R(\%) + T(\%)) \) were acquired from the measurement of reflectance \( R \) and transmittance \( T \) spectra of each structure. The reflectance and transmittance spectra are shown in Figures 8b and 8c. The reflectance measurements include specular reflectance from the planar thin film and diffusely reflected light from the nanostructures. It can be observed that the optical absorption in CdTe planar thin film is strongly dependent on the wavelength with a maximum absorption of 41\% at \( \lambda = 350 \text{ nm} \) and a low-range absorption between 6\% to 12\% is observed beyond 600 nm wavelength. Nanostructuring has significantly enhanced the optical absorption along with less dependency on wavelength, as observed for the CdTe nanowires. The maximum total absorption is 63\% at 350 nm and the variation in the absorption is within 63\% to 48\% over a wavelength range of 350 nm to 1400 nm. Interestingly, the 3D hierarchical structure of CdTe shows substantial improvement in total optical absorption as high as 90\% with almost insignificant wavelength dependence over 350 nm–1400 nm. The 3D hierarchical CdTe structures exhibits a drastic improvement in total absorption by ~30\% for a broad wavelength (350 nm – 1400 nm) as compared to the nanowires and thin film of CdTe of same amount. This is due to high reduction in both transmittance and reflectance over a broad wavelength for the CdTe hierarchical structures.

Figure 9 corresponds to photoluminescence emission spectrum for CdTe nanowires and hierarchical structures at different excitation wavelengths. The photoluminescence emission spectrum shown in Figure 9a for CdTe nanowires exhibited a near band-edge emission at 604 nm (2.05 eV) with a FWHM of 40 meV. The estimated energy bandgap value for the CdTe nanowires is 2.1 eV as obtained from the diffused reflectance measurement (Kubelka-Munk theory) as well as absorbance measurement by Tauc relationship. Other photoluminescence emission peaks were also obtained at lower energies corresponding to 619 nm and 642 nm (shown in supplementary Figure S4 (a) and S5 (a)). These emissions were probably due to other shallow/deep level defects in the nanowire structure. The defect states most likely originated due to the Cd vacancies caused with excess of Te content in these structures or due to other surface defect states.

XRD graph in Figure 7 also exhibited prominent peaks corresponding to elemental Te indicating the presence of vacant Cd sites. Near band-edge emission for the hierarchical CdTe structure was obtained at 600 nm (2.07 eV) as shown in Figure 9b. The optical bandgap of the hierarchical CdTe structures was estimated to be 2.08 eV (using Kubelka-Munk and Tauc relationship), which was slightly lower than the CdTe nanowires. A minor shift in the optical bandgap was probably due combined structural effect and residual strain in the CdTe hierarchical structure. Another very interesting observation was 10-fold increase in the band-edge emission intensity corresponding to the hierarchical structures than the CdTe nanowires, moreover the FWHM was also lowered by half from 40 meV to 20 meV. This decreased value of FWHM for hierarchical CdTe was evidenced due to the increase in its grain size which can also be verified.
from the SEM images (Figure 3). Other defect related emission peaks at 619 nm and 642 nm (supplementary Figure S4 (b) and S5 (b)) were also obtained for the hierarchical CdTe structures. These peaks were at the same wavelengths as observed for the CdTe nanowires. Significantly enhanced photo-response in the form of band edge emission peak for the CdTe hierarchical structures indicates that the diverse shapes of CdTe can be favorably and efficiently employed for several optical and optoelectronic applications.

**Discussion**

The non-uniform branched PA template is believed to be formed due to two major reasons. Firstly, the 1st step anodization performed in this experiment was only for 1 hour which was insufficient to remove all the defects from the surface of the Al substrate. The defect sites may have been one of the branching initiation sites. Secondly, during the oxide barrier thinning process using sequential reduction in anodization voltage; as the potential changes from the established equilibrium condition for uniform pore formation, the oxide continues to grow and simultaneously dissolution process also competes, i.e. a re-anodization occurs at a different voltage leading to smaller pore sizes. Several repeated attempts of stepping down the voltage affects the equilibrium condition as required for the vertical growth of uniform pore and leads to the formation of smaller pores not constrained to vertical growth, thus forming branches inside the porous alumina channels.

It is understood from literatures that, handling and transferring of thin PA membrane and its adhesion to the substrate are the major reasons that limit the electrodeposited growth of long semiconductor nanowires. While transferring thin PA membranes onto a substrate, it often tends to crack as PA is quite fragile. Literatures have often reported the use of polymer fillers like polymethyl methacrylate (PMMA) or polystyrene to handle thin PA membrane. However, PA membrane still remain fragile even when filled with these polymer fillers. This work (as mentioned in the Results section), fragility of polystyrene filler has been reduced by adding a plasticizer additive. This step ensured an easy transfer and positioning of the PA membrane using a simple plastic fork followed by complete removal of the polymer filler with chloroform vapors. Previous literatures by Haddad et al. and Meng et al. demonstrated large area fabrication and transfer of PA membrane onto perfect flat Silicon (Si) substrate.53,58 However, authors used sophisticated ion milling technique to remove and flatten the barrier layer for transfer onto Si substrate, which needs a high precision as well as a high expense. Moreover, PA membrane transfer onto atomically flat substrate like Si is much simpler than onto relatively rough surfaces like ITO or FTO coated glass. Overall it is established that a moderate to poor adhesion of PA onto a substrate often delaminates the membrane when electroposition of nanowires is attempted for a longer duration of time, because electrodeposition is always performed in a harsh chemical environment. Comparatively, electrochemical growth of nanodots or metal nanowires require much less time duration, hence, these structures are the one that are being often reported in the literatures till date.28,35,39,58

In the current work, dense hyperbranching observed in the electrochemically grown CdTe through the non-uniform PA template can provide a complete new aspect toward optoelectronic applications. Moreover, the overall duration for fabrication of 3D CdTe structures is only 2.5 hours (including the fabrication time of PA template), as compared to more than 32 hours reported elsewhere.55 It has been discussed by Manna et al. and W Nie et al.52,53 that hyperbranching in CdTe is most likely due the existence of polytypism, where two crystalline phases i.e. cubic zinc blende and hexagonal wurzite have very less difference in their internal energies, thus can occur at the same temperature and pressure. It is shown in this work that the PA template structure plays a major role to generate densely arranged hierarchical structures. It is likely that as the nanowires of CdTe try to grow randomly through the branched porous channels, they tend to optimize their pathway through the interconnected PA channels and self-assemble on each other. Especially, at a high bath temperature of 60 °C, these nanowires tend to self-assemble and aggregate onto each other to form a 3D hyperbranched structure providing it a leaf-like shape. It is also predicted in a previous literature that as more and more hyper-branching originates from a nucleus, it is an indication of dominance of wurzite over cubic zinc blende phase or a phase conversion from zinc blende to wurzite phase.54

A similar observation was made through the XRD analysis (Figure 7) where hierarchical CdTe structure showed dominant wurzite phase than in the CdTe nanowires however XRD peaks for CdTe nanowires also marks the presence of wurzite phase.

As stated earlier, in comparison to room temperature bath temperature of 60 °C was found to be most appropriate for growth of 3D hierarchical structure. In addition, it was observed that branching in PA template plays a major role in hyperbranching effect of CdTe. Parameters like, CdTe precursor concentration and role of organic stabilizer in solution phase growth of hyperbranched CdTe has also been discussed in other literatures.52,65 Such studies can be undertaken with the current electrodeposition growth method as an extension in future.

**Conclusions**

We summarize that the high aspect ratio diverse shapes of CdTe nanostructures can be obtained by simple and minor structural engineering of a PA template. High aspect ratio (~47) uniform CdTe nanowires have been directly grown on chemically modified FTO coated glass substrates. These CdTe nanowires can potentially be utilized for solar cell application when combined with a suitable energy band matching n-type material such as CdS. Especially, if grown on conductive flexible substrates, can possibility be used for developing conformal nanowire based solar cell. PA template assisted rapid electrochemical growth of high density 3D hierarchical structures of CdTe is reported in this work. It is revealed that the PA template architecture and electrochemical bath temperature plays important role in generating the hierarchical CdTe nanostructure. Presence of several nanowires on each microstructured leaf of CdTe hierarchical structure is an apparent indication of significantly enhanced surface area to volume ratio. As observed through enhanced photoluminescence emission and high optical absorption, these CdTe hierarchical structures can be extremely beneficial by offering increased interactive area for light harvesting and other enhanced optoelectronic applications.

**Acknowledgment**

The authors are grateful to the Department of Science and Technology and Amity University Uttar Pradesh for financial support and characterization facilities. We are thankful to Mr. Shiv Chaudhary and Dr. V. K. Jain, Amity Institute of alternative and renewable energy sources (AIARS) for the scanning electron micrographs.

**ORCID**

Ranu Nayak © https://orcid.org/0000-0002-5879-6860

**References**

1. Z. Tang, N. A. Kotov, and M. Giersig, Science (80-.), 297, 237 LP-240 (2002).
2. C. Ma and Z. L. Wang, Adv. Mater., 17, 2635 (2005).
3. S. Kar, B. Satpati, P. V. Satyam, and S. Chaudhuri, J. Phys. Chem. B, 109, 19134 (2005).
4. T. Zhao, X. Fang, L. Li, Y. Bando, and D. Golberg, Nanoscale, 2, 168 (2010).
5. X. Duan, Y. Huang, R. Agarwal, C. M. C. M. Lieber, and C. G. Fast, Nature, 421, 241 (2003).
6. J. S. Jie et al., Nano Lett., 6, 1887 (2006).
7. S. C. Kung, W. E. van der Veer, P. Yang, K. C. Donavan, and R. M. Penner, Nano Lett., 10, 1481 (2010).
8. C. J. Barrelet, A. B. Greytak, and C. M. Lieber, Nano Lett., 4, 1981 (2004).
9. L. Li et al., Microelectron. Eng., 126, 27 (2014).
10. K. Deng and L. Li, Adv. Mater., 26, 2619 (2014).
11. G. Xing et al., ACS Nano, 6, 10835 (2012).
