

Synthesis and Application of DNA–CdS Nanowires within a Minute using Microwave Irradiation

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A very fast, electroless, microwave method is described to synthesize electrically conductive CdS nanowires on DNA just within 60 s. The electrical characterization indicates that the CdS wires are continuous, have very low contact resistance, and exhibit Ohmic behavior. Highly selective deposition on DNA is obtained by specific complexation between the Cd(II) ion and DNA, followed by decomposition of thioacetamide to S²⁻ to form CdS. The nanowires are found to have a diameter of 140–170 nm and a length of ~8–12 μm. The one-step process developed here does not perturb the overall conformation of the DNA chain. The nanowires we fabricated can be used as building blocks for functional nanodevices, tiny computers, sensors, and optoelectronics.

1. Introduction

In recent years, the synthesis and characterization of one-dimensional (1D) nanostructured materials have attracted much attention due to their unique optical,¹ electrical,² and biological³ applications. Among the various materials studied, CdS is one of the most important group II–IV semiconductors having vital applications in optoelectronics,⁴ solar cells,⁵ and electronic⁶ devices. The CdS nanowires represent a broad class of nanoscale building blocks that have been used to assemble a range of electronic and photonic structures,² electronic devices,⁶ light-emitting diodes,⁷ laser,⁸ and others. Well-known biomolecules such as amino acids, nucleic acids, proteins, and peptides with the ability to self-assemble have been used as templates to metalize metal nanostructures and nanowires.^{9,10} Among the above biomolecules, DNA has been widely investigated for this purpose because of its various important properties: (a) the double-stranded, rigid chain structure gives the DNA higher

strength¹¹ in comparison to single strands; (b) the versatile chemical structure containing polymeric sequences allows DNA to self-assemble into complex structures such as squares,¹² cubes,¹³ and “T” junctions¹⁴ that may be leveraged to make complete circuit elements; (c) the negative charge on DNA allows binding to metal cations^{15,16} and metal nanoparticles,^{17,18} functionalizing the DNA structure with a thiol (S–H) or disulfide (S–S) group; and (d) the intermolecular interactions in DNA are readily programmed and reliably predicted. Among the four base molecules present in DNA, adenine (A) pairs with thymine (T), and guanine (G) pairs with cytosine (C). This chemical nature makes DNA an effective genetic material for programmed self-assembly. Different noble metals like Pd,¹⁹ Pt,²⁰ Au,¹⁹ Ag,¹¹

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and Cu²¹ have been metalized on DNA, leading to electrically conducting nanowires. Coffey and co-workers were the first to utilize DNA as stabilizer to form CdS nanoparticles.²² Their original work was the synthesis of CdS nanoparticles using DNA molecules by exposing H₂S gas over Cd²⁺/DNA complex for more than 1 h. Wong et al. reported that self-assembled DNA membrane templates can be employed in the molecular imprinting of biomineralized CdS nanostructures.²³ Braun et al. reported that the attachment of metal nanoparticles to DNA can protect specific regions of the DNA strands.¹⁹ The most studied methods for the synthesis of CdS nanoparticles involve direct reaction of metal salt with sulfur powder,²⁴ thermal decomposition of sulfur-containing salts, or the utilization of H₂S as the S²⁻ source²⁵ at high temperatures. To date, various methods have been reported for achieving the synthesis of CdS nanowires. Chen's group²⁶ and Cheon's group²⁷ synthesized CdS nanowires in a micellar environment. Qian's group utilized a chemical route to synthesize CdS nanowires using solvothermal growth.²⁸ Leiber's group developed a vapor-liquid-solid (VLS) method to synthesize CdS nanowires.²⁹ Peng's group synthesized small size semiconductor quantum rods and wires by exploiting high molecular weight amine ligands at very high temperatures.³⁰ The other well-known methods are γ -irradiation,³¹ photochemical reduction,⁶ ion-irradiation,³² etc. However, most of the above methods need surfactant, micelles, and high molecular weight nitrogen- or phosphorus-containing ligands to stabilize the CdS particles, which might decrease the purity of the final product. It is believed that the CdS synthesized using the above methods at higher temperature was either amorphous or cubic and required crystallization after the synthesis.

Recently, the microwave method has been used to synthesize nanoparticles of metals^{33,34} and semiconductors.³⁵ The microwave enables selective heating of dielectrics, enhancing the reaction rates. Using the microwave as a heating source offers great advantages in making nanoparticles. These include flexibility, simplicity, short reaction time, fast nucleation of metal ions, and ease of use. Zhu et

al.³⁶ reported the synthesis of CdS nanoparticles by heating a mixture of Cd(II) and thioacetamide in aqueous solution. The synthesized particles are found to be polydispersed with no specific shapes. To date, there are no reports on the synthesis of one-dimensional CdS nanowires by microwave irradiation directly on DNA scaffolds.

Here, we report a fast, one-step in situ process to synthesize electrically conductive CdS nanowire on DNA scaffolds within 60 s by microwave irradiation in aqueous solution. The CdS nanowires are synthesized in a mixed solution containing DNA, cadmium perchlorate [Cd(ClO₄)₂], and thioacetamide (t-NH₂; CH₃CSNH₂) in the presence of microwave heating. The synthesized nanowires are found to be electrically conductive and the process is straightforward, simple, and cost-effective.

2. Experimental Section

2.1. Reagents. Cadmium perchlorate dihydrate [Cd(ClO₄)₂·2H₂O] and thioacetamide were purchased from Aldrich and used without further purification. The λ -phase DNA, sheared to an average size of 48 500 bp was purchased from Sigma. The DNA is a polydispersed mixture of DNA chains with broad size distribution. Other chemicals include a tris-EDTA buffer (pH 7.4) and adenosine 5'-triphosphate disodium salt (ATP) that were purchased from Sigma and used as received. UltraPure DNase/RNase-free distilled water (UPD water) (Invitrogen Corp.) was used in all synthesis experiments.

2.2. Instruments. The ultraviolet-visible (UV-vis) absorption spectra were recorded with a Hitachi (model U-4100) UV-vis-NIR spectrophotometer equipped with a 1 cm quartz cuvette holder for liquid samples. A high-resolution transmission electron microscope (HR-TEM, ZEOL ZEM-2010) was used at an accelerating voltage of 200 kV. Field emission scanning electron microscopy (FE-SEM) images were obtained using a Hitachi S-4700. The X-ray diffraction (XRD) patterns of the CdS nanowires were collected with a scanning rate of 0.020 s⁻¹ in the 2 θ range 20°–60° using a Bruker, D8 advance X-ray diffractometer with Cu K α (λ = 0.154 178 Å) radiation operating at 40 kV, 50 mA. The energy dispersive X-ray spectra (EDS) were recorded with the instrument connected with the HR-TEM during TEM experiments. A atomic force microscope (AFM) probe used for scanning the surfaces for the conductivity study was a multimode AFM instrument from Pacific Nanotechnology Inc. (shown in the Supporting Information). The tip was coated with a double layer of chromium and platinum-iridium approximately 25 nm thick on both sides of the cantilever. The tip side coating enhanced the conductivity of the tip and allowed electrical contacts. The detector side coating enhanced the reflectivity of the laser beam by a factor of 2 and prevented light from interfering within the cantilever. The coating process was optimized for stress compensation and wear resistance. The bending of the cantilever due to stress was less than 3.5% of the cantilever length. The gas chromatography-mass spectrometry (GC-MS) study was done using a micromass HP-5970 mass spectrometer (Manchester, UK) with OPUS V3.1X data system. The Fourier transform infrared spectroscopy (FT-IR) spectrum was done with a Bruker IFS 113v spectrophotometer. A domestic microwave oven (Gold Star, EM-Z200S, 1000 W, 60 Hz) was used for microwave irradiation for all the synthesis experiments.

2.3. Synthesis of CdS Nanowires on DNA by Microwave Irradiation. A stock solution of DNA (60 μ g/mL) was prepared in tris-EDTA buffer (pH 7.4) by dissolving appropriate amounts

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of DNA with UPD water and was stirred overnight using a magnetic stirrer. The buffer solution helps to prepare a homogeneous DNA solution without any pop off of A or G bases from DNA and was stored in a refrigerator. Stock solutions of 10^{-2} M cadmium perchlorate and 10^{-2} M t-NH₂ were made in UPD water.

In a typical synthesis, we fixed the DNA concentration and varied the molar ratio of cadmium salts to t-NH₂ from 0.5 to 5. The Cd²⁺ ion initially formed a DNA–Cd²⁺ complex, confirmed by the observed shift in the UV–visible spectrum of the mixed solution compared to that of pure DNA. The mixed solution containing DNA, Cd salt, and t-NH₂ solution was placed in a microwave oven and irradiated for a total of 60 s with an intermittent pause after every 5 s to cool the reaction vessel. The CdS formation started just after 15 s of microwave irradiation, as observed from the UV–vis spectrum and the appearance of a light yellowish coloration to the solution. After the reaction was completed, the solution become yellowish and the UV–vis spectrum was again recorded, showing the formation of CdS nanoparticles.

2.4. Preparation of Samples for FE-SEM, TEM, and *I–V* Studies. The FE-SEM studies were done on Si chips with 100 nm SiO₂ layer. The DNA–CdS nanowires were deposited over the chip and dried. Finally, the chips were washed with UPD water and allowed to dry again in the air were ready for characterization. The samples for the TEM study were prepared by placing a drop of fresh CdS–DNA solution on carbon film coated copper (Cu) grids followed by slow evaporation of solvent at ambient conditions. The samples for the conductivity (*I–V*) study were prepared on a substrate. The substrate was thoroughly cleaned with ethanol and piranha solution (30% H₂O₂ and 70% H₂SO₄), followed by treatment with HF and rinsing with ethanol. Subsequently, the substrate was washed with UPD water and then dried in air. The substrate was then placed in the CdS–DNA solution for about 2 h, followed by a gentle wash with UPD water. After that, the substrate was dried in vacuum at 25 °C for 2 h and was ready for characterization.

The *I–V* measurements were performed using a AFM conductive probe scanning the substrate in contact mode. The AFM probe was in contact with the nanowire, and electrical potentials were applied through the nanowire by the AFM probe. The applied electrical potentials through the nanowire and AFM probe were increased from –10 to 10 V in 1 V steps increments. For each potential, the current flow through the nanowire was recorded by the LabView program of the AFM computer. The results were plotted as the *I–V* curve.

3. Results and Discussion

3.1. UV–Visible Spectroscopy Study. For the synthesis of CdS–DNA nanowires we varied the molar concentration ratios of cadmium salt to t-NH₂ from 0.5 to 5 while that of the DNA solution was kept fixed. Then the solution mixture was irradiated in a microwave oven for about 60 s (see details in the Experimental Section). Figure 1 shows the UV–vis spectra at different stages of the reaction. The aqueous solution of DNA itself has an absorption band at 260 nm (curve A, Figure 1). The average diameter of hydrated DNA is ~3 nm and that of hydrated Cd²⁺ ion is ~0.4 nm. With addition of Cd²⁺ salt, the absorption peak shifted a little bit with a slight increase of absorbance value, indicating the initial formation of DNA–Cd²⁺ complex (curve B, Figure 1). After the addition of t-NH₂ to the DNA–Cd²⁺ complex, the absorption peak remained unchanged, although absorption of Cd²⁺ on DNA partially neutralized the DNA's negative

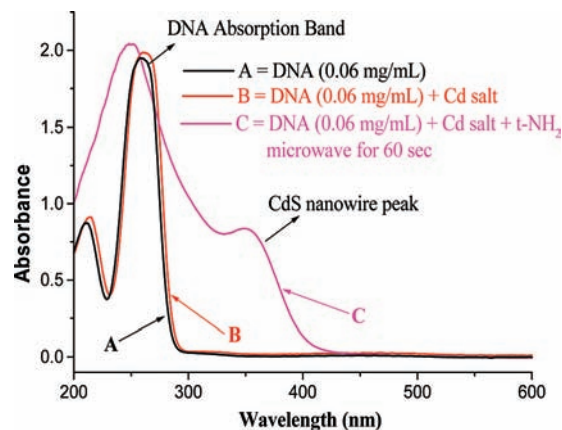
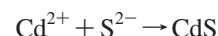
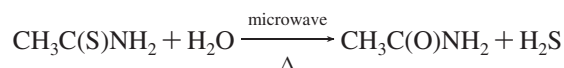


Figure 1. The UV–vis absorption spectra of DNA–CdS nanowire at different stages of synthesis. Absorption spectra of (A) DNA strands itself in water, (B) mixture of DNA–Cd²⁺ complex, and (C) mixture of DNA, Cd salt, and t-NH₂ after microwave irradiation for 60 s. The absorption band 340–420 nm corresponds to the excitonic peak of CdS nanowire.

charge. With microwave heating (1000 W, 60 Hz) for 60 s, the clear solution turns slightly yellowish in color, indicating the formation of CdS nanoparticles having a new absorption band in the range 340–420 nm (curve C, Figure 1), in correlation with reported results.^{37,38} Here three basic preparative steps took place: (a) formation of DNA–Cd²⁺ complex, (b) reaction of the DNA–Cd²⁺ complex with the S^{2–} generated from the decomposition of t-NH₂ to form CdS nuclei during MW heating, and (c) stabilization of the formed CdS on the DNA chain.

Once the CdS particles formed, they grew in the selective crystallographic directions on DNA, leading to the formation of a nanowire. According to the literature, thermal decomposition of aqueous solutions containing thio groups like thioacetamide, thiourea, or thiosulfate leads to the formation of S^{2–} ions.^{39,40} Once the S^{2–} ions formed, they reacted with the Cd²⁺ ions present in the solution to form CdS-stabilized on DNA. The generalized equations for CdS formation are expressed as follows:



The microwave irradiation time of the solution mixture was optimized as 60 s. We varied the molar ratios of Cd²⁺ ion to t-NH₂ from 0.5 to 5, but after they increase beyond 2.5, the solution became deep yellow in color and precipitates formed, indicating the formation of larger sized, aggregated particles. A similar observation was also found when the solution was microwave irradiated for more than 180 s. Results showed that microwave irradiation of a pure DNA solution for more than 180 s leads to a small shift of the absorption peak at 260 nm. This is attributed to microwave-influenced supercoiling and cross-linking of DNA strands

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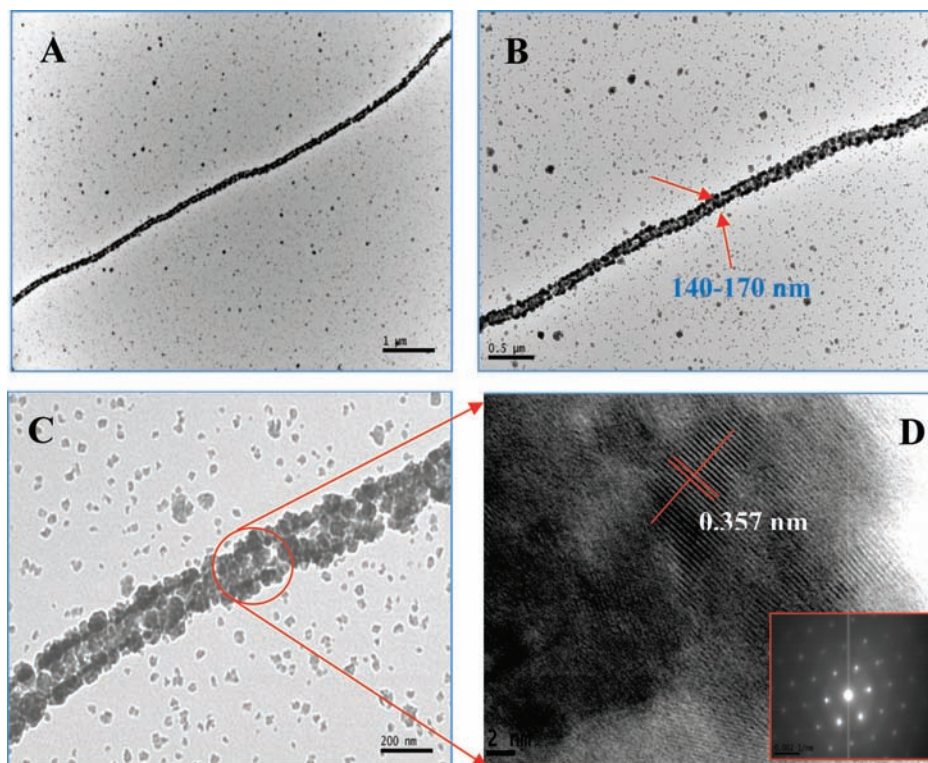


Figure 2. TEM images and diffraction patterns of the DNA–CdS nanowires when the Cd^{2+} to t-NH_2 molar concentration is 1:2 for 60 s microwave irradiation. (A) DNA–CdS nanowire at low magnification indicates the growth of the particles in wirelike morphology with an average diameter of $\sim 140\text{--}170$ nm. (B) A single straight chain of DNA–CdS nanowire at low magnification from the other part of the TEM sample indicates the CdS particles on DNA with wirelike structure having average diameter $\sim 140\text{--}170$ nm and length $8\text{--}12$ μm . (C) Highly magnified image of the CdS nanowire. (D) A very highly magnified TEM image of DNA–CdS nanowire from a specific part of image C, synthesized under identical conditions. The inset of Figure 2D showing the selected area electron diffraction pattern of the CdS nanowires indicates the crystalline nature of the particles. The smallest spacing between two crystal planes is ~ 0.357 nm.

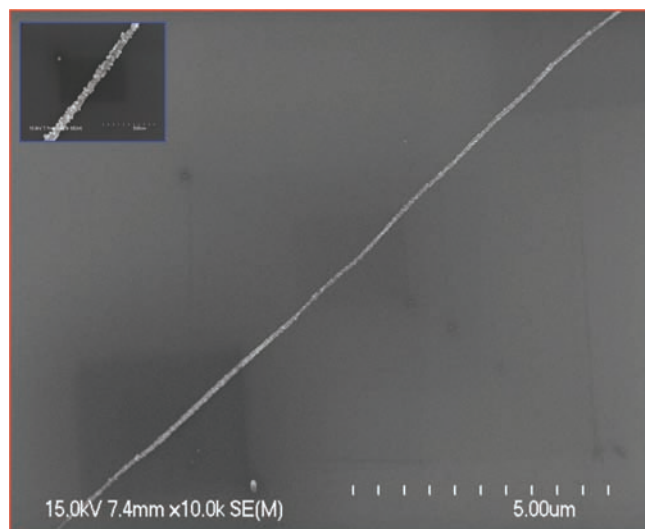


Figure 3. FE-SEM images of the DNA–CdS nanowires when the Cd^{2+} to t-NH_2 molar concentration is 1:2 for 60 s microwave irradiation. The inset shows the corresponding higher magnified image of the same samples.

due to trimeric complex⁴¹ formation. A similar observation was also found during the synthesis of CdS nanowires in the presence of UV irradiation.⁶ Both phenomena prove that DNA itself is not very stable in the presence of longer UV or microwave irradiation and formed the trimeric complex⁶ due to cross-linking of DNA strands. CdS nanoparticles were not observed in the sample solutions irradiated for less than

15 s, suggesting the presence of a threshold for the release of S^{2-} ions from t-NH_2 . The optimum conditions for the synthesis of CdS nanowire are 60 s of MW irradiation with a Cd^{2+} ion to t-NH_2 molar ratio of 2.

3.2. Transmission Electron Microscopy and Field-Emission Scanning Electron Microscopy Study.

Figures 2 and 3 are the images obtained using TEM of our reaction products at various conditions. Figure 2A shows a typical long nanowire formed when the Cd^{2+} to t-NH_2 molar ratio is 2 at low magnification. The DNA itself is transparent to the electron beam, so the image is mainly constructed from the CdS bound to the DNA chain. Figure 2B shows another nanowire at a different magnification. The CdS nanowires are normally $8\text{--}12$ μm long, while average diameters of the chains are $140\text{--}170$ nm. Figure 2C shows the corresponding high-magnification image. Most of the CdS particles formed in the solution are bound to the DNA chain, although a few separate particles ($\sim 7\%$) were also found. We calculated that $\sim 93\%$ of the CdS particles are directly bound with the DNA chains when the Cd^{2+} to t-NH_2 molar concentration was 1:2. Figure 2D shows a highly magnified TEM image taken over an area of the image 2C. According to the image, it is clear that the particles are crystalline and the smallest spacing between two crystal planes is calculated to be ~ 0.357 nm. The inset of Figure 2D shows the corresponding SAED pattern, which indicates the crystallinity of the CdS particles. Figure 3 shows the FE-SEM images of the DNA–CdS

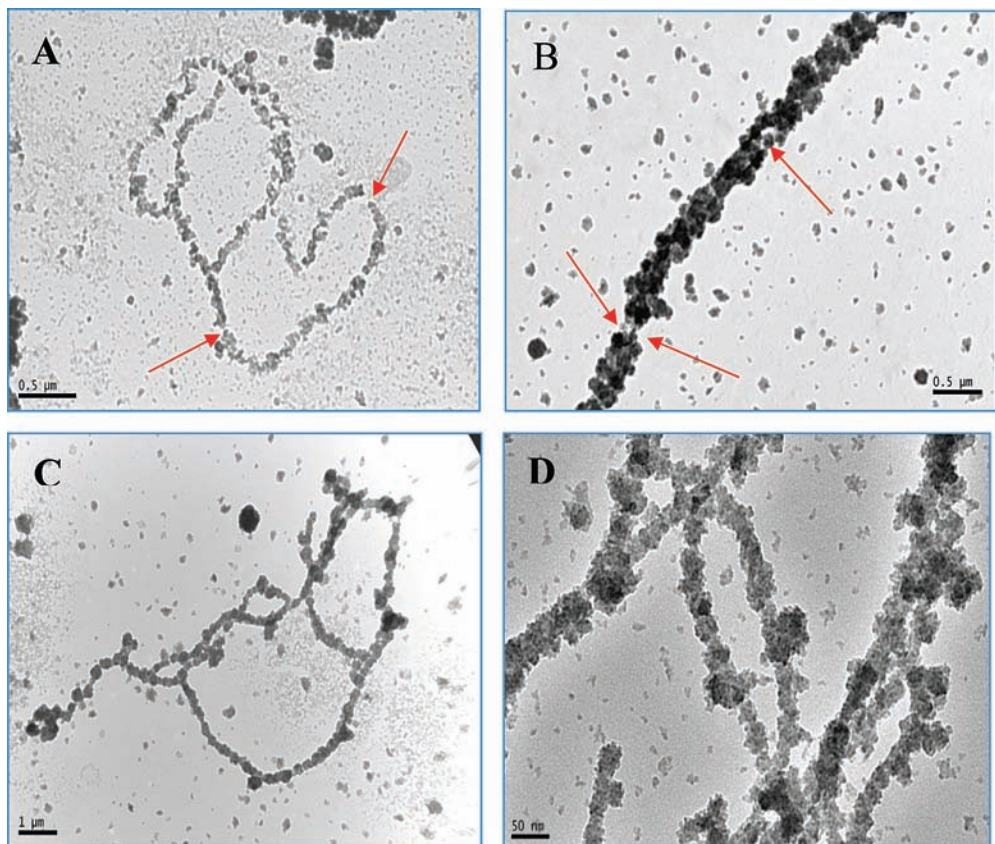


Figure 4. TEM images of the DNA–CdS nanowires at different molar ratios of Cd^{2+} to t-NH_2 after 60 s microwave exposure time. (A) Cd^{2+} to t-NH_2 molar ratio is 0.5 and (B) Cd^{2+} to t-NH_2 molar ratio is 1; in both cases the CdS nanowires are not fully developed. (C) Cd^{2+} to t-NH_2 molar ratio is 3 and (D) Cd^{2+} to t-NH_2 molar ratio is 5; in both the cases the DNA chains are cross-linked each other and aggregated/agglomerated with an increase of the particles' diameter.

nanowires when the Cd^{2+} to t-NH_2 molar concentration is 1:2 for 60 s microwave irradiation. From Figure 3 it is shown that the length and the diameter of the nanowires are consistent with the TEM images above. The inset of Figure 3 shows the corresponding higher-magnification image. Figure 4 shows TEM images of the CdS particles with different molar ratios of Cd^{2+} to t-NH_2 . Parts A, B, C, and D of Figure 4 are the TEM images of the CdS particles when the Cd^{2+} to t-NH_2 molar ratios are 0.5, 1, 3, and 5, respectively. Figure 4A,B shows that CdS particles are formed but not fully developed on the DNA chain, as indicated with red arrows. Figure 4C,D shows that the DNA chains are cross-linked with each other and aggregated/agglomerated as the particles' diameter increased.

3.3. Energy Dispersive X-ray Spectroscopy Analysis. The chemical composition of the synthesized product was examined by EDS during TEM analysis. The spectrum is shown in Figure 5. The spectrum of the nanowire is mainly composed of Cd, S, C, Cu, and Cr. The Cd and S peaks arise from the CdS nanowire. The additional C and Cu peaks come from the carbon-coated Cu TEM grid, and the small Cr peak came from the sample holder used for TEM.

3.4. X-ray Diffraction Analysis. The XRD pattern of the CdS nanowires (Figure 6) was collected in the 2θ range 20° – 60° with a Bruker, D8 advance X-ray diffractometer

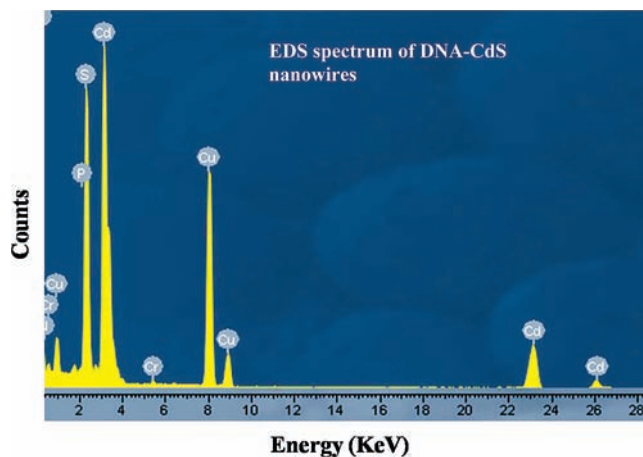


Figure 5. EDS of the DNA–CdS nanowires. The spectrum consisted different peaks for cadmium, sulfur, carbon, copper, and chromium.

using $\text{Cu K}\alpha$ ($\lambda = 0.154\ 178\ \text{\AA}$) radiation operating at 40 kV, 50 mA. In the 2θ range 20° – 60° , the diffraction peaks are assigned to (100), (002), (101), (102), (110), (103), and (200) planes of the hexagonal phase of CdS. The (002) peak is unusually narrow and strong, indicating a preferential growth along the c -axis in the product, with a wirelike structure.⁴² All the peaks for the hexagonal phase of CdS are well-matched with the literature values (JCPDS file No

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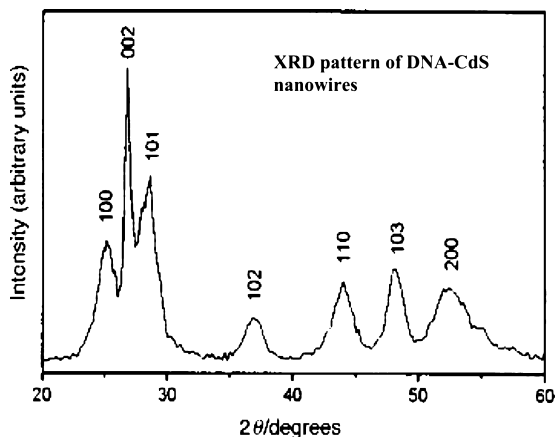


Figure 6. Powder X-ray diffraction pattern of the DNA–CdS nanowire. The peaks are assigned to the diffraction from (100), (002), (101), (102), (110), (103) and (200) planes of the hexagonal phase of CdS.

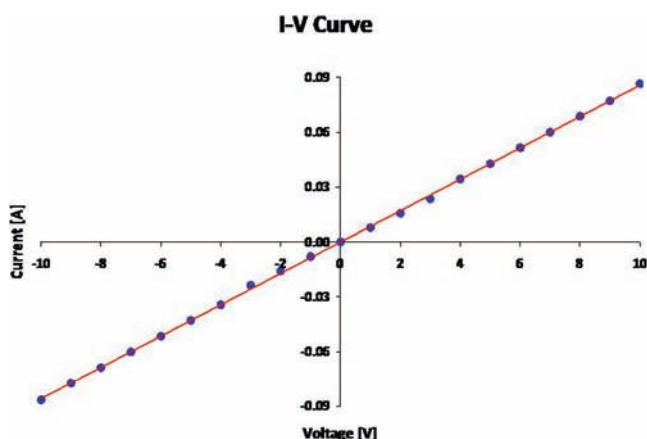
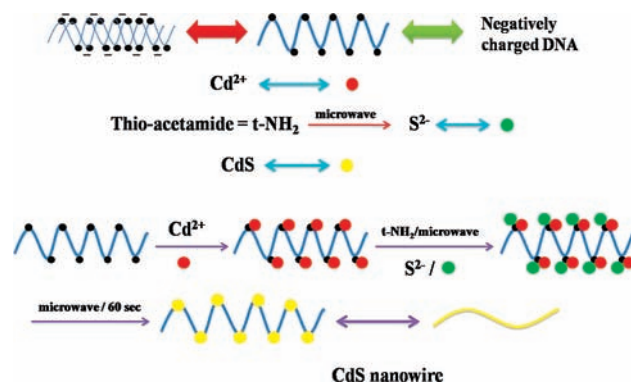


Figure 7. Current–voltage (I – V) curve for the CdS nanowires. The Ohmic resistances for the linear fit is 115.78Ω , indicating the continuous structure of the CdS nanowire.

41–1049). The EDS and XRD, in combination with the TEM images, exclusively prove that we successfully formed controlled mesoscale assemblies of single crystal CdS nanowires in DNA.

3.5. Conductivity (I – V) Measurement. The use of highly aligned DNA strands as molecular combs is of great utility in device construction, such as positioning the DNA on microgap electrodes.⁴³ The CdS nanowires are deposited on a substrate to measure their conductivity using an AFM probe. The AFM probe has been used widely to image and manipulate atoms and structures on a variety of surfaces. In the present study, we constructed I – V curves using an AFM with external applied potential and measured current. Details of the conductivity measurement are discussed elsewhere.⁴⁴ The simple diagram for the conductivity measurement is shown in the Supporting Information. Figure 7 shows the corresponding I – V curve of the DNA–CdS nanowires. As shown in the figure, the current is increasing linearly with the applied potentials and maintains Ohm's law, indicating very good contact of the CdS nanowires with the substrate.

Scheme 1. Schematic Presentation for the Synthesis of CdS Nanowire on DNA Using Microwave Irradiation



We did not find any hysteresis in the I – V measurement, which indicates the continuous structure of the CdS nanowires. The resistance of the nanowires is calculated to be 115.78Ω , which is an upper bound on the resistance of the nanowire itself, as nanowire/substrate contact resistance might be significant. The measured conductivity was slightly higher than previously reported results by Patel's group for semiconductor/metal junctions.⁴⁵ We suggest that the contact resistance of the nanowire/substrate and the phosphate groups of the DNA backbone might play some crucial role in enhancing conductivity.⁴⁶ The synthesized nanowires are composed of tiny particles of CdS and DNA molecules. To check the stability of the wires for device application, we measured the conductivity experiment just after synthesis and 3 months after the synthesis for the same samples. We observed almost same resistance in both the cases, which proves the high stability of the DNA–CdS nanowires in ambient condition for device application. Again, the EDS study of the same sample after 3 months did not show any peak for oxide formation.

3.6. Reaction Mechanism for the Nanowire Synthesis.

The synthesis of CdS nanowires was carried out at room temperature, under ambient pressure in a microwave oven. As we discussed earlier, the CdS nanowire synthesis on DNA is a three-step process. In the first step, positively charged metal ions (Cd^{2+}) form a complex with DNA having similarity to the formation of Ag^+ –DNA complex.⁴⁷ A similar type of CdS–DNA complex formation was also reported earlier.²² In the second step, the thermal decomposition of t-NH_2 in presence of microwave irradiation releases S^{2-} , which reacts with Cd^{2+} to produce CdS nuclei. The growth of the particles takes place in multistep on the DNA chains present in solution (Scheme 1). The smaller sized CdS nuclei crystallize in the preferential direction, aggregated and stabilized on the DNA chain. In the absence of DNA, with the presence of Cd^{2+} salt and t-NH_2 , the preformed CdS particles precipitate immediately after the microwave irradiation, due to absence of a specific stabilizer in the solution. We tested our reactions with another biomolecule,

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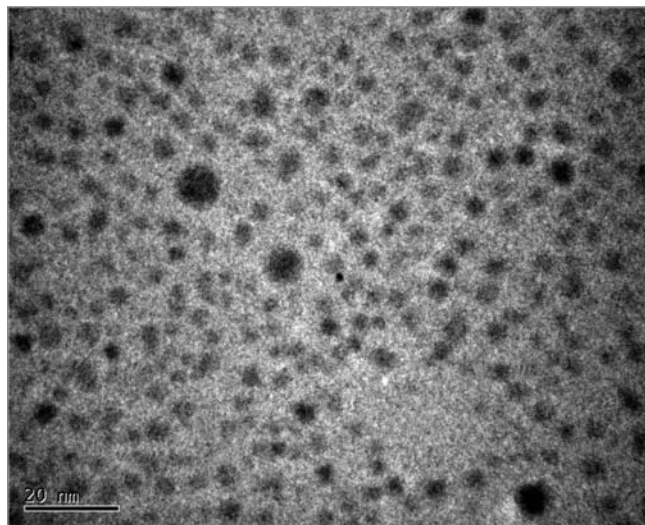


Figure 8. TEM images where the presence of adenosine 5'-triphosphate (ATP) resulted in \sim 5–8 nm spherical CdS nanoparticles.

adenosine 5'-triphosphate (ATP), having a similar charge to DNA. The process produced small spherical CdS nanoparticles (5–8 nm, Figure 8) after 60 s microwave irradiation. But the particles were not stable and precipitated after a few hours due to the absence of any proper stabilizer. Therefore, we believe that DNA itself acts as a stabilizing agent as well as nonspecific capping agent for the synthesis of the CdS nanowires. Logically, the synthesis of continuous wires on any macromolecules will result in loss of functionality of the molecule for subsequent use due to complete coverage by the metal species. The functionality of DNA is critical in our process for the synthesis of conductive CdS nanowires. The microwave exposure process is subsequent to the formation of CdS nanowires; thus, the small degradation of DNA due to microwave exposure will not affect the nanowire formation nor the versatility of DNA. We characterize our final product using FT-IR and GC–MS to check if there is any organic impurity present with the nanowires or not. We did not find any from the FT-IR study, but the GC–MS study showed there are three low intensity peaks having m/z values 206.4, 327.1, and 404.8. These small peaks are probably due to the degradation of the DNA molecule in the presence of microwave irradiation. However, this small degradation does

not affect any of the nanowire formation we already discussed above. The present microwave method was compared with a previously reported method,⁶ and we found that it is much faster and produced more uniform, longer nanowires in solution than before. In presence of UV light, it took 6 h to complete the formation of nanowires,⁶ whereas using microwave it took only 60 s. We believe that the present process of the synthesis of conducting CdS nanowire by microwave irradiation within 60 s is the fastest process of any other reported methods. Having this idea in mind, one will also able to synthesize other semiconductor (ZnS, PbS, NiS, CuS, etc.) and metal–semiconductor hybrid nanostructures within a short time.

4. Conclusion

To summarize, we have demonstrated an innovative method for the rapid synthesis of electrically conductive semiconductor nanowire in DNA using microwave irradiation within just 60 s. The synthesized nanowires are 140–170 nm in diameter and 8–12 μ m long and are stabilized on DNA chains. The one-step process does not perturb the overall conformations of the DNA chains. This method could be extended to fabricate intricate circuitry using DNA's ability to form complex shapes by hybridization. In the future, the present approach may lead to a quick synthesis method for single and composite nanowires having applications such as building blocks for functional nanodevices, miniature computers, sensors, and optoelectronics.

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Supporting Information Available: Details of conductivity measurements using AFM and a schematic for I – V measurement. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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