

# CHAPTER 1

## INTRODUCTION

### 1.1 BACKGROUND

Over the past three decades into today's powerful disciplines and knowledge that allow the engineering of advanced technical device has been developed based on fundamental chemistry, biotechnology and material science. They are focus on current approaches emerging at the intersection of materials research, nanosciences, and molecular biotechnology. The novel and highly interdisciplinary field of chemistry is closely associated with both the chemical and physical properties of organic and inorganic nanoparticles (NPs), as well as to the various aspects of molecular cloning, recombinant DNA and protein technology, and immunology. Today's materials research is used to develop instruments and techniques for basic and applied studies of fundamental biological processes [1]. The pioneering work of Pedersen, Cram, and Lehn on supramolecular aggregates held together by weak non-covalent interactions in a highly interdisciplinary effort has developed over the past 30 days into a well-established discipline. Supramolecular chemistry concerns the investigation of nature's principles to produce fascinating complex and functional molecular assemblies, as well as the utilization of these principles to generate novel device and materials, poteneially useful for sensing, catalysis, transport, and other applications in medicinal or engineering science. In this area, the enormous advance attained so far is illustrated impressively by comparing materials used in last centuries electrical devices such as millimeter-sized copper wires to today's submicrometer-sized optical and electronical parts, comprised of modern conducting and electro-luminescent organic polymers [1]. The significant property of nanotechnology is its "interdisciplinary nature". The chemistry is the central science for the development of applied disciplines such as material science and biotechnology as shown in Fig. 1.1. Material science, which

is based on classic chemical research fields and engineering technologies, has led to enormous advances in tailoring advanced modern materials, such as ceramics, nanoclusters, and conducting polymers. For biotechnology, combined with tailored biomolecules, like proteins, nucleic acids, compartments, and organelles. We can merge these disciplines to take advantage of the improved evolutionary biological components to generate new smart materials and develop future nanodevices composed of various advanced modern materials [1].

As we can see in Fig. 1.2, both biotechnology and materials science meet at the same length scale. A gap currently exists in the engineering of small-scale devices. Whereas conventional top-down processes hardly allow the production of structures smaller than about 100 nm, the limits of regular bottom-up processes are in the range of about 2-5 nm. Their own dimensions show a result, two different types of compounds appear to be suited for addressing that gap: (1) biomolecular components, such as proteins and nucleic acids, and (2) colloidal NPs comprised of metal and semiconductor materials. The main concepts in the development of human civilization are the conventional *top-down processes*. As human technology develops, people tend to fabricate more and more delicate tools or functional devices. However, this strategy will eventually reach a limit that people cannot easily go beyond based on available technologies. For example, the structural dimensions of computer microprocessors are currently in the range of about 65 nm, which is already the highest level of conventional top-down technology. “There is plenty of room at the bottom”, as Nobel physicist Richard Feynman pointed out more than 40 years ago, which best describes the central idea of nanotechnology [1]. Today’s nanotechnology research puts a great emphasis on the development of bottom-up, which concern the self-assembly of molecular and colloidal building blocks to create larger, functional device. Inorganic NPs are particularly attractive building blocks for the generation of larger superstructure. Such NPs can be prepared readily in large quantities from various materials by relatively simple methods. It can be controlled the sizes of the NPs from one to several hundred nanometers. Most often, the particles are comprised of metals, metal oxides, and semiconductor materials, such as Ag<sub>2</sub>S, CdS, CdSe, and TiO<sub>2</sub>. The NPs have highly interesting

optical and electrical properties, which are very different from those of the corresponding bulk materials and which often depend strongly on the size of particles in a highly predictable way. Moreover, some types of NPs can be considered as “artificial atoms” since they are obtainable as highly perfect nanocrystals, which can be used as building blocks for the assembly of larger two- and three-dimensional structures [1].

Inorganic NPs are attractive building blocks for the construction of nanostructured materials and devices with adjustable physical and chemical properties. With a variety of inorganic NPs now at hand, the identification of chemical methods for the selective linkage of these nano-building blocks to produce nanostructured aggregates, or clusters, of controllable structure becomes increasingly important. The amine modified SiO<sub>2</sub> and carboxylic acid modified Au and CdSe NPs has been self-assembly in aqueous solution to give well-defined core-shell type cluster, whose composition can be controlled with the pH. Ligand modified 50 nm SiO<sub>2</sub>, 7 nm Au, and 6 nm CdSe NPs were employed for the electrostatic assembly [2]. Transmission electron micrographs of SiO<sub>2</sub>@Au and SiO<sub>2</sub>@CdSe composites formed at the indicated solution pH values are shown in Fig. 1.3 and 1.4, respectively.

Recently, semiconductor NPs are being vigorously investigated as new materials for traditional electronic and optical applications, as chemical and biological sensors, and as building blocks for conceptually novel molecule-based devices. Most of these practical implementations of nanotechnology will require the immobilization of NPs on various substrates in the form of thin films. One of the new techniques that can be used for NP processing in thin films is the layer-by-layer assembly on polyelectrolyte has been proposed. It affords a high degree of structural control and quality of the coatings. [3]. However, the forces that make the assembly to happen are similar to those that involve in the interaction between molecules, such as **hydrogen bonds**, **coulombic force**, and **Van der Waals force** [1] [2] [3].

In general, with work involving self-assembly processes, nucleotides with various lengths were employed to take advantage of their self-recognition and self-assembly abilities [4]. The synthesis of

~ 15 nm Au NPs by Citrate Reduction method and ~ 5 nm CdSe NPs by Tyramine-modification method was reported in literatures, which provide negative-charged and positive-charged on the surface of the NPs, respectively [4][5]. For further study, the resulting solution consisting of Tyramine-modified CdSe NPs was vacuumed to dryness and re-dissolved in D.I. water [6]. In order to modify the silicon oxide substrate provide amino groups ( $-NH_3^+$ ) for assembling of Colloidal Au NPs, the silicon oxide substrate was immersed in a 10% N-[3-(trimethoxysily)propyl] ethylene diamine (TMSPED) / methanol solution for several time and further washed by methanol to remove excess TMSPED [7]. Recent research in several of nanodevices / nanostructures with unique optical and electrical properties has increased significantly. Among these nanodevices / nanostructure, semiconductor NPs exhibited spectacular size-dependent properties when the particles size is less than 10 nm, and producing the quantum-effect [8][9][10]. As the particles size becomes smaller, the band gap becomes larger, resulting in the blue shift of UV-visible absorption spectrums [11]. For metal NPs, the Fermi level lies at the center of one continuous band. As a result in literatures, across the entire size range, the optical and electrical behaviors of metal NPs are described using classical equations for corresponding bulk metal material rather than quantum mechanical concepts [12]. Most recently, a 350 nm diameter Au-CdSe-Au nanowires were fabricated using a template growth method, and can function as sensitive photo sensors, which can potentially be massively multiplexed in devices of small size [13]. However, the fabrication process and the electrofluidic alignment method of nanowires as described in the study were not feasible with conventional silicon chip. Consequently, since the potential application of this device on silicon chip is severely limited, a new nanomaterials and/or a new process for the fabrication of nanodevice on silicon chips arise. The process of assembling negative-charged Au NPs and positive-charged CdSe NPs onto the silicon chip has been developed and proposed in [14].

## 1.2 REVIEW ON NANODEVICES

Several of the assembly processes, inorganic nanoparticles (NPs) and nanoclusters are the most attractive ones. Recently, the researches on the synthesis, characterization and applications of inorganic NPs have been increasing significantly. The inorganic NPs have some advantages: (1) Many well-developed synthesis methods of the NPs has been proposed, which are often simple and cheap for large quantity preparation. (2) The NPs have their unique optical, electronic, and catalytic properties, which are quite different from those of their corresponding bulk materials. For example, when the size of NP becomes smaller than its Bhor exciton radius ( $\sim 6$  nm for CdSe NP), the photo-excited electrons are delocalized. (3) The size of NPs, conventionally ranging from one to hundreds of nanometers, is particularly suitable for them to serve as building blocks for the assembly of larger nanostructures and contact closely with the micro systems, like the silicon chips.

In this section, we review some significant experiments about nanodevices composed of nanomaterials or NPs. One of the methods to construct nanodevices is the self-assembly techniques, which provide a means to realize structures such as quantum dots (QDs), NPs and other electronic / optoelectronic device configurations. Because these techniques do not rely on lithography to realize the specific nanostructures and assemblies, they can represent efficient, high throughput fabrication approaches. For self-assembled semiconductor structures, the electronic device functionality has been limited by the difficulty in achieving suitable interfaces for passivating and contacting the resulting islands or dots [15]. A patterning method of trapping and deposition of NPs in a submicron narrow gap have been developed in recently year. It demonstrated a light-emitting device, which consists of NPs trapped in the gap of lateral electrodes. The CdSe/ZnS NPs in the solvent were electrostatically trapped as a dielectric material in the gap by lateral electric field. The NPs were deposited in the gap as the solvent was evaporating. Electroluminescence from the NPs in the gap was observed when current was applied through the lateral electrodes [16]. Fig 1.5(a) shows a schematic diagram of the method. It was able to fabricate an ultra small light source smaller than the

wavelength of visible light. This small light source can be applied to optical devices, such as scanning probes, integrated photonic crystals, and so on. The fabrication process of the submicron sized light source was shown in Figure 1.5(b). At first, an electrode structure on p-type SOI was made with DRIE (The Alcatel A601E), and then a submicron gap was fabricated by cutting the electrode structure with Focused Ion Beam (FIB) that can enable us to fabricate a submicron narrow gap easily. Next, the wafer was immersed in NPs solution of toluene solvent, and applied the voltage to the gap between the lateral electrodes to trap NPs. At last, wafer was annealed at 400°C to remove excess organic molecules such as toluene and TOPO. After annealing, junctions between p-type Si and CdSe/ZnS NPs were built [16].

The synthesis of quasi-one-dimensional (1D) nanostructures has been developed, many of which have interesting electronic, optical, and chemical sensor properties that derive from size, composition, and shape. One-component systems are now quite common, but there are few examples of methods for synthesizing multi-component 1D materials composed of organic and inorganic materials. The hybrid multi-component (i.e. organic-inorganic) nanorods that have either diode or resistor properties has been proposed in [17]. In a typical experiment, the synthesis of segmented metal-polymer nanorods by electrochemical deposition of gold into alumina templates, followed by electrochemical polymerization of pyrrole (Ppy). During the electrodeposition process, it can control the length of each block by monitoring the charge. Other metals (e.g. Ag and Cd) with low work functions and inorganic semiconductors (e.g. CdSe), also can be deposited on top of the polymer block and polyaniline can be used in place of polypyrrole. This allows one to prepare multi-component rod structures with tailorable electronic properties that derive from the choice of the individual compositional blocks. For the Au portions of the nanostructure (contacts 1-2 and 3-4) exhibit linear I-V characteristics and bulk metallic behavior at room temperature as shown in Fig. 1.7(A), and demonstrate Ohmic behavior. For the Au-Ppy-Au system, one can see dark Ppy domains sandwiched between two bright segments of gold as shown in Fig. 1.6(A). Significantly, Fig. 1.7(B) shows the I-V measurements across the Ppy block of the Au-Ppy-Au nanorod (2-3 and 1-4 contacts)

also exhibit a highly reproducible, linear response at room temperature but nonlinear behavior at low temperature ( $<175$  K), characteristic of a semiconductor. The I-V curves and the corresponding electrical conductivities provide two important observations. First, the conductivity of the polymer block at room temperature, is 6 orders of magnitude lower than the metallic blocks, and all data are consistent with Ohmic contact between the Ppy-Au junctions. Second, the I-V response for the Au-Ppy-Au nanorod becomes slightly nonlinear as the temperature decreases [Fig. 1.7(B)]. Since the Ppy for the nanostructures discussed herein were generated by oxidative polymerization, they are p-type semiconductor. Continuously, four-segment nanorods (Au-Ppy-Cd-Au) also can be prepared via an analogous procedure [Fig. 1.6(B)]. I-V measurements on devices constructed from single Au-Ppy-Cd-Au rods exhibit “diode” behavior at room temperature as shown in Fig. 1.7(C), and the typical response is asymmetric and non-Ohmic. In the forward bias, there is a positive voltage on the Au block adjacent to the Ppy and negative potential on the Au block interfaced with the Cd block. Therefore, holes move from the Ppy block to the Cd block during the forward bias. In reverse bias, current does not flow until the bias overcomes the breakdown potential ( $-0.61$  V). The turn-on voltage for these diode nanorods is approximately  $0.15$  V. The I-V characteristics of the Au-Ppy-Cd-Au nanorods at room temperature suggest that a Schottky-like junction is formed at Ppy/Cd due to the difference in work functions of the two materials and an Ohmic junction at the Ppy/Au interface due to the similarity in work functions for the two materials. It is a powerful method for deliberately producing structures with desirable electrical properties with a straightforward synthetic procedure that offers a high degree of reproducibility [17]. These structures could be useful for a wide range of electronic and sensor devices.

Now, we will introduce the state of current and coming solar photovoltaic technologies and their further development. The emphasis is on R&D advances and cell and module performances, with indications of the limitations and strengths of crystalline (Si and GaAs) and thin film (a-Si:H, Si, Cu(In,Ga)(Se,S)<sub>2</sub>, CdTe). The contributions and technological pathways for *now and near-term* technologies (silicon, III–V, and thin films) and status and forecasts for next-next generation



photovoltaic (organics, nanotechnologies, multi-multiple junctions) are evaluated. Recent advances in concentrators, new directions for thin films, and materials/device technology issues are discussed in terms of technology evolution and progress. Insights to technical and other investments needed to tip photovoltaic to its next level of contribution as a significant clean-energy partner in the world energy portfolio [18]. The research progress over the past 25–30 years has been substantial and steady, as shown in Fig. 1.8. Photovoltaic is poised at what may be its most critical tipping point; the one that will cause this technology to “spread like wildfire” as it finally becomes a major part of our world’s energy portfolio.

Recently, in order to provide innovative strategies for designing next generation energy conversion devices, people efforts to design ordered assemblies of semiconductor and metal NPs as well as carbon nanostructures. Renewable energy such as solar radiation is ideal to meet the projected demand but requires new initiatives to harvest incident photons with higher efficiency, for example, by employing nanostructured semiconductors and molecular assemblies. Dye sensitization of mesoscopic  $\text{TiO}_2$  has been widely used in this context. Power conversion efficiencies up to 11% have been achieved for such photochemical solar cells. Semiconductors such as CdS, PbS,  $\text{Bi}_2\text{S}_3$ , CdSe, and InP, which absorb light in the visible, can serve as sensitizers as they are able to transfer electrons to large band gap semiconductors such as  $\text{TiO}_2$  or  $\text{SnO}_2$ . CdSe quantum dots (QDs) have been assembled onto mesoscopic  $\text{TiO}_2$  films by using bifunctional surface modifiers (SH-R-COOH) [19]. During visible light excitation, CdSe QDs inject electrons into  $\text{TiO}_2$  nanocrystallites. The injected charge carriers in a CdSe-modified  $\text{TiO}_2$  film can be collected at a conducting electrode to generate a photocurrent. The  $\text{TiO}_2$ -CdSe composite, when employed as a photoanode in a photoelectrochemical cell, exhibits a power conversion efficiency of 12%. Significant loss of electrons occurs due to scattering as well as charge recombination at  $\text{TiO}_2/\text{CdSe}$  interfaces and internal  $\text{TiO}_2$  grain boundaries. Fig. 1.9 shows the assembled  $\text{TiO}_2$  and CdSe nanoparticles using bifunctional surface modifiers of the type HS-R-COOH. Fig. 1.10 shows the sequence of steps followed.



One approach to facilitating electron transport in nanostructured semiconductor films involves applying a positive bias to the working electrode. The photocurrent generated at different applied potentials for OTE/TiO<sub>2</sub> and OTE/TiO<sub>2</sub>/CdSe electrodes is shown in Fig. 1.11. Excitation of TiO<sub>2</sub> and TiO<sub>2</sub>/CdSe films was carried out using light with wavelengths greater than 300 and 400 nm, respectively. Both films show anodic photocurrents when subjected to band gap excitation. The observed photocurrents increase as the potential is swept toward positive values. The potential at which we observe zero current is a measure of the flat band potential and reflects the maximum attainable open-circuit voltage ( $V_{oc}$ ). We observe zero current at potentials of -0.78 and -0.88 V vs SCE for TiO<sub>2</sub> and TiO<sub>2</sub>/CdSe films, respectively. The 100 mV shift represents the improved energetic of the TiO<sub>2</sub>/CdSe films and shows the advantage of using composite nanostructures for boosting  $V_{oc}$  [19].

### 1.3 MOTIVATIONS



As we have discussed previously, interactive forces between molecules, such as **hydrogen bonds**, **Van der Waal force**, and **coulombic force**, are also effective for NPs and play an important role in the assembly process. The researches on the synthesis of organic and inorganic NPs have been increased significantly. Among the semiconductor NPs, CdSe NPs or QDs is the most suitable for harvesting light energy in the visible region of the solar spectrum. So much researcher always choose the CdSe NPs or QDs to realize the nanodevices, optical devices, and solar-like devices. Recently, the photo-sensing nanodevice composed of negative-charged Au and positive-charged Tyramine-CdSe NPs has been developed and proposed. This functional nanodevice composed of inorganic NPs directly on the surface of silicon chip is the simplest and most effective process and without damage of the circuits in silicon chip. However, the method of Tyramine modification on CdSe NPs will seriously damage the optical and electrical properties of CdSe NPs. Therefore, it is important to develop more efficient methods. In our works, we propose another modify method of

CdSe NPs and follow the ‘dipping-and-washing’ process to improve the performance of Au / CdSe nanodevice, continuously, we also construct another nanodevice composed of CdSe- modified NPs based on “ionic interaction system” .

## 1.4 THESIS ORGANIZATION

The background has been introduced in section 1.1, including the basic concepts, the trend of nanotechnology development in the world, the synthesis methods of Au and CdSe NPs, and several of assembly methods of NPs on silicon substrate. Then, we have some reviews on the most representative experiments about nanodevices based on nanomaterials, Qds, and NPs in section 1.2. At last, the motivations of this work and thesis organization will be proposed in section 1.3 and section 1.4.

In chapter 2, the optical and electrical properties of metal and semiconductor will be introduced in section 2.1. For semiconductor NPs, we will focus on the mechanism of photoconductivity of CdSe NPs and the electron transportation between NPs, like quantum confinement of CdSe NPs. In section 2.2, the review on nanodevice composed of Au and CdSe NPs will be proposed and explained about the mechanism of the photo-sensing properties. Finally, we will introduce the CMOS sensing circuit in section 2.3.

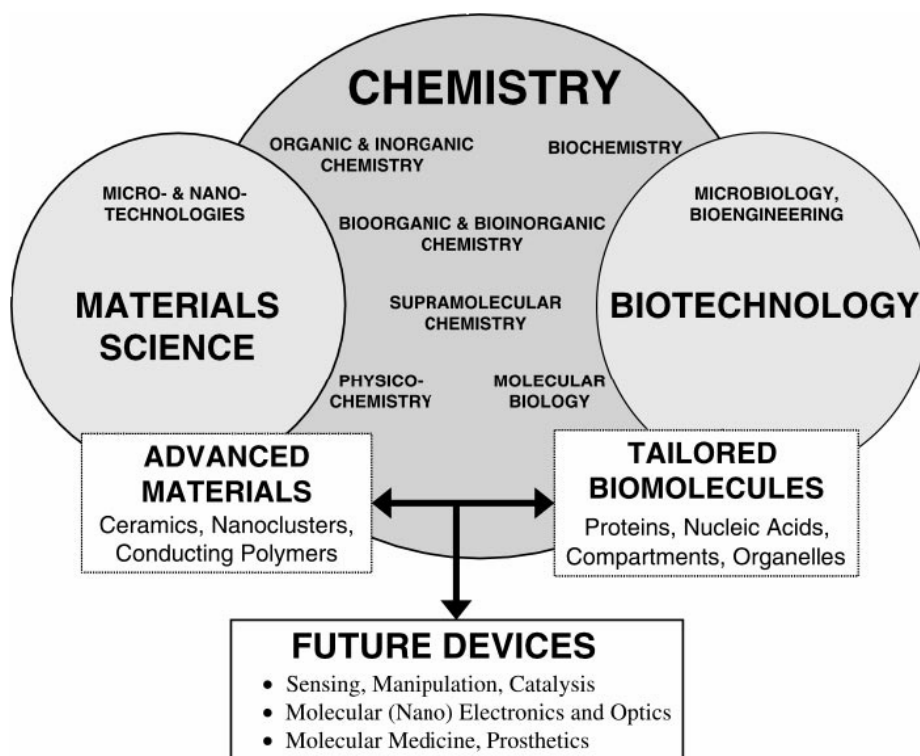
In chapter 3, we will develop the one system--- Coulombic force system, which is able to control NPs in nanostructure formation on silicon oxide substrate. In section 3.1 and 3.2, the synthesis and modification process of Au NPs and CdSe/ZnS (core/shell) NPs will be illustrated clearly. In section 3.3, the assembly process based on ionic interaction system will be proposed to construct two kinds of nanostructures.

In chapter 4, section 4.1 introduces the environment setup for measurement. SEM images and UV-visible / PL intensity spectra of the experimental results will be shown with no exception in section 4.2. In section 4.3, the measurement results of CMOS sensing circuits are shown. Then, the

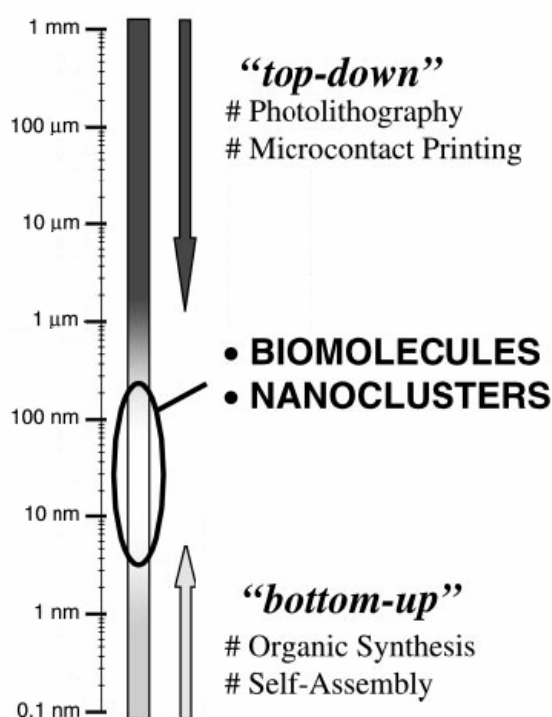
measurement results of nanodevices on silicon chip are shown in section 4.4 and 4.5. At last, we will consider the power efficiency of Au / AET-CdSe/ZnS nanodevice on silicon chip in section 4.6.

In chapter 5, the conclusions and future works are given in section 5.1 and 5.2.

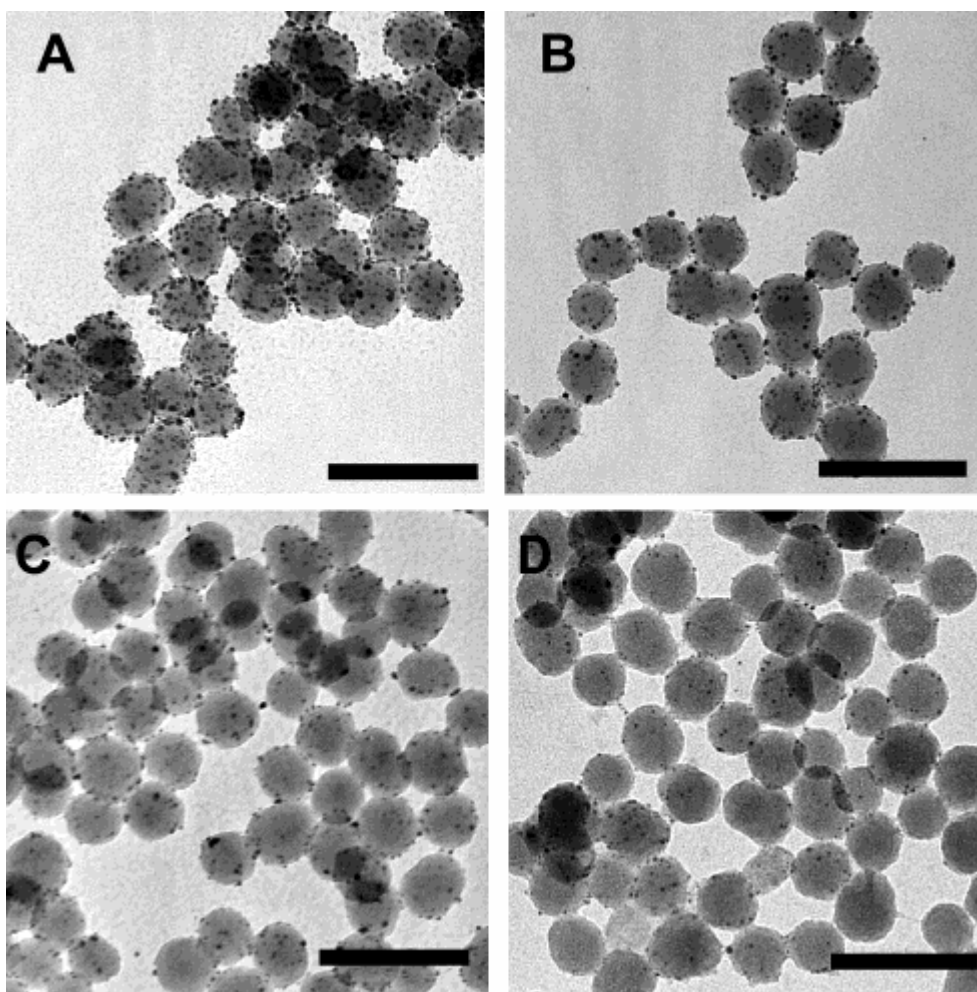




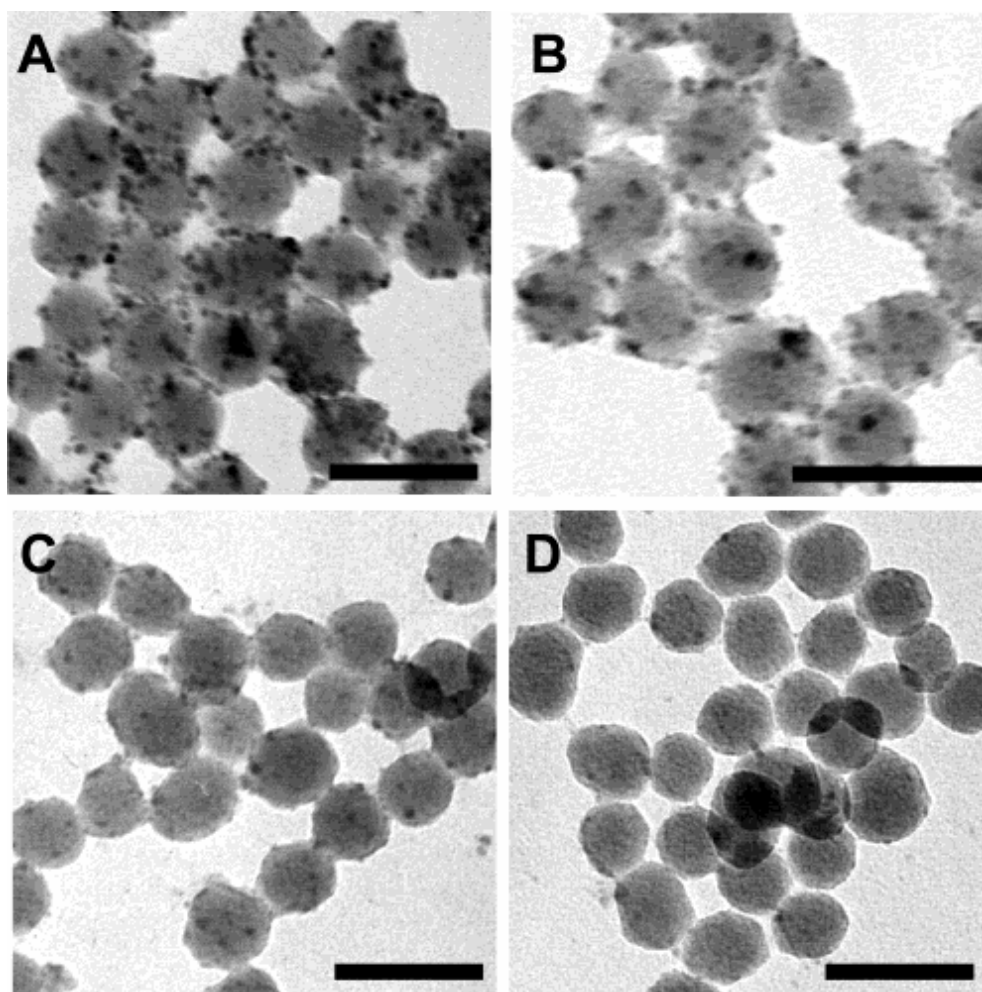
**Fig. 1.1** Chemistry is the central science for further applications such as materials science and biotechnology. The combination of advanced materials and tailored biomolecules will produce the future nanodevices [1].



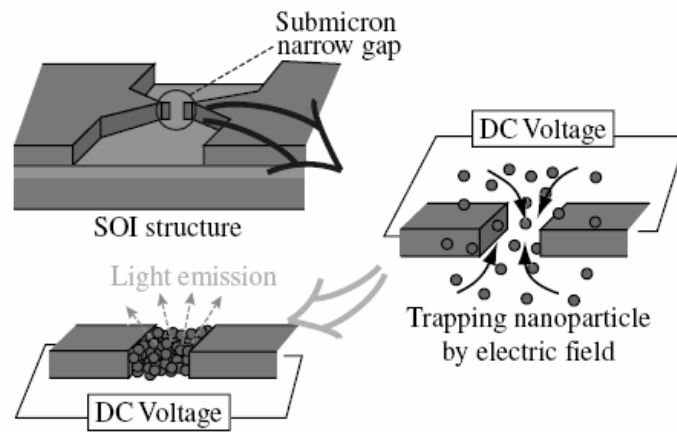
**Fig. 1.2** A gap currently exists in the engineering of small-scale devices. The top-down processes will have their limit below 100 nm, and the bottom-up processes will also have a limit at 2~5 nm. The gap will be filled by nanoclusters and biomolecules [1].



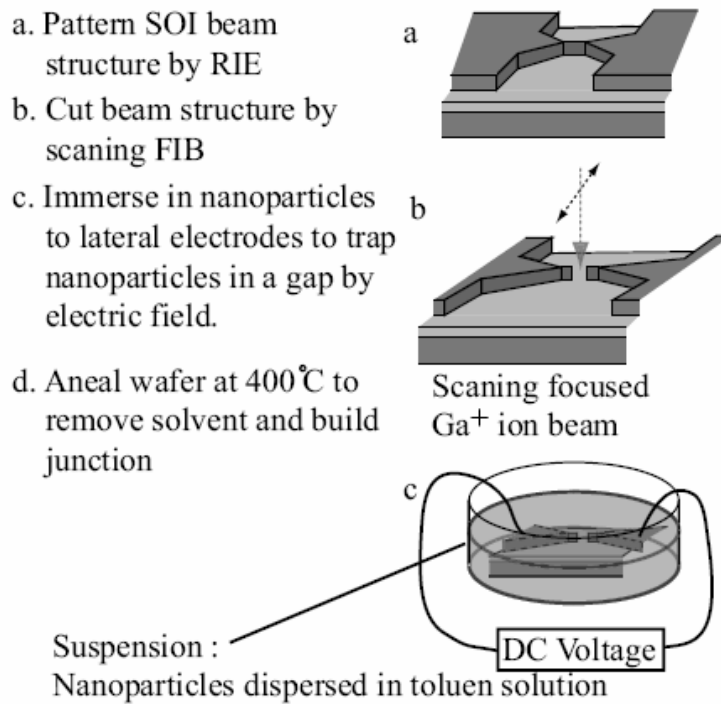
**Fig. 1.3** The TEM images of SiO<sub>2</sub>@Au NP clusters synthesized at (A) pH=8.4, (B) pH=8.6, (C) pH=10.2, (D) pH=11.1. The scale bar for all micrographs is 200 nm [2].



**Fig. 1.4** The TEM images of SiO<sub>2</sub>@CdSe NP clusters synthesized at (A) pH=6.8, (B) pH=7.2, (C) pH=10.2, (D) pH=11.1. The scale bar for all micrographs is 100 nm [2].



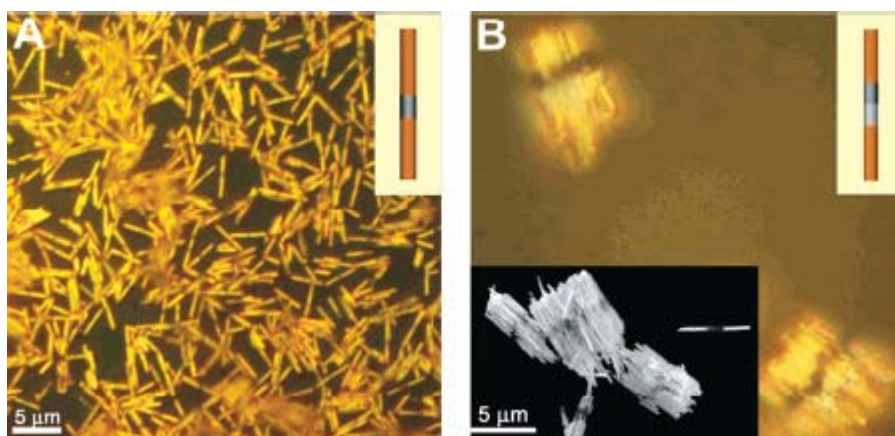
(a)



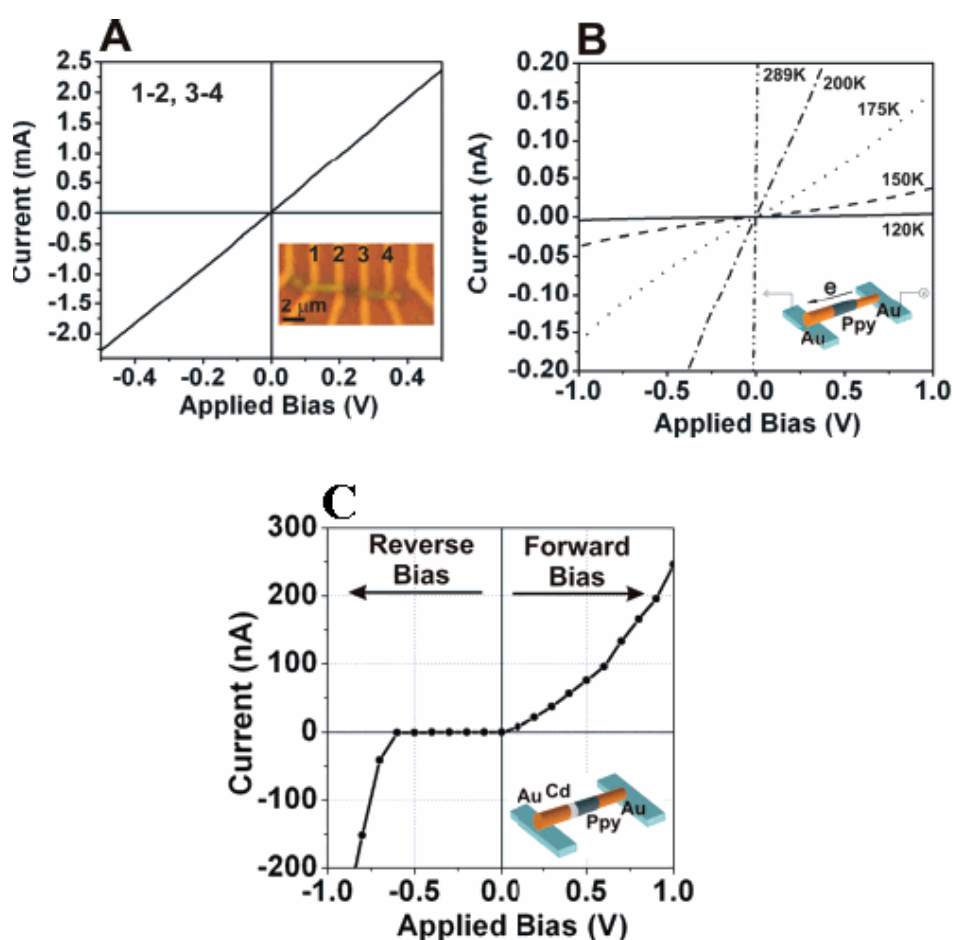
(b)

**Fig. 1.5** (a) The schematic diagram of trapping NPs in a submicron narrow gap ( $5 \mu\text{m} * 5 \mu\text{m} * 1 \mu\text{m}$ ) and a submicron sized light source. (b) The fabrication process of a submicron sized light source based on SOI and CdSe/ZnS NPs [16].

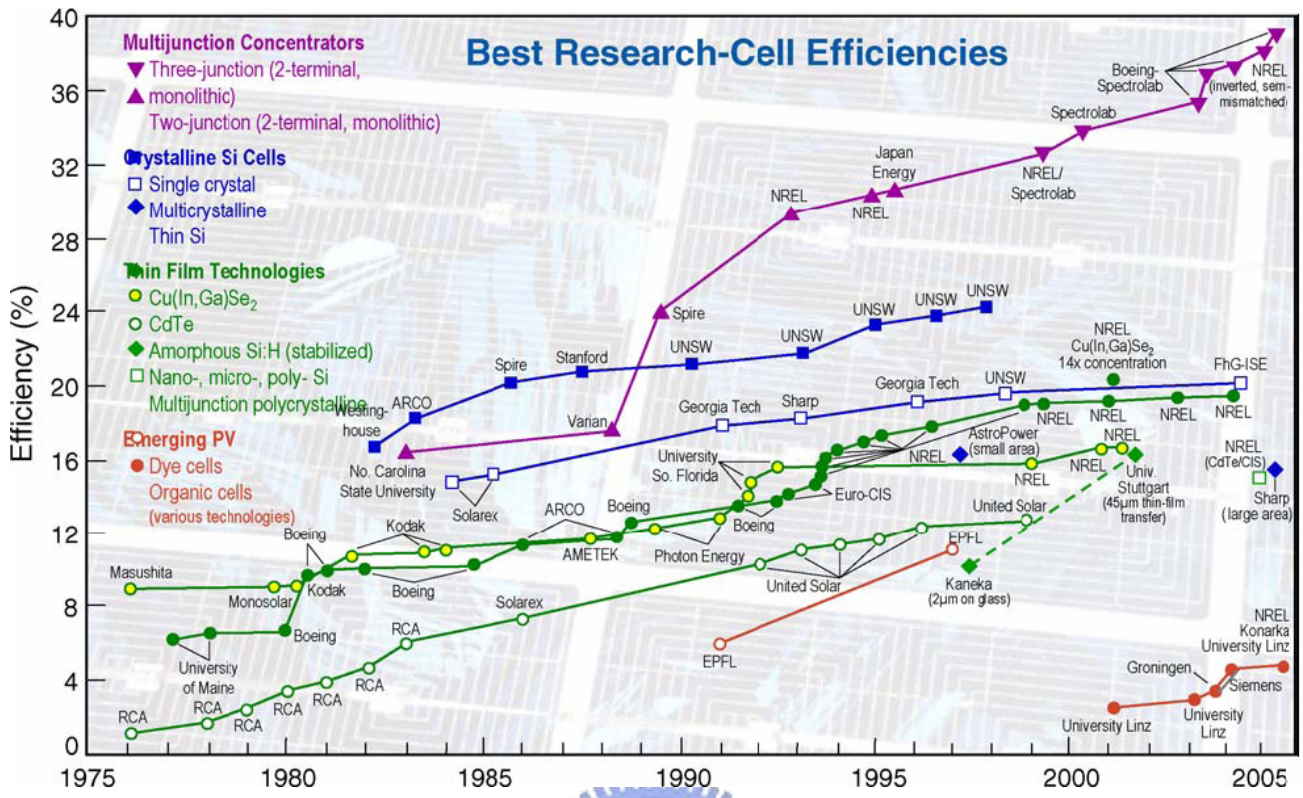




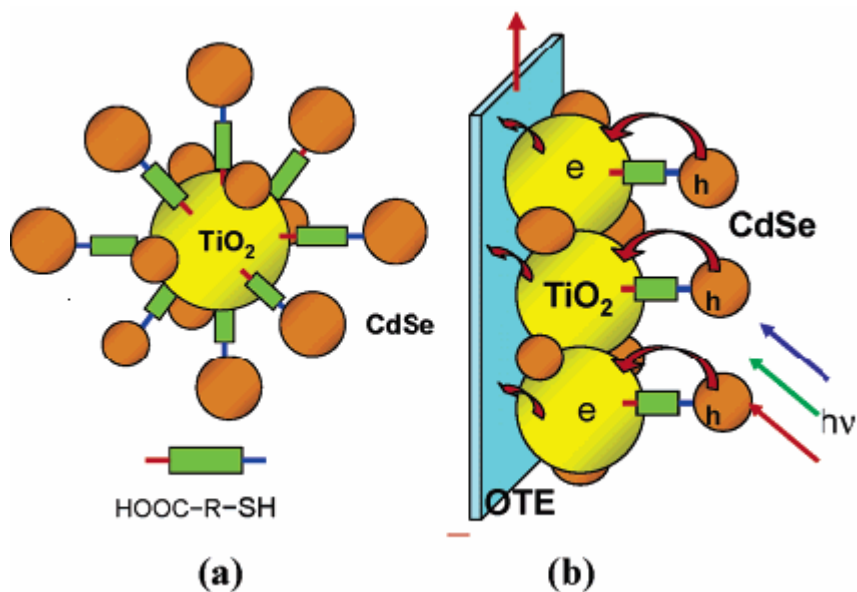
**Fig. 1.6** (A) Optical microscope image of Au-Ppy-Au rods. (B) Optical microscope image of Au-Ppy-Cd-Au rods. The lower left inset shows the corresponding FESEM image [17].



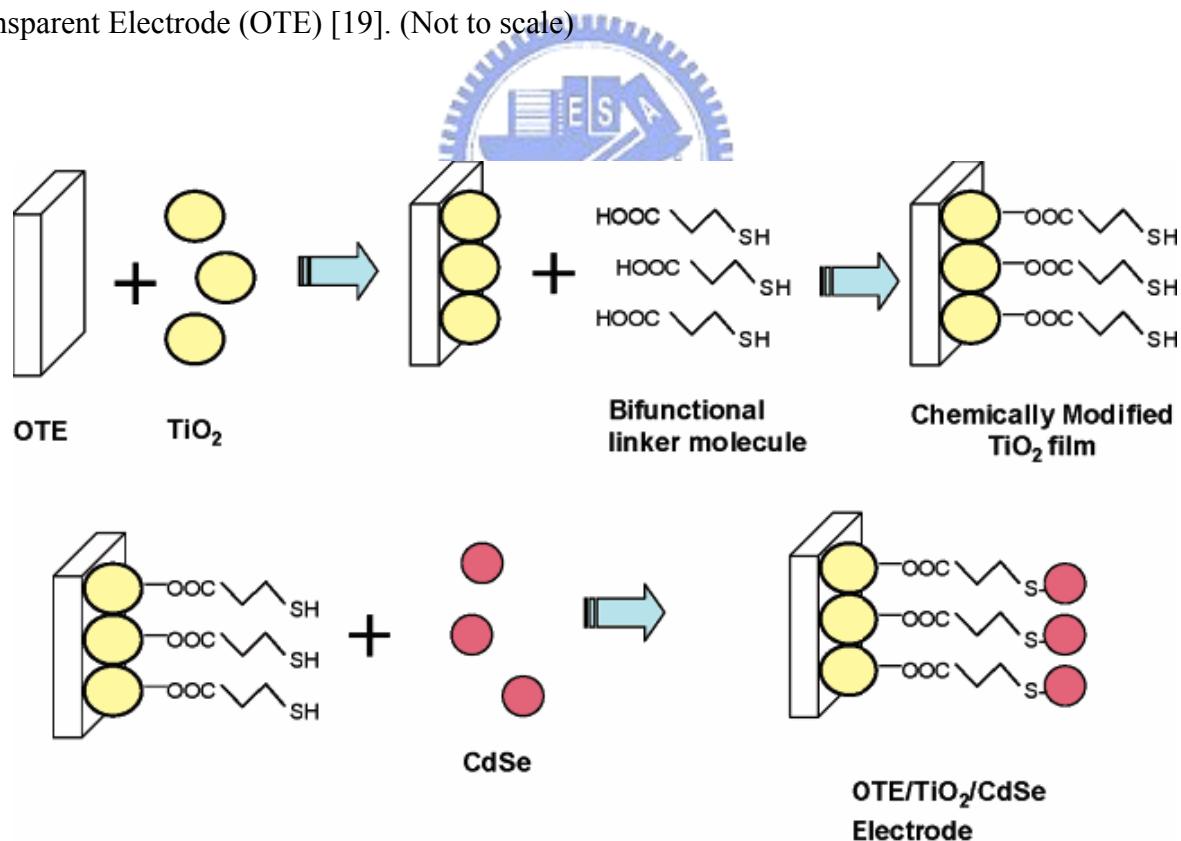
**Fig. 1.7** The measurement results of I-V characteristics. (A) For the gold blocks (1-2, 3-4) within a single nanorod at room temperature. Inset shows the optical microscope image (1000 magnification) of a single Au-Ppy-Au rod on microelectrodes. (B) Temperature-dependent I-V curves for measurements across electrodes 2 and 3. (C) For a single Au-Ppy-Cd-Au rod at room temperature [17].



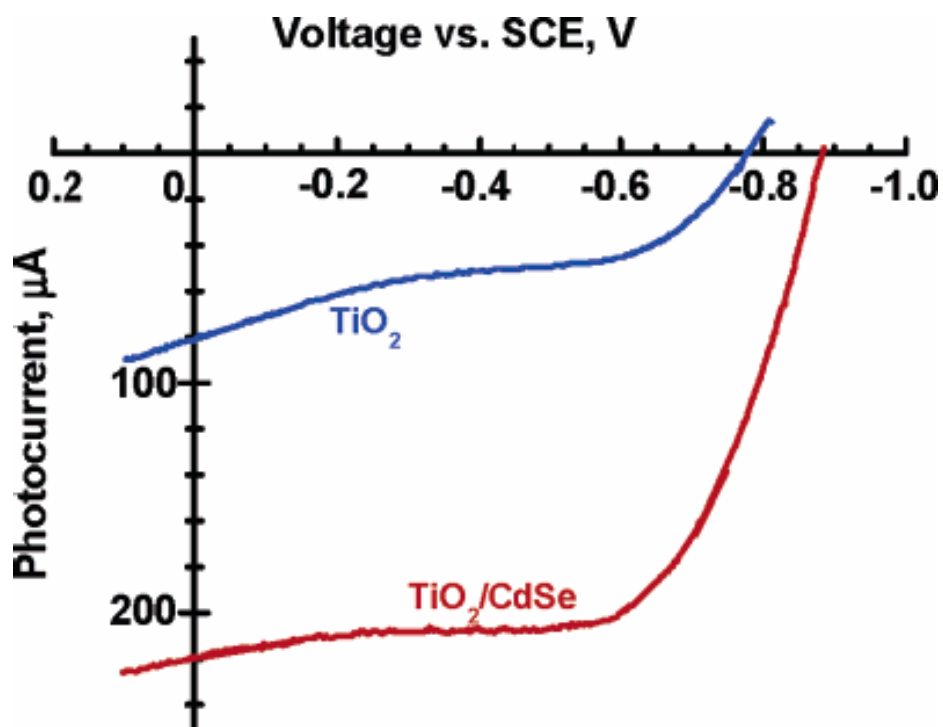
**Fig. 1.8** The efficiency evolution of best research cells by several of technology types. This table identifies those cells that have been measured under standard conditions and confirmed at one of the world's accepted centers for standard solar-cell measurements [18].



**Fig. 1.9** (a) Linking CdSe QDs to  $\text{TiO}_2$  particles with bifunctional surface modifier (HS-R-COOH); (b) Light harvesting assembly composed of  $\text{TiO}_2$  film functionalized with CdSe QDs on Optically Transparent Electrode (OTE) [19]. (Not to scale)



**Fig. 1.10** The sequence of steps for linking CdSe QDs to  $\text{TiO}_2$  surface with a bifunctional surface modifier [19].



**Fig. 1.11** I-V characteristics of (a) OTE/TiO<sub>2</sub> and (b) OTE/TiO<sub>2</sub>/MPA/CdSe films. The filtered lights allowed excitation of TiO<sub>2</sub> and CdSe films at wavelengths greater than 300 and 400 nm, respectively [19].

