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Quantum Dots: A Metaphor for Advancement of Technology

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ABSTRACT

Quantum dots have attracted the attention of many researchers since their discovery in the last decade. Quantum Dots (QDs) which are also known as semiconductor nanocrystals, have become an indispensable tool in bio-medical research, especially for multiplexed, quantitative and long-term fluorescence imaging and detection. QDs are nanometer-scale semiconductor crystals composed of groups II-VI or III-V elements and are defined as particles with physical dimensions smaller than the Bohr radius. Now the most useful QDs are semiconductor QDs, such as ZnS-capped CdSe nanocrystals. QDs possess unique chemical and physical properties due to their size and highly compact structure. Due to their tuneable band gap property they have shown promising applications in almost in each and every field. They can be a useful tool for monitoring cancerous cells and providing a means to better understanding of its evolution as they offer a wide broadband absorption spectrum while maintaining a distinct, static emission wavelength. In future, they could also be armed with tumour-fighting toxic therapies to provide the diagnosis and treatment of cancer. The success of using QDs in biological imaging, sensing and detection has encouraged scientists to further develop this technology for defence, clinical and translational research. One of the most important emerging applications of QDs appears to be traceable drug delivery, because it has the potential to elucidate the pharmacokinetics and pharmacodynamics of drug entity and to provide the design principles for drug carrier engineering. This review intends to highlight the latest developments in quantum dots that have greatly affected the human life in various fields.

Key words: Quantum dots, fast drug testing, solar paints, biosensors, drug-delivery, lasers

INTRODUCTION

Many scientist in the field of chemistry, polymer, composite and materials have given significant contribution to science and technology by utilizing the natural resources (Chauhan and Kaith, 2012; Aan *et al.*, 2011; Abd El-Hady, 2011; Abd El-Hady and Abd El-Baky, 2011; Abdi *et al.*, 2010; Raja and Thilagavathi, 2011; Issaoui *et al.*, 2011; Das *et al.*, 2011; Rocco, 2011; Adedayo, 2012). Nano science and technology are the emerging field of interest for various researchers. Nanostructured materials are materials which fall in the size range between 1-100 nm. Increased relative surface area and quantum confinement effect are the two factors that are responsible for the sudden change in properties when material are reduced to nanoscale (Qi and Gao, 2008; Roduner, 2009). There are three types of nanostructured materials depending on the confinement of electrons. These are nanorods, thin films and quantum dot (Cao, 2004). QDs are semiconductor nanocrystals having size range between 2-10 nm. They have unique properties such as band gap, tuneable absorption and photoluminescence, molecular coupling, electronic and magnetic property. These properties make quantum dot a material that has influenced nearly each field such as healthcare, sensor, detection, non-renewable energy source, defence etc. Therefore, the objective of this review was to highlight the latest developments in quantum dots that have greatly affected the human life in various fields.

QUANTUM DOTS AND ITS USE

Quantum dots in health care: Cancer is the second most common cause in the US, exceeded only by heart disease that accounts for one in every four death. The 2011 count rate for the death by cancer was 1500 people per day. Therapies like chemotherapy combined with radiation is the usual treatment of choice for different types of cancer but patients undergoing these therapies have to undergo repeated therapies as the cancer often returns and rejuvenates (Cao, 2004; American Cancer Society, 2005).

Quantum dots in cancer imaging, detection and targeting: Nanotechnology has generated new hopes by introducing nanostructured materials called QDs, the semiconductor nanoparticle. These nanoparticles have shown marvellous change in the imaging, detection and targeting of cancer cells. QDs act as multifunctional nanoparticles which can be employed for various purposes such as photosensitizer, carriers of photosensitizer molecules and carriers of multiple functions. These nanoparticles are functionalized with different moieties such as photo-sensitizers, antibodies against cancer cells, carbohydrates etc.

Photodynamic therapy is also a new therapy for cancer treatment in which cancer cells are destroyed by light-induced local production of a reactive oxygen species, such as singlet oxygen. The only disadvantage of photodynamic therapy is that it affects the non-cancerous cells also. Nann (2011) studied the direct generation of singlet oxygen by QDs quantum dots technique that foster resonance energy transfer in which energy absorbed by quantum dot is transferred to nearby photosensitizes.

But the use of cadmium or selenium quantum dots is not acceptable for photodynamic therapy because of their toxicity. The investigators created a nanoparticle with indium phosphide core and a zinc sulphide shell that results the quantum dots fluoresced brightly at 710 nanometers, a wavelength of light that passes through biological tissues and can be seen from within the body. QDs has their pharmacological properties of the ability to travel unimpeded through the blood stream, penetrate tissues and reach biological targets-the researchers coated the nanoparticles with a biocompatible polymer known as a dendrite. This coating also served as a convenient attachment point for a three amino acid peptide arginine-glycine-aspartic acid, known as RGD that targets many types of tumours. Tests with cancer cells and tumour-bearing animals demonstrated that these nanoprobes clearly imaged tumours known to bind to RGD. Bio distribution tests showed that approximately 60% of an injected dose of the new quantum dots was cleared from the body within a day and that 100% clearance was achieved within one week. Equally important, animals dosed with this new type of nanoparticle experienced no apparent ill effects. QD710-Dendron and RGD-modified nanoparticles had some favourable in vivo pharmacokinetics and successful tumour imaging properties (Gao *et al.*, 2012).

Quantum dot in RNA interference: Gene silencing using short interfering RNA (siRNA) is an effective approach to probe gene function in mammalian cells (Fig. 1). Although there have been

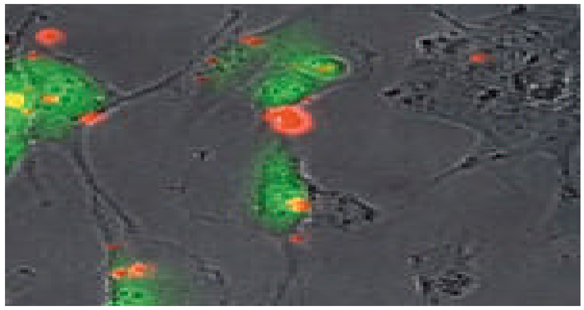

Fig. 1: RNA interference technique inhibiting the expression of targeted tumour cells

some success in the delivery of siRNA using various methods but tracking their delivery and monitoring their transfection efficiency but it is hard without a suitable tracking agent. Therefore, a challenge lies with the design of an efficient, self-tracking, transfection agent for RNA interference. Chitosan nanoparticles (NPs) with encapsulated QDs were synthesized and used to deliver HER2/neusiRNA. Using such a construct, the delivery and transfection of the siRNA can be monitored by the presence of fluorescent QDs in the chitosan NPs. Targeted delivery of HER2siRNA to HER2-overexpressing SKBR3 breast cancer cells was shown to be specific with chitosan/QD NP surface labelled with HER2 antibody targeting the HER2 receptors on SKBR3 cells. Gene-silencing effects of the conjugated siRNA were also successful using the luciferase and HER2 ELISA assays (Tan *et al*., 2007).

QUANTUM DOTS IN ENERGY CONSERVATION

Scientific breakthroughs are required for meeting the future energy needs to generate efficiently, store, transmit and use large amounts of power. For this, there is a need to develop cost-effective methods for capturing and converting energy from the sun but because of irregular nature of solar and other renewable energy sources, we must be able to store this energy for use when demand is high. New innovative scientific methods are needed to separate electric charges from solar radiations. Researchers from Los Alamos on demonstrating, nanoscale crystals, called "quantum dots," concluded that these nanocyrstals on absorption of a single photon of light can generate multiple charge carriers. This phenomenon is called "carrier multiplication" or "Multiple Exciton Generation (MEG)". Carrier multiplication could provide with its next generation solar energy conversion devices such as solar panels, solar cells, photovoltaic cells etc. (Qi and Gao, 2008; Roduner, 2009; Cao, 2004).

Quantum dots in solar paint: Researchers experimented with the composite mixture of CdS/TiO_2 and CdSe/TiO_2 nanoparticles. Different ratio of quantum dots in paint was experimented by the whole mixture of composite. Paste is applied over the glass electrode which is annealed at 473 k, the paint has an overall power efficiency exceeding 1% under ambient conditions. When CdS and CdSe quantum dots were deposited directly on the TiO_2 nanoparticles as a coating by using multi-film quantum dots it increased the efficiency to 5%, due to various size dependent optical and electronic properties. Solar paint can generate photocurrent by excitation in semiconductor nanocrystal that as a result produces electron injection into TiO_2 nanoparticles which are then collected by collecting electrode, generating photocurrent (Fig. 2) (Genovese *et al*., 2012).

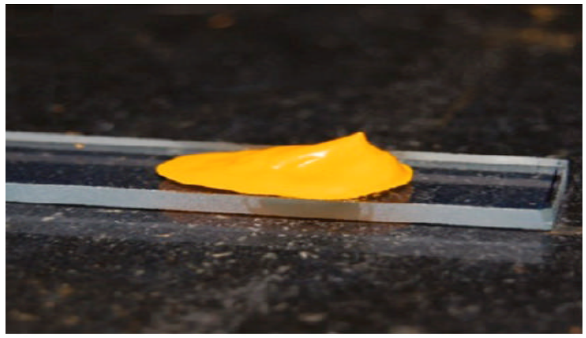

Fig. 2: Solar Paint (Image credit: Genovese *et al.*, 2012 American chemical society)

Quantum dots in photovoltaic cell: Multiple exciton generation is the most powerful feature of quantum dots. Due to this feature quantum dot can generate multiple electrons for every photon incident on it. Different devices such as photovoltaic cell, photonic devices and photodetectors are based on this feature. Graphene sheet modified with CdSe QDs is designed in flexible photo electrode. Current conversion efficiency of 17% has been achieved when incident with photon with flexible photovoltaic cell (Chen *et al.*, 2012).

Quantum dot in counter measure system: It has immense use in defence. Researchers have successfully developed a counter measure system to protect these space assets such as satellite from missiles attack. For this researchers designed the decoy consisting of quantum dots. Quantum dots unique size-dependent electro-optical properties and controllable size, shape, strength of confinement potential and their ability to tune and emit radiation of desired wavelength are the main factors for designing a decoy system (Mintz *et al.*, 2012; Tang *et al.*, 2011).

Mixture of different kinds of quantum dots (InSb, PbTe, HgTe, HgSe, CdTe, CdSe and CdS) in various sizes in the required ratio, when dispersed in space like a cloud copies exactly with target so efficiently that even advanced sensor technology are unable to detect the original target as clearly shown by Fig. 3, because the sensor technology is not able to distinguish between original target and decoy. Quantum dots cloud can be created either by spraying a mixture of quantum dots from a storage tank or by exploding a small pack of quantum dots dispersed in an inert gas (Argon/Helium) (Mintz *et al.*, 2012; Tang *et al.*, 2011).

Quantum dot in solar cells: Researchers from the University of Toronto have created the most efficient solar cell based on Colloidal Quantum Dots (CQD). The researchers used inorganic ligands i.e., single layer of atoms around the quantum dot instead using organic molecules that was using less space. Researchers not only showed the same colloid characteristics but also showed highest electrical characteristics and highest power conversion efficiency that was one of the striking feature of Colloidal quantum dot. Quantum dot solar cells with (MEG) multiple exciton generation have been demonstrated by National Renewable Energy Laboratory that has measured very high MEG quantum yields (up to 300%) for charge carrier generation in Pb-VI QDs (VI = S, Se, Te) (Tang *et al.*, 2011).

Quantum dot in hybrid solar cells: Hybrid solar cells are the combination of unique properties of one or more kind of inorganic nanoparticles, combining the properties of polymers when formed

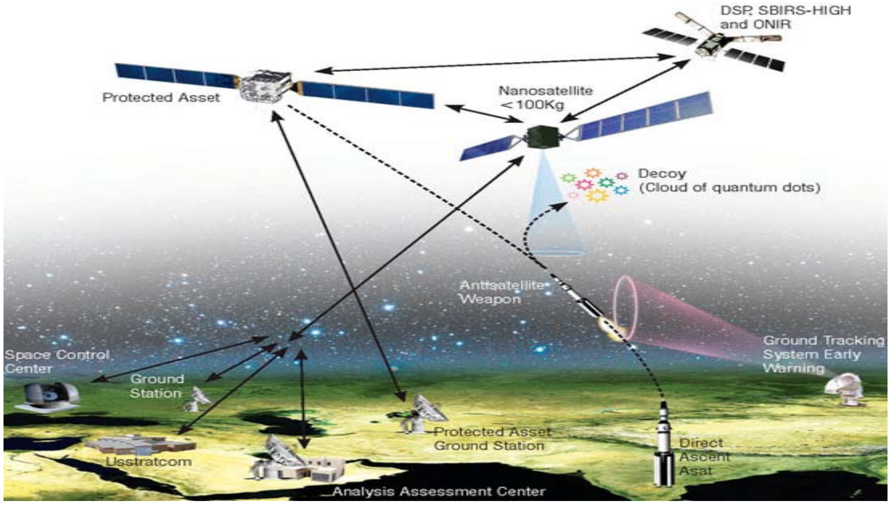

Fig. 3: The counter measure system based on quantum dots. Anti-satellite weapon based on advanced sensor technology seeks the decoy cloud of quantum dots instead of the target satellite (Mintz *et al.*, 2012)

as films. Organic/inorganic as thin hybrid material are opening doors for the construction of new class of devices in which both components are photovoltaically active. The prime requirement in inorganic/organic hybrid solar cell is to blend a high concentration of inorganic nanoparticle onto polymer matrix, to form an interpenetrating network. Phase separation in macroscopic scale should be avoided. There are two different configurations for solar cell configuration one is bilayered configuration and the other is interconnected structure of p and n type material. An efficient charge transfer from the nanocrystalline inorganic semiconductor so the conduction band of wide band gap semiconductors (such as TiO_2, ZnO, TaO.) in combination with high extinction coefficient nanocrystals in the visible range makes them very attractive for dye sensitized solar cells (Arici *et al.*, 2004; Ellingson *et al.*, 2005).

QUANTUM DOTS IN DIAGNOSTICS

Researchers developed a nanoprobe, 100 times less than the size of human cell. This nanoprobes helps in visualizing *in vivo* proteolytic activity. Near-infrared light also passes harmlessly through skin, muscle and cartilage; the new probes could help doctors to catch tumours and other disease sites deep in the body without biopsy or invasive surgery. Quenching technique is being used to attach gold nanoparticle via peptide sequence, keeping the gold nanoparticle close to quantum dot that prevents quantum dot to give its own light. Quantum dots are programmed such that they get light up by specific proteases such as cancer, atherosclerosis and many other diseases (Chang *et al.*, 2005). Researchers have successfully demonstrated the silicon quantum dots as these are non-toxic and environmental friendly. They have fabricated the colloidal, water dispersible and optically stable quantum dots. Si quantum dots with the size range of 1-5 nm and emission range from Blue to NIR has been obtained (Quek and Leong, 2012).

QUANTUM DOTS IN ELECTRONIC DEVICES

Colloidal quantum dots are now becoming the most attractive application for nanoscale fluorescent emitters. Through, a simple spin coating technique a new class of hybrid optically

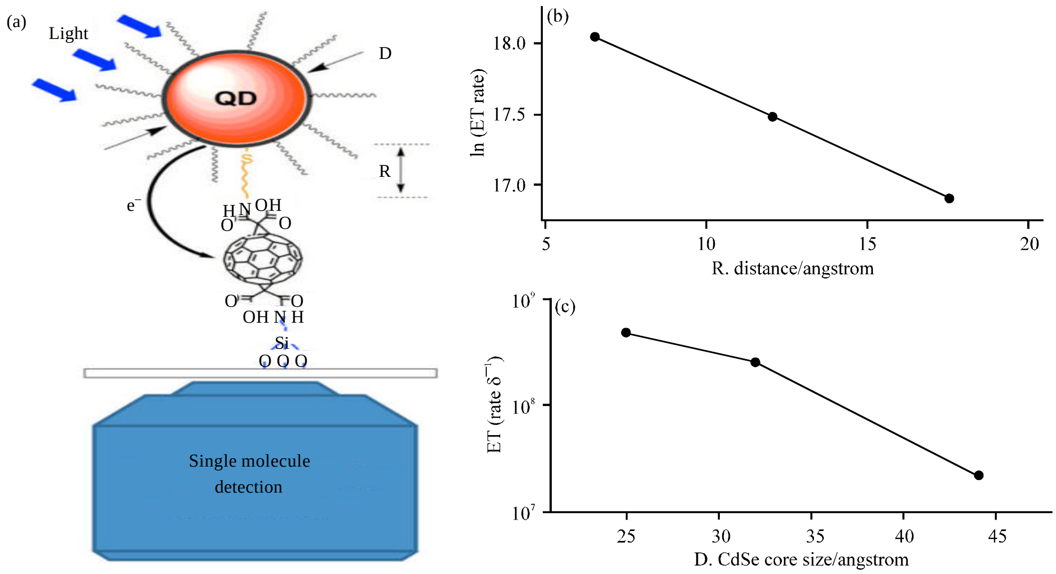

Fig. 4(a-c): (a) Photo induced electron transfer occurring in quantum dot-bridge-fullerene here rodimers and observed with single molecule microscopy, (b) controlling electron transfer (ET) rate by variation of interparticle distance (R) and (c) Quantum dot size (D) (Credit: Image courtesy of DOE/Brookhaven National Laboratory)

pumped surface emitting laser has been realized that combines the advantages of organic and inorganic systems representing significant step towards low-cost, mechanically flexible lasers that have efficient luminescence properties, can cover a wide spectral range and can confine to any shape. Researchers successfully experimented by incorporating CdSe quantum dots into photosensitive polymer host like SU8 and other waveguides and micro cavity structures using soft lithography. Various devices such as vertically coupled waveguides and micro disk resonators can be fabricated. Practical ultrafast optical switches, flexible emitters, modulators and room temperature single photon sources can be fabricated through these techniques (Menon *et al*., 2009).

QUANTUM DOTS IN MOLECULAR ELECTRONICS

Scientists have developed organic (DBA) donor-bridge-acceptor systems as these systems are useful due to their wide range of charge transport properties which can be controlled by varying its chemistry. Quantum dots in this DBA system will acts as a bridge and combined with electron-accepting materials such as dyes, titanium oxide fullerenes to produce dye-sensitized hybrid solar cells. Quantum dots light-absorbing and size-dependent emission properties would boost the efficiency of devices incorporating DBA system such as hybrid solar cell. Figure 4 shows that the electron transfer rate can be enhanced and fluctuations caused by electron transfer can be reduced by reducing quantum dot size and the length of the linker molecules.

Through the pairing of such nano particles miniature, power sources can be developed that could help to boost molecular electronics (Xu and Cotlet, 2011).

PURE QUANTUM DOTS SHINES BRIGHTER FOR IMPURITY PROFILING

Recent advancements have shown that quantum dots made of multiple components in solution via exchange of cations are poor light emitters because of impurities left in the final product. They

Fig. 5: Luminescence of CdSe/CuS nanocrystals prepared by cation-exchange. Left picture showing crystals before purification and the right picture are the same nanocrystals after purification in which impurities have been removed. (Credit: Image courtesy of DOE/Lawrence Berkeley National Laboratory)

demonstrated that by heating these nanocrystals to 100 degrees Celsius, not only increases their luminescence by 400-fold within 30 h but also able to remove the impurities as shown in Fig. 5 (Jain *et al.*, 2012).

ROLE OF DOUBLE QUANTUM DOTS IN COMPUTERS

A new method has been developed for handling the effect of the interplay between vibrations and electrons on electronic transport that could help in understanding the transport of discrete amount of information as qubits (electrons) in quantum computers. A model was created to assess the electron current fluctuations when subjected to phonons (quantized modes of vibrations).Phonons were induced by nano-mechanical resonator and double quantum dots were used to enhance it its ability to confine by two or more electrons. They have shown that when the excess energy between the two quantum dots of the DQD system is sufficient to create an integer number of phonons, electrons start resonance and tunnel from one quantum dot to the other. In strong electron-phonon coupling regimes, multi-phonon excitations can thus enhance the electron transport. Coherent phonon states method is used to de-couple the electron-phonon interaction and reach the resonance modes of phonon. The fluctuations of electron current could therefore be controlled by tuning the electron-phonon coupling which makes it a good quantum switch to control the transport of information in quantum computers (Wang *et al.*, 2012).

COATING QUANTUM DOTS WITH POLYMER

The studies have described a procedure for the preparation of quantum dots coated with an amphiphilic polymer, a polymer that contains both water-attracting and repelling components, aimed to develop a robust approach for the preparation of QD for use as fluorescent tags for bio imaging, sensing and therapeutics. This method is applicable to any nanoparticles, not just QDs. Conventional methods of ligand exchange shell are unstable as it might release toxic material such as cadmium into solution. QDs disperse in water by coating them with a polymer that has both hydrophilic and hydrophobic moiety associated with them. The hydrophobic parts of the polymer

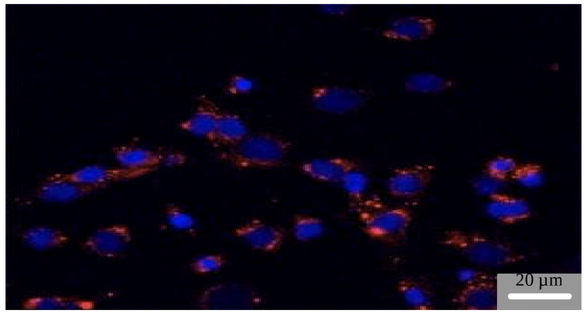

Fig. 6: Image of red light-emitting quantum dots incubated with mammalian cancer cells. The cell nuclei are stained blue (Janczewski *et al*., 2011)

attract hydrophobic ligands that stabilizes the QDs and hydrophilic parts of the polymer attract water molecules in solution. Polymer coating can be used to attach various functional groups to quantum dot surface that can help in imaging cancer cells as shown Fig. 6 (Janczewski *et al*., 2011).

CONCLUSION

Bulk heterojunction hybrid solar cells are the new scientific advances that have occurred recently and many such advances are expected in near future. In future by making the best use of the existing approaches, researchers will be able to reach the incredible applications from quantum dots. Defence sector includes applications like Quantum Dot Infrared Photodetectors (QDIP) are currently proving very powerful and sensitive as compared to other sensors. Quantum dots are proving beneficial as they are not only helping to conserve our natural resources but also help in fighting diseases like cancer and helping in the development of science and technology.

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