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ZnO quantum dots a novel nanomaterial for various applications: Recent advances and challenges

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Globally, in the recent era of 22[nd] century, ZnO quantum dots has gained huge attention of researchers towards its various applications in nano-biotechnology industry. This review article provides substantial approach on several aspects of ZnO quantum dots,its properties, synthesis process, factors affecting the synthesis process. Recent advances and challenges in QDs synthesis and their applications. Though the use of ZnO QDs has shown huge progress, but still so many challenges are there at present like economically cheaper level commercialization of quantum dots, proper *in vitro* and *in vivo* application of ZnO quantum dots, so that it can fulfil the need of the industry for various applications.

Keywords: Biomolecules, Nano-bioconjugation, Quantum confinement, ZnO QDS

Nanomaterials

Nanomaterials are the materials having at least one of the dimensions in range of 1-100 nm[1–3]. Nanomaterials, inspired from natural molecules[4,5]are the bridge stone of bio-nanotechnology, *i.e.*, interfacing biology with nanotechnology is recently a powerful tool for application to almost all the fields of science and technology including health improvement. Plenty of inorganic and organic nanomaterials are naturally available to synthesize nanomaterials of various size and shape. Nanomaterials are mainly composed of organic[6] or inorganic[7,8] materials having covalent, ionic and metallic bonds with high potential for being applied in various fields of technologies including health and diagnosis[9], bioimaging[10] drug discovery[11], drug targeting[12] drug deliveries[13], antimicrobial agents[14], wound dressing[15], transfection vectors[16] and labeling agents[17]. Recently, integrating biomolecules with biocompatible nanomaterials contrast agents, diagnostic devices, and important tools in cancer therapy are developed[18]. Some of these nanomaterials occur naturally, but most are engineered for specific interest like cosmetics[19–21], sunscreens, stain resistant, clothing[22,23], tires[24] electronics[25], *etc*. Thus, the science and technology of nanomaterials is a wide and interdisciplinary research which resulted in rapid transition into the technology with better performance in the past few years worldwide[26].

At this scale nanomaterials have high surface area to volume ratio[27] than their bulk counterparts leading to improved chemical, physical, mechanical[28], magnetic, optical[29] optoelectronic[30] and other properties[31]. The nanomaterials have potential to targeted drug delivery which can be controlled using some externally applied field such as magnetic, applied electric or irradiated photons[32]. Nanomaterials are used as source for renewable and clean energy to meet the global energy demand[33,34]. Nanomaterials as potential candidates are studied for improved engine efficiency, replacing to light emitting diode (LED)[35], efficient water purification systems[36] and defense systems[37]. Nanomaterials will revolutionize technology and industrial processes with improved performance same as the silicon technology did.

Zero-dimensional (0D) Nanomaterials

Zero dimensional (0D) nanomaterials have dimensions of a few nanometers with less than 10 nm in all direction and exhibit quantum confinement effect leads to discrete energy levels; known as quantum dots (QDs)[38–41] QDs are generally referred as an artificial atom[42], where time-space distributions of the excited electron-hole pairs get confined within a particular small volume, which results into enhanced properties[43].

One-dimensional (1D) Nanomaterials

1D nanomaterials has size restriction in two dimensions whereas in third dimensionlimitation is relaxed and hence, quantum confinement is in

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two directions[44]. Quantum wires, nanowires, nanofibrils, nanofibers, nanotubes, *etc*. are the 1D nanomaterial. 1D nanocomposite have potential and are used in nanodevices, nanoelectronics, alternative energy resources and national securitydata storage, biochemical and chemical sensors[45].

Two-dimensional (2D) Nanomaterials

2D nanomaterials have quantum confinement in only one direction since there is no size limitation in two directions[46]. Quantum well, nanosheet like structures are the examples of 2D nanomaterials.

Three-dimensional (3D) Nanomaterials/Superlattices

3D nanomaterials are basically dispersions of nanostructured materials *e.g*. bundles of nanofibers/ belts etc. making bulk materials in which thefree electron can move in all three dimensions *i.e*. X, Y and Z directions[47]. Nanomaterials with 3D architectures, like nano superlattices show some exceptional properties and functionalities having wide range of applications. The distribution of the density of states for nanomaterials of 0D, 1D, 2D and 3D are shown in (Fig. 1)

Types of QDs

Nanostructured materials/QDs (QDs) can be produced for all kinds of materials viz. metals, semiconductors, insulators and polymers. Their properties can be tailored as per the requirement such as magnetic, optical, chemical, catalytic, hydrophobic, hydrophilic nanostructured materials. Therefore, QDs are also prepared to have high luminescence properties at specified energy in different medium. Semiconductor QDs have wide range of materials like II-IV, I-III, I-V, II-VI, *etc*. Metal/semiconductor QDs can exhibit high intensity of fluorescence useful for various applications including tags, biomarkers and probes. The fluorescent QDs unveil transitions having high polarizability and size scale in accordance with equation: $E_{fermi}/N^{1/3}$ [49,50]

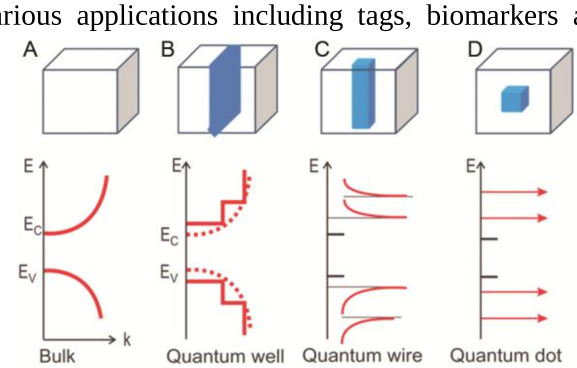

Fig. 1 — Schematics of density of states as system dimensionality is reduced as moving from left to right *i.e*., from (A) the bulk; (B) 2D quantum well; (C) 1D nanowire; and (d) 0D quantum dot. The valence bands and conduction bands are distributed into overlapping sub-bands that goes on becoming narrow and narrow successively as the movement of electron is restricted[48]

QDs depict quantum size effects as their size is of the order of Bohr's radius *i.e*., electron-hole pairs in solid materials[51]. The transition energy from highest occupied molecular orbital (HOMO) tolowest unoccupied molecular orbital (LUMO) decreases with size of QDs. The bandgap and emission wavelength of QDs are tuned between ultraviolet (UV) to near infrared (IR) by controlling the size and composition of nanocrystals. The emissions from QDs are bright and stable at room temperature. These specific properties make the QDs suitable for manufacturing LED, photonic crystals, Single Electron Transistor(SET), chromophores in solar cells, semiconducting polymer matrix, bio-imaging quantum optics[52,53]. Fluorescent QDs are also used as fluorescent indicators to monitor biological reactions as they can bind/attach to DNA or protein through sulfide linkage.

Fluorescent QDs

The fluorescent QDs are produced having the emission at any wavelength in the entire visible and near infra-red region. In metallic QDs of a few atoms can give fluorescence which is characterized by intra-band transitions of free conduction electrons. At this trivial size, metallic clusters behave as 'molecular species' and discrete states showing very strong fluorescence[54].

On the other hand, fluorescent semiconducting QDs are gaining attention due to sharp single wavelength and highly intense emission due to quantization effect. It also hasa possibility of tailoring the band gap from UV to near IR range of electromagnetic spectrum, chemical and thermal stability. The nature of fluorescence strongly depends on the physical environment of electron-hole pair just before they recombined. Strong confinement of the exciton in QDs, yields quantum mechanical effects with quantization of the fluorescence peaks which was first discovered in semiconductor nanocrystals by A. Ekimov in a glass matrix[55] and L. Brus in colloidal solutions.

Fluorescent ZnO QDs

Fluorescent ZnO QDs are bio-compatible, water-dispersible, stable in aqueous medium, environmentally friendly inorganic material having strong fluorescence as compared with traditionally used QDs of CdTe or CdSe, which makes it attractive for practical applications. Due to their relative non-toxicity, ZnO QDs have higher biological importance including bio imaging, optical imaging, drug delivery, gene therapy, antigen and allergen detection, DNA detection, bio-sensing including cancer cell sensing and antibacterial agents[56–59]. The high abundance of ZnO in nature and its low toxicity makes it an excellent substitute for II-VI compound semiconductor nanocrystals that may produce toxicity via generation of light induced reactive oxygen species (ROS). Till date, the most affluent method to fabricate ZnO QDs in dispersions is sol-gel method though, colloidal solutions of ZnO nanomaterials have tendency of aggregation. Zhang *et al*. has prepared ZnO QDs using sol-gel method show enhanced activity of ZnO QDs[60]. The diameter of ZnO QDs and cadmium doped ZnO QDs with wurtzite structures (hexagonal) were 3-6 nm, exhibit sharp absorption and fluorescence. The intensity further enhanced using surface modification of such QDs using different surfactants like Octadecyl amine/Trioctylphosphine oxide (ODA/TOPO). Different groups synthesize ZnO nano powders via sol-gel approachof size ~4 nm, aggregated into larger spherical particles. Jagvir Singh *et al*., have studied the importance of alkali metal hydroxide (LiOH, KOH, NaOH) to control the size of ZnO nanomaterial in non-aqueous solution and discussed the role of alkali hydroxide in controlling the size of ZnO nanoparticle within 10 nm[61]. Zhang *et al*. have modified the surface of ZnO nanomaterials using various capping agents; like APTMS(aminopropyl trimethoxysilane), TEOS (tetraethyl orthosilicate), MS (mercaptosuccinic acid), MPTMS (3-mercaptopropyl tri-methoxysilane) and PVP (polyvinylpyrrolidone) to limit the particle size below 10 nm depicted from transmission electron microscopy (TEM)[62].

Properties of ZnO QDs

Optical Properties

ZnO QDs show novel optical properties lead by quantum confinement. As the size of QDs decreases, the energy gap between the valence band & conduction band increases, therefore, QDs of same material exhibit diverse colorspectrum as a function of size, as shown in (Fig. 2). ZnO QDs with size less than 10 nm exhibit strong quantum confinement effect in three directions hence, density of states of this 0D structure has limited spatial correlation between electrons and holes. Fluorescent ZnO QDs exhibit wide emission range subject to the particle size having direct band gap having high excitonic binding energy (~60 meV) suggesting the possibility of excitonic transition at room temperature in ZnO QDs[63–68].

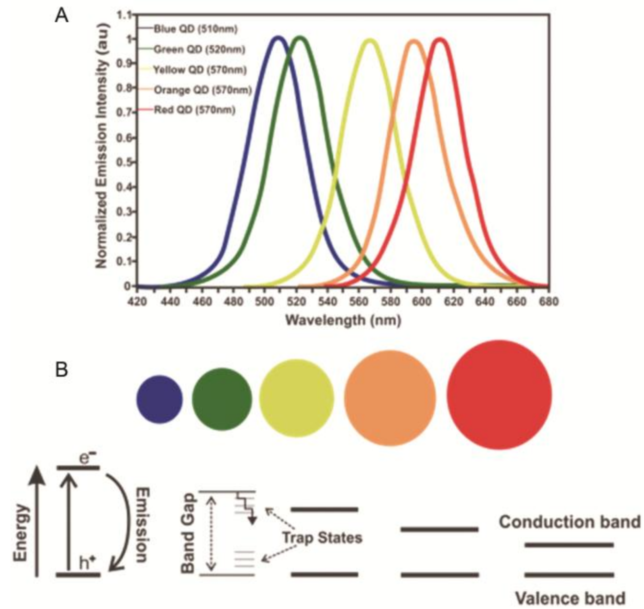

Fig. 2 — (A) Emission spectra of water soluble CdSe/ZnS QDs having excitation wavelength 350 nm; and (B) QDs with different size and formation of electron-hole pairs after excitation facilitated by fluorescence or relaxing *via* trap states

Physicochemical Properties

In nano-regime, the physicochemical properties of ZnO QDs are different from that of bulk counterpart. ZnO QDs has mainly two distinct crystallized forms *i.e.*wurtzite hexagonal structure and zinc blend in cubic form[69]. The wurtzite structure in hexagonal form exists at optimum pressure and temperature only. The ideal wurtzite structure is close-packed lattice in hexagonal form, with c_o = 0.52069 nm and a_o= 0.32495 nm as lattice parameters with ratio c_o/a_o =1.602 and sp^3hybridized. The polarity of ZnO is characterized by tetrahedral symmetry arises along axis of hexagonal symmetry. Piezoelectricity and continuous polarization are produced due to polar symmetry of ZnO along axis of hexagonal symmetry. Based on the first principle Hartree-Focklinear combination of atomic orbitals(LCAO) theory, the wurtzite structure is considered to be most stable phase among different phases of ZnO. The intrinsic n-type characteristics of ZnO is mainly due to the sensitivity of lattice constants of ZnO, existence of vacancies and interstitials &planar dislocations/ threading which are generally seen in ZnO materials inducing non-stoichiometric behavior useful for various applications[69].

Other Properties

ZnO QDs have modest stability in water making itis useful for cell labeling. At low pH, water molecules can target the surface states/defects of ZnO destructing the luminescence properties[71].ZnO QDs are useful for various biological applications due to high isoelectric point (IEP) of ~9.5 biomolecules of low IEP can be immobilization *via*coulomb's electrostatic attraction. The transparency in visible light having environmental and electrical stability makes it suitable candidate for bio-sensing applications. Prachi Joshi *et al*. have investigated the role of surface bound charge species on ZnO QDs for antibacterial activity[57]. Authors show that antibacterial activity of ZnO-Nt (nitrate) and ZnO-Ac (acetate) QDs are different relating to surface ionic charges which is significantly observed under radiation. The irradiation results photo-excitation of surface density producing high density of ROS resulting in the inhibition bacterial growth.

$O_2 + e^- \rightarrow O^{2-}$

$O^{2-} + H^+ \rightarrow \bullet HO_2$

$\bullet HO_2 + e^- + H^+ \rightarrow H_2O_2$

$OH^- + H^+ \rightarrow \bullet OH$

The O^{2-} formation results in high density of ROS leads to lipid peroxidation of cell walls and results the increased permeability of membrane and internalization of ZnO QDs.

Bioconjugation of Nanomaterials

ZnO quantum dots in nano-bioconjugations

The binding of nanostructured materials with biomolecules is known as nano-bioconjugation. Conjugation of biomolecules such as oligonucleotides, peptides, and proteins to the QDs without altering the structure &function of biomolecules is becoming important to various applications like bio-sensing, drug designing, test markers and other bioanalysis. Commonly used methods for conjugation of QDs with various biomolecules include covalent linkage, multivalent chelation, nonspecific adsorption, and mercapto (-SH) exchange[70,71].

Various biomolecules, like serum albumins, oligonucleotide andprotein get adsorbed easily on the surface of QDs dispersed in water[72,73] The binding is affected by temperature, pH, ionic strength, and surface charge on QDs and the biomolecule. The covalent interaction of functional groups of biomolecules with QDs forms stable nano-bioconjugate using cross-linker molecules, for example sulfhydryl coupling, formation of amide that is mediated by carbodiimide, formation of amine mediated by maleimide ester. These induced conjugation with $-NH_2$ and -COOH groups are advantageous as proteins contain carboxylic acid and amine groups which leads conjugation without any external linkage[74,75]. Figure 3 depicts the various steps (i)-(v) involved for nano-bioconjugation of QDs.

ZnO quantum dots showing various kind of interactions. Ionic interaction between negatively charged QDs surface and a protein having positive charge or between a positively charged QDs surface and an oligonucleotide having negative charge. Formation of amide bond between -COOH and $-NH_2$ groups by NHS/EDC linkers. Linkage between thiol (-SH) and amine ($-NH_2$) groups through cross-linker like Succinimidyl-4-(N-maleimidomethyl) cyclohexane-1-carboxylate (SMCC). Attachment of hydroxyl (-OH) and thiol (-SH) groups.Hydrophobic interaction of lipid or liposome and alkyl on QDs surface.

ZnO QDs-Protein Interaction

The higher surface to volume ratio of nanomaterial is several orders of magnitude higher than that of bulk counterpart having high free energy of surface making nanomaterials highly reactive[76]. Therefore, upon exposure to fluid system of protein; the proteins and other complex biomolecules start binding with the surface charge on nanomaterial resulting into capping. The surface adsorption of protein may result into unfolding and aggregation of protein subject to the shape size and chemical content of nanomaterials. Interaction of ZnO nanomaterials with various kinds of proteins have been studied by enormous groups

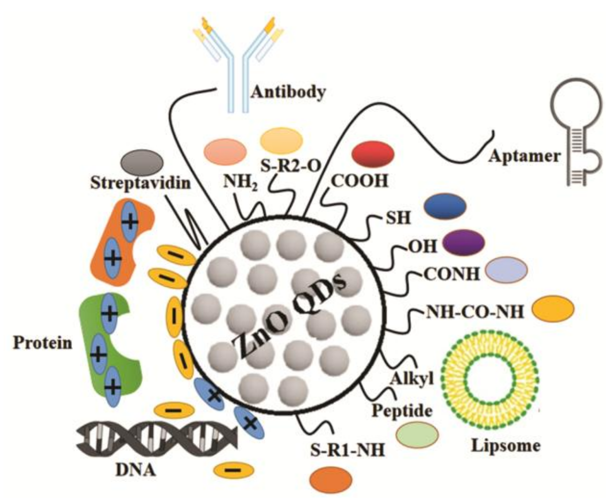

Fig. 3 — Schematic representation of various methods to prepare QDs-bioconjugates

worldwide. Bardhan *et al*. have discussed theground state complex formation between ZnO nanomaterials and Bovine Serum Albumin (BSA) showing static quenching of BSA[77]. Prachi Joshi *et al*. has discussed functionalized ZnO QDs with polyethyleneimine (PEI) conjugated BSA[78]. Mandal *et al*. have discussed the interaction between ZnO nanomaterial and bovine hemoglobin (BHb) results into the formation of ground state complex through static quenching effect[79,80].Bhogale *et al*. have conjugated ZnO nanomaterials (~7.5 nm) with BSA at different temperature and based on thermodynamic studies reported that binding sites (n) and binding constant (K) are inversely related to temperature[81]. Bhunia *et al*. have explained the corona formation and influence of on same while interacting with ZnO nanomaterial resulted in quenching of fluorescence and unfolding of protein[82,83]. Wahab *et al*. have adopted CD (circular dichroism) and fluorescence quenching approach to study the interaction of ZnO QDs with BSA & BHb and they observed that, quenching occurs in the fluorescence intensity of BSA as the concentration of ZnO QDs increases and reported about 91% decrease in fluorescence intensity at 2 μM concentration of ZnO QDs with blue shift of 3 nm[84].

Surface Modification of ZnO QDs

Enormous reports have been published regarding monodispersed, stable and fluorescent ZnO QDs in several organic media. ZnO QDs being highly active sometimes undergo agglomeration which leads to poor dispersion and loses all their fluorescence. Several methods and techniques are therefore, established to overcome the challenges such as modification of surface of ZnO nanomaterials making use of water soluble/organic ligands, silanes or by capping of ZnO nanomaterials with polymer. Prachi Joshi *et al*. have gone through synthesis of highly fluorescent polyethyleneimine (PEI) capped ZnO QDs having high stability and dispersibility using trisodium citrate as a linker between ZnO and PEI. The fluorescence spectra showed defect related emission around 555 nm in water as dispersion medium and no agglomeration of ZnO showing long range degradation in luminescence. It was evident that surface modification may produce excellent binding affinity for several biomolecules like nucleic acid, monosaccharide and protein etc., which can make the ZnO QDs as an excellent candidate as fluorescence contrast agent for bioimaging, bioconjugation and other applications[85,86].

Fluorescent ZnO QDs for Diabetes

Recently, diabetesis a major issue causing death & disability of human being across the globe, involving blindness, kidney failure, heart disease etc. and ~200 million people are afflicted with diabetesand is expected to rise up to 300 million or more by 2030.Therefore, it is important to make an instrument for monitoring of glucose content in the bodyto prevent further spreading of disease and protect the existing patients from sever hazards. Device based on electrochemistry has a set of problems leading the scientiststo develop an alternative approach for sensing glucose and one of the possibilitiesis optical measurement using fluorescence from UV to near IR region. Some of the examples are concanavalin A (Lectin) receptors and various enzymes like GO_x, glucokinase/hexokinase and glucose dehydrogenase have been used to detect glucose in fluorescence-based biosensors. Fluorescence resonance energy transfer (FRET) that deals with energy transfer between coupled donor & acceptor fluorophores are one of the powerful tools which can be utilized for glucose detection. FRET is highly sensitive to change in size, conformation and dielectric properties of the donor and acceptor, therefore, inter and intra molecular interactions or changes can be monitored. Some metal oxide fluorescent QDs like ZnO has high IEP, good biocompatibility, and simple fabrication procedure of nanomaterial, high surface to volume ratio can be used to detect glucose followed by immobilization of GO_x using FRET as biosensor probe to monitor blood glucose level at nano level[87,88].

Fluorescent ZnO QDs for cancer diagnosis and therapy

Fluorescent QDs and nanoparticles are widely used in biomedical and biochemical studies, immunoassays and contrasting agents for various diagnosis applications. Photodynamic therapy is promising and emerging method for non-invasive treatment of cancer[89]. Photosensitizers once up taken by cancer cells, illuminated with light of suitable wavelength can generate ROS which may induce necrosis or cell death.

Amongst all, ZnO QDs being highly luminescent semiconductor nanomaterials have biological significance for cancer cell detection. A novel ZnO nanomaterial having red fluorescence and its conjugation with radioactive Cu^{64}having half-life of 12.7 h & TRC105; a monoclonal chimeric antibody against CD105 were successfully applicable for fluorescence imaging like positron emission tomography (PET) imaging of the tumor vasculature. ZnO nanomaterial are emerging as an important ingredient for cancer therapy in near future[90–92].

Fluorescent ZnO QDs for drug delivery

Photoluminescent semiconductor QDs are promising candidates in fields of biological and nanomedicine because of distinct photochemical properties such as sharper spectra and photostability.ZnO QDs are being biocompatible and economically viable has potential to perform better for application as drug delivery systems.ZnO QDs are known to have an ability of rapid dissolution to Zn^{2+} at pH lower than 5.5 therefore, has been accepted as multifunctional smart drug delivery nano-carriers. ZnO-chitosan-folate are studied as carrier for delivery of doxorubicin; an anti-neoplastic material used in tumor treatment via chemical interactions. Water dispersible ZnO QDs have been investigated as a platform for pH based targeted intracellular DOX delivery and drug release carriers[93].

Fluorescent ZnO QDs for Bioimaging

Fluorescent QDs are useful for increasing contrast and improving the sensitivity in real time imaging and their use can improve the spatial resolution during imaging and enable to translate 2D information into3D surgical field. Therefore, fluorescent QDs *e.g*. Gd ion in ZnO QDs are usedin magnetic resonance imaging as nanoprobes. These nanoprobes due to sharp emission provide better reliability in clinical diagnosis through modern medical criteria[94,95].

Fluorescent ZnO QDs for Other Biomedical Applications

Fluorescent QDs in general and ZnO QDs in particular are used for different biomedical applications such as fluorescence labeling, image contrasting agent, immunoassays, fluorescence imaging and other diagnosis and treatment purposes. Being pH sensitive, ZnO QDs are promising candidates for drug carriers, delivery and sustainable drug delivery systems. ZnO QDs have been used as labeling probes due to its high aspect ratio, electronic and optical signal amplification and specific coding property[96,97].

Conclusion

ZnO quantum dots has been emerged as a novel nanomaterial and has been used as diverse range of applications for so many decades. From defence to diagnosis, from textiles to cosmetics. It has been used for various applications in biomedical fields as nano-bioconjugates as well. It is a promising candidate for drug carriers, delivery and sustainable drug delivery systems. Fluorescent ZnO QDs in particular are used for different biomedical applications such as fluorescence labelling, image contrasting agent, nano probing, bioimaging, immunoassays, fluorescence imaging and other diagnosis and treatment purposes. In this review article we are trying to provide substantial approach on the theory, synthesis process, various applications of ZnO quantum dots. ZnO quantum dots has enormous excellent properties and shown lots of advantages over other nanomaterials. Though the use of ZnO quantum dots is vast and has sown huge progress, but still so many challenges are there like maintain its fluorescence in aqueous system, commercialization of ZnO quantum dots at large scale, so that it can fulfil the need of society at economically cheaper rate. We adventurously imagine that in coming future there will be advance use of engineered ZnO quantum dots that can be utilized in several applications in efficient way.

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Conflicts of interest

All authors declare no conflict of interest.

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