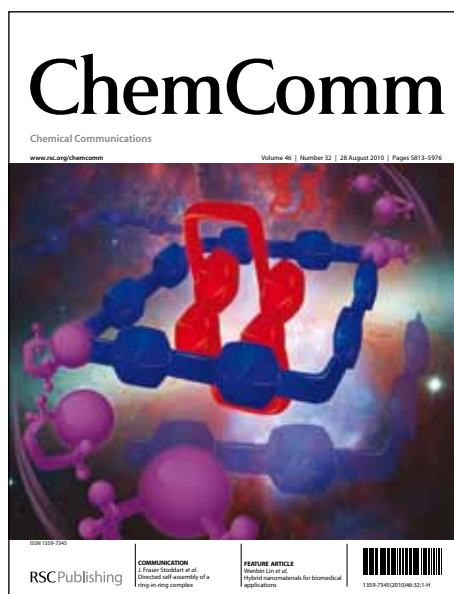


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ARTICLE TYPE

## Brilliant sandwich type fluorescent nanostructure incorporating compact quantum dots layer and versatile silica substrates

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A "hydrophobic layer in silica" structure was designed to integrate compact quantum dots (QDs) layer with high quantum yield into scalable silica hosts containing desired functionality, which was based on metal affinity driven assembly of hydrophobic QDs with versatile silica substrates and homogeneous encapsulation of organosilica/silica layers.

Assembling hydrophobic nano-building blocks directly with solid or colloidal substrates in organic phase<sup>1-2</sup> brings new opportunity to achieve high particle packing density, exceeding the limitation of aqueous-based layer-by-layer self assembly where electrostatic repulsion among same charged particles exists.<sup>3-4</sup> For the issue of semiconductor nanocrystals, namely quantum dots (QDs), skipping the conventional hydrophilic ligands exchange<sup>5</sup> before assembling particularly favors their surface passivation to maintain bright and sharp emission. These characters make such assembling technic attractive for fabricating high performance QDs based fluorescent structure which have broad applications in multiplex analysis by color encoding,<sup>6</sup> simultaneously visualizing intracellular targets<sup>7</sup> and ultrasensitive fluorescent imaging.<sup>8</sup>

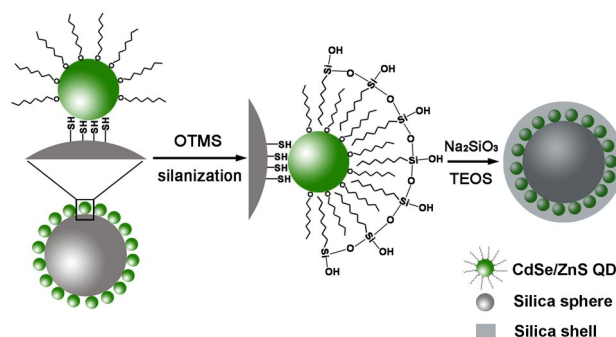
The primary concern of such hydrophobic QD assemblies toward potential high fluorescence, multi-functionality and biocompatibility for end use comes the structural engineering. Unfortunately, the fluorescent sensitivity of QDs towards native organic ligands passivation makes their processing a challenging issue, considering an irreversible quantum yield (QY) loss, in either assembling process requiring pre-modification of QD surface<sup>9-11</sup> or post-grafting of immobilized QD layer with hydrophilic coatings.<sup>8</sup> Despite using multi-inorganic shell passivation could render QDs less sensitive to surface damages,<sup>8,12-13</sup> yet the synthetic protocol is rather complicated compared with that of generally available QDs (CdSe/ZnS in most cases). In that sense, exploring an "minimally invasive" incorporation of intact QD layer into processible substrates would favor the fluorescent nanostructure design.

Silica is one superior candidate as both supporting substrate and hydrophilic coating layer regarding its convenient processability, high stability in aqueous media and good biocompatibility.<sup>14-15</sup> The strong coordination of thiolated silica with metal contained nanoparticles<sup>2b</sup> may serve efficiently in achieving high QY and simplified protocol, since no pre-modification for hydrophobic QDs is required. On the other hand, the combination of hydrophobic bilayer with silica shell<sup>16</sup> would

largely preserve both the QY and QDs loading amount towards bright and stable water dispersible QD structures. Although the surfactant encapsulation has been adopted to mediate phase transfer of hydrophobic particle assemblies,<sup>2b</sup> however, this may promote mesoporous subsequent silica shell<sup>17</sup> instead of homogeneous coating due to the aggregation of silica together with surfactant micelles.<sup>18</sup>

Herein, a QD based fluorescent nanostructure simultaneously possesses high QY and homogeneous silica coating was prepared, using silica anchoring surface and alkyl-chain derived organosilica shell to sandwich a compact layer of hydrophobic QDs. As shown in Scheme 1, the QDs were efficiently immobilized by SiO<sub>2</sub> substrates via thiol-metal coordination to achieve a high loading. The hydrophobic assemblies underwent an ultrasonic assisted silanization by n-octyl trimethoxy silane (OTMS) to derive an amphiphilic organosilica layer, which was critical to achieve high QY and homogeneous silica coating from silicate deposition and desired Stöber growth. Current assembling and coating strategy was further extended to fabricate variable sized and bi-functional fluorescent nanostructures.

Colloidal silica substrates were first grafted with mercaptopropyl groups for anchoring with QD surface metals. The thiolated spheres exhibited good monodispersity (Fig S1A) and enhanced hydrophobicity to disperse in nonpolar solvents, which favored their proper interaction with CdSe/ZnS QDs (Fig S1B). The high efficient thiol-metal coordination driven assembly produced approximately surface saturated silica spheres by QDs (Fig 1A) which rendered them totally dispersible in organic phase. To confirm the driving force of QDs assembling with thiolated



Scheme 1 Preparation procedure of sandwich type SiO<sub>2</sub>@QDs@SiO<sub>2</sub> fluorescent nanostructure