Inorganic-Ligand Quantum Dots Meet Inorganic-Ligand Semiconductor Nanoplatelets: A Promising Fusion to Construct All-Inorganic Assembly

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ABSTRACT: By the reaction of inorganic-ligand CdS/Cd^{2+} quantum dots (QDs) with inorganic-ligand $CdSe/CdS/S^{2-}$ nanoplatelets (NPLs), semiconductor CdS QDs were fused with CdSe/CdS NPLs to yield all-inorganic assemblies, accompanied by great photoluminescence-enhancement. These all-inorganic assemblies facilitate charge transport between each other and open up interesting prospects with electronic and optoelectronic nanodevices.

olloidal semiconductor nanocrystals (NCs) exhibit unique size and shape dependent optical and electronic properties¹⁻⁸ and are of great interest in optoelectronics⁹ and biological applications.¹⁰⁻¹² High molecular weight polymer ligands, particularly, dendritic polymers,¹³ block polymers,¹⁴ and proteins,¹⁵ and organic capping ligands such as short-chain thiols¹⁶ are often used for the aqueous synthesis of semiconductor NCs. Long-chain hydrocarbon organic capping ligands^{17,18} and trioctylphosphine oxide/trioctylphosphine (TOPO/TOP) ligands¹⁹ are usually applied to nonaqueous synthesis of semiconductor NCs. These semiconductor NCs always have inorganic/organic hybrid structures. A big challenge is that the organic capping ligands are usually insulated; this makes nanodevices or nanostructured materials made from such NCs behave like insulators. Posttreatment after the synthesis of NCs to remove the insulating ligands is a prerequisite for electrical and optoelectronic applications. Talapin et al.²⁰ established molecular metal chalcogenide (MCC) ligands²⁰ such as $CdTe_2^{2-}$ and simple metal-free inorganic ions²¹⁻²³ such as S^{2-} , Se^{2-} , OH^- , NH_2^- to modify the surface of NCs. The replacement of traditional long hydrocarbon ligands by small inorganic ligands facilitated the charge transport between individual NCs and opened up interesting opportunities for device integration of nanostructures. Nag et al.²⁴ proposed a simple and general method for in situ preparation of inorganic-ligand luminescent metal sulfide NCs. These inorganic-ligand NCs were able to be directly used in electrical and optoelectronics devices.

In this paper, we would like to construct integrated allinorganic assembly based on inorganic-ligand two-dimensional nanoplatelets (NPLs) and quasi-zero-dimensional quantum dots (QDs). Different from traditional assembly or selforganization of NCs containing both organic molecules and NCs, all inorganic assembly based on inorganic-ligand NPLs and QDs was established here.

The oleylamine (OLA) and oleic acid (OA) capping ligands of core/shell CdSe/CdS NPLs were replaced by S^{2-} to get

negative charge on the surface. Similarly, small S^{2-} was used instead of traditional ligands with long hydrocarbon tails on CdS QDs and then Cd²⁺ was introduced to get a positive ζ potential for CdS QDs. As illustrated in Scheme 1, with the

Scheme 1. Illustration for Fusion of CdSe/CdS NPLs and CdS QDs $% \left(\mathcal{A}_{\mathrm{S}}^{\mathrm{C}}\right) =\left(\mathcal{A}_{\mathrm{S}}^{\mathrm{C}}\right) \left(\mathcal{A}_{\mathrm$



reaction of the S²⁻ capped CdSe/CdS NPLs with CdS QDs capped with Cd²⁺, the fusion of CdSe/CdS NPLs and CdS QDs could be realized, due to the reactions of S²⁻ and Cd²⁺, resulting a new kind of all-inorganic assembly without ligands. After fusion, the photoluminescence of this all-inorganic assembly was also greatly enhanced compared to that of CdSe/CdS/S²⁻ NPLs due to the elimination of S²⁻ photoluminescence quencher. Most importantly, there were only S and Cd atoms at the fusion locus and no organic ligands were on the assembly surface, facilitating their electronic and

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Figure 1. (a) Phase transfer of CdS QDs from hexane to N-methylformamide (NMF) upon exchange of the original organic surface ligands with S^{2-} . (b) UV–vis spectra of CdS QDs capped with organic ligands in hexane, CdS/S²⁻ QDs in NMF, and CdS/Cd²⁺ QDs in NMF, respectively. (c) FT-IR spectra of CdS QDs capped with organic ligands and S^{2-} , respectively. (d) ζ -potential of CdS/S²⁻ QDs and CdS/Cd²⁺ QDs in NMF.



Figure 2. (A) UV–vis spectra of CdSe/CdS NPLs in hexane, CdSe/CdS/S^{2–} NPLs in NMF, CdS QD/CdSe/CdS NPLs in NMF, and CdS QD/CdSe/CdS NPLs in hexane, respectively. (B) Photoluminescence (PL) spectra of CdSe/CdS NPLs in hexane, CdSe/CdS/S^{2–} NPLs in NMF, CdS QD/CdSe/CdS NPLs in NMF, and CdS QD/CdSe/CdS NPLs in hexane. The inset pictures a and b, made under a UV lamp, correspond to CdS QD/CdSe/CdS NPLs in NMF and CdS QD/CdSe/CdS NPLs in hexane, respectively.

optoelectronic applications compared to organic moleculecontaining nanostructures.

The CdS QDs and CdSe/CdS NPLs used in this work were prepared following protocols^{25–30} using long hydrocarbon chains as stabilizers. For a typical ligand change procedure, the CdS QDs capped with organic ligands in hexane were combined with a *N*-methylformamide (NMF) solution of Na₂S or $(NH_4)_2S$. The immiscible two phase mixture was gently stirred for several minutes under an Ar atomosphere, and then CdS QDs could be completely transferred to NMF phase in the form of CdS/S^{2–} QDs, which can be evidenced by yellow color of QDs shown in Figure 1a. Figure 1b compares the absorption spectra of CdS QDs capped with organic ligands, S^{2–} and Cd²⁺, respectively. The excitonic features in the absorption spectra of CdS QDs changed little from 445 to 447 nm after introducing S^{2–}, implying the effect of surface environment change on CdS QDs. Long alkyl chain ligands were replaced by small S^{2–}, resulting in a fundamental distance decrease between each quantum dot (QD). For the CdS/Cd²⁺ QDs, they could be synthesized easily by deposition of Cd²⁺ on CdS/S^{2–} QDs. The absorption peak of CdS QDs shifted to 457 nm, implying that a new layer of CdS was formed on CdS QDs by the reaction of S^{2–} and excess Cd²⁺.

Figure 1c exhibits FT-IR spectra of CdS QDs before and after the exchange of organic ligands with S^{2-} . After phase transfer, the bands at 2855 and 2927 cm⁻¹ corresponding to

C–H stretching in the original organic ligands completely disappeared, and new bands at 2887 and 2947 cm⁻¹ corresponding to C–H stretching in NMF solvent appeared. These results confirm that long hydrocarbon organic ligands can be completely replaced by S^{2-} and thus all-inorganic CdS QDs can be obtained.

Figure 1d shows the ζ -potential of purified CdS/S²⁻ QDs is -35.7 mV, implying a negative charge on the surface of CdS QDs. The purified S²⁻ capped CdS QDs were further reacted with Cd(AC)₂ in NMF to get CdS/Cd²⁺ QDs in NMF. Their ζ -potential which displays in Figure 1d is +13.2 mV, indicating that a positive charge on CdS QDs could be realized by introducing Cd(AC)₂. TEM images of CdS QDs with average size of 3.3 nm in different stages are shown in Figure S1.

Layer-by-layer atomic deposition assembly is a common method for preparing core/shell CdSe/CdS NPLs. By the reaction of Cd²⁺ with CdSe/S²⁻ NPLs, one monolaver of CdS shells can be formed. After the deposition of several layers of CdS, core/shell CdSe/CdS NPLs with red emission were formed and then they were transferred into the hexane phase by the addition of OA and OLA organic ligands. By the exchange of organic ligands with S^{2-} , NMF solutions of CdSe/ CdS/S^{2-} NPLs were obtained. Figure 2 compares the absorption and photoluminescence spectra of CdSe/CdS NPLs capped with organic ligands in hexane and CdSe/ CdS/S²⁻ NPLs in NMF. Both the absorption and emission peaks had slight increases after S^{2-} capping. As the initial CdSe/CdS NPLs had a Cd-rich surface, the initial surface Cd ions on the CdSe/CdS NPLs could react with S²⁻ to get a thin CdS layer, resulting in a minor increase of absorption peak and an enhancement of photoluminescence. After aging for several days, the quantum yield (QY) of CdSe/CdS/S²⁻ NPLs could reach 2.8%, which is a great enhancement compared with that of CdSe/CdS NPLs (QY: 0.6%). When the inorganic-ligand CdSe/CdS/S²⁻ NPLs met with inorganic-ligand CdS/Cd²⁺ QDs, a fusion occurred between them, resulting in QDs-inlaid NPLs called as CdS QD/CdSe/CdS NPLs, which are illustrated in Scheme 1.

The fusion between inorganic-ligand CdSe/CdS/S²⁻ NPLs and CdS/Cd²⁺ QDs can be proved by the absorption and emission spectra. As shown in Figure 2A, the absorption peak of CdSe/CdS/S²⁻ NPLs shifts from 620 to 635 nm after the mixing with CdS/Cd²⁺ QDs. CdS QD/CdSe/CdS NPLs could be formed due to the reactions between Cd^{2+} on the CdS/ Cd²⁺ QDs and S²⁻ on the CdSe/CdS/S²⁻ NPLs. The corresponding photoluminescence peak shifts from 631 to 643 nm shown in Figure 2B also imply the interactions between CdS/Cd²⁺ QDs and CdSe/CdS/S²⁻ NPLs. For the QY, the QY of CdS QD/CdSe/CdS NPLs was 17.8%, which was greater than that of CdSe/CdS/S²⁻ NPLs due to the diminishment of S²⁻ PL quenchers by the reaction of S²⁻ and Cd²⁺. CdS QD/CdSe/CdS NPLs in NMF phase could be extracted to hexane phase in the presence of OLA and OA. After purification, the QY of CdS QD/CdSe/CdS NPLs in hexane was 15.1%.

TEM images in Figure 3a show the fusion between CdSe/ CdS/S²⁻ NPLs and inorganic-ligand CdS/Cd²⁺ QDs in NMF after mixing for 6 h. Small black dots on the NPLs with a size about 3.3 nm can be assigned to CdS/Cd²⁺ QDs which have no remarkable size change before and after fusion with CdSe/ CdS/S²⁻ NPLs. In order to further confirm that CdS/Cd²⁺ QDs were inlaid on the CdSe/CdS/S²⁻ NPLs, they were transferred from the NMF phase to the hexane phase and



Figure 3. TEM images of CdS QD/CdSe/CdS NPLs in NMF (a) and in hexane (b). The scale bars are 50 and 20 nm for images a and b, respectively.

purified by size-selective precipitation to remove free CdS/ Cd²⁺ QDs. From Figure 3b, CdS/Cd²⁺ QDs could still be seen on the CdSe/CdS/S²⁻ NPLs, which further proves the fusion of CdS/Cd²⁺ QDs and CdSe/CdS/S²⁻ NPLs. The lateral dimensions of CdS QD/CdSe/CdS NPLs are 42 nm × 12 nm, and the thickness is 3.2 nm. It is worth mentioning that fusion between CdS/Cd²⁺ QDs and CdSe/S²⁻ NPLs can also be realized. The corresponding UV–vis spectra, PL spectra and TEM images can be seen in Figures S4 and S5 in the Supporting Information, respectively.

In summary, the fusion of semiconductor CdS QDs and CdSe/CdS NPLs was realized by the reaction of inorganic-ligand CdS/Cd²⁺ QDs with inorganic-ligand CdSe/CdS/S²⁻ NPLs. Different from the organic molecule linker method for connecting two types of nanomaterials, CdS QDs were fused with CdSe/CdS NPLs by the reactions of Cd²⁺ (from CdS/Cd²⁺ QDs) and S²⁻ (from CdSe/CdS/S²⁻ NPLs), thus no insulating ligands exist. Furthermore, this promising fusion also resulted in great photoluminescence-enhancement of NPLs. These all-inorganic assemblies open up interesting opportunities for integrated nanodevices which can be directly used for electronic and optoelectronic applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c00880.

FT-IR details, TEM images of CdS QDs in different stages and CdS QD/CdSe NPLs in NMF, XPS spectra, HR-TEM images and XRD spectra of CdS QD/CdSe/CdS NPLs, UV-vis and PL spectra of CdSe NPLs, CdSe/S²⁻ NPLs in NMF and CdS QD/CdSe NPLs in NMF, and experimental procedures (PDF)

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Notes

The authors declare no competing financial interest.

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