Molybdenum and Tungsten Sulfide Ligands for Versatile Functionalization of All-Inorganic Nanocrystals

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Supporting Information

ABSTRACT: We report a strategy toward the synthesis of colloidal nanocrystals capped with inorganic molybdenum and tungsten sulfide ligands. MoS$_2^{2−}$ and WS$_2^{2−}$ thiometalates were utilized to replace organic ligands capping a wide range of nanocrystals such as metals, semiconductors, and well-conserved primary properties of nanocrystals in polar media. Especially, MoS$_2^{2−}$ and WS$_2^{2−}$-capped CdSe nanocrystals showed the dramatic enhancement of photoluminescence properties by the photo-oxidation treatment, which originated from the preferential formation of MoS$_x$O$_y$ layers on the CdSe surface. The highest quantum yield reached up to 51%. Furthermore, we studied the charge-transport properties of MoS$_4^{2−}$-capped PbS nanocrystals by the fabrication of a field-effect transistor and photodetectors. Finally, MoS$_2^{2−}$ and WS$_2^{2−}$-capped nanocrystals were used for the production of two-dimensional MoS$_2$ and WS$_2$ thin layers on nanostructures by heat treatment. Such versatility of these thiometalate ligands offers an additional degree of control over the functionality of nanocrystals for optoelectronic and catalytic applications.

Over the last 2 decades, impressive progress has been made in the synthesis of various colloidal nanocrystals (NCs) such as semiconductors, metals, oxides, and other functional materials.¹⁻⁴ These nanomaterials have extensively been utilized in various technological areas due to their size- and shape-dependent optical, electronic, and magnetic properties.⁵⁻⁷ Most of the synthetic routes to these NCs are based on the use of long-chain organic ligands, which play a key role in the formation of NCs and stabilization of the NC surface against agglomeration.¹⁻⁴,⁸ Furthermore, these ligands effectively passivate the surface trap states of the semiconductor NCs, securing their superior luminescence properties.⁹⁻¹¹ However, long-chain bulky hydrocarbons of organic ligands act as an electrically insulating barrier for charge transport, blocking the access of other species, thereby limiting their device or catalytic applications. Recently, a variety of inorganic ligands have been reported for NC capping, which remarkably improves the charge-transport properties of NC solids via strong electronic coupling arising from contraction of the interparticle distance.⁷,¹²⁻¹⁵ Although these ligands provide excellent all-inorganic NC building blocks for electronic applications, they usually generate multiple trap sites on the NC surfaces that are undesirable because of the deleterious effects on the luminescence properties of semiconductor NCs.¹³,¹⁶

Most of the recently developed inorganic ligands are based on post-transition metal chalcogenides anions such as In$_2$Se$_6^{2−}$, Sn$_2$Se$_6^{2−}$, and Sb$_2$Te$_6^{2−}$ with hydrazinium, ammonium, and alkali metal cations.¹²,¹⁷ Development of transition-metal-based anionic ligands can offer an additional degree of control over the functionality of NC surfaces, improving the basic understanding of the NC surface chemistry.¹⁸⁻²⁰ Recently, molybdenum and tungsten sulfide have been recognized as next-generation two-dimensional (2D) materials analogous to graphene.²¹ These nanoscale materials have intensively been studied owing to their unique electronic, optical, and chemical properties in a broad range of disciplines.²¹⁻²⁴ More recently, Kovalenko et al. suggested the possibility of MoS$_2^{2−}$ as inorganic ligands capping NCs.¹⁷ However, the optical, electronic, and structural properties of NCs capped with these compounds have not been studied systematically. In this work, we report transition-metal sulfide ligands such as molybdenum sulfide (MoS$_2^{2−}$) and tungsten sulfide (WS$_2^{2−}$) in anionic forms for capping of colloidal NCs. The generality of MoS$_2^{2−}$ and WS$_2^{2−}$ ligands was demonstrated for a wide range of colloidal NCs including CdSe, PbS, Au, Bi, and CdS (Figure 1). In particular, we showed that the photoluminescence (PL) properties of the semiconductors, MoS$_2^{2−}$ and WS$_2^{2−}$-capped CdSe NCs, was dramatically enhanced by photo-oxidation treatment. We found that this treatment led to the preferential formation of stable MoS$_x$O$_y$ layers on the CdSe core, which enhanced the quantum yield (QY) up to 51% without a notable peak shift. Finally, we showed that the MoS$_2^{2−}$ and WS$_2^{2−}$ ligands were decomposed and formed short 2D MoS$_2$ and WS$_2$. © 2016 American Chemical Society
layers on nanostructures upon heat treatment. These versatile thiometalate ligands can provide a great potential for various applications in optoelectronics, catalysts, and biomedical imaging.25,26

Ammonium tetrathiomolybdate ((NH4)2MoS4) and ammonium tetrathiotungstate ((NH4)2WS4) were used as chemical sources of MoS4<sup>2-</sup> and WS4<sup>2-</sup> ligands, respectively. These compounds are widely used as sources of MoS<sub>2</sub> and WS<sub>2</sub> for the fabrication of solution-processed thin films due to their excellent solubility in polar solvents and the simplified transformation into crystalline 2D phases by thermal decomposition.27 Solutions of these compounds in commonly used polar solvents of N-methylformamide (NMF), formamide, dimethyl sulfoxide (DMSO), dimethylformamide (DMF), and H2O produce the anions MoS4<sup>2-</sup> and WS4<sup>2-</sup>, displaying red and yellow colors, respectively. The MoS4<sup>2-</sup> and WS4<sup>2-</sup> anions exhibited optical absorption characteristics throughout the visible range with peaks at 468 and 393 nm, respectively (see Supporting Information, Figure S1). The NCs studied here for capping with MoS4<sup>2-</sup> and WS4<sup>2-</sup> were synthesized by previously reported procedures on organic ligands with long hydrocarbon chains such as trioctylphosphine oxide (TOPO), octadecylphosphonic acid (ODPA), oleylamine (OAm), oleic acid (OA), and dodecanethiol (DDT) (Figure 1a).28−32 The ligand exchange process was carried out as a typical two-phase reaction in a mixture of nonpolar organic and immiscible polar solvents (Figure 1b).

Transmission electron microscopy (TEM) images of the all-inorganic MoS4<sup>2-</sup>- and WS4<sup>2-</sup>-capped CdSe NCs show that ligand exchange did not lead to a change in size and shape of the NCs, when compared with the as-synthesized organic-capped CdSe NCs (Figure 1c−e). In addition to CdSe NCs, these ligands were applied to various spherical NCs, such as PbS, Au, Bi, and CdS (Figure 1f−i), and TEM analyses confirmed that the primary sizes and shapes were well maintained. Furthermore, identical X-ray diffraction (XRD)
patterns for CdSe, PbS, and Bi NCs (Figure S2) were observed before and after the ligand exchange process, and no peaks related to impurities were detected. We also conducted the ligand exchange process for ultrathin CdS nanoplates (NPs) with a thickness of 1.2 nm. The TEM image of the MoS$_4^{2-}$-capped CdS NPs (Figure 1j) shows an unchanged morphology of the NPs, revealing their ultrathin characteristics. These results demonstrate the versatility of these new types of anionic MoS$_4^{2-}$ and WS$_4^{2-}$ ligands in the realization of different kinds of NCs and diversity in shapes.

The degree of the ligand exchange was studied with Fourier transform infrared (FT-IR) absorption spectroscopy. The strong absorption arising from the C–H stretching modes (2700–3000 cm$^{-1}$) in the organics-capped CdSe NCs disappeared after ligand exchange, which indicates the complete replacement of the organic ligands with anionic MoS$_4^{2-}$ and WS$_4^{2-}$ ligands. The broad bands between 3000 and 3700 cm$^{-1}$ in the FT-IR spectra of MoS$_4^{2-}$- and WS$_4^{2-}$-capped CdSe NCs were attributed to the vibrational modes of the NH$_4^+$ balance cations (Figure S3a). In addition, similar changes in the FT-IR absorption spectra were observed for Au, PbS, and Bi NCs capped with the ligands DDT, OAm, and OA after ligand exchange (Figure S3b).

Similar to other anionic ligands, the $\zeta$-potentials of MoS$_4^{2-}$- and WS$_4^{2-}$-capped CdSe NCs were found to be negative, with values of $-15.2$ and $-13.9$ mV, respectively, due to the formation of an electrical double layer around the NCs. These NCs can sufficiently stabilize in NMF via electrostatic interactions (Figure S4). NMF has an exceptionally high dielectric constant ($\epsilon \approx 182$); therefore, it is widely used as a

Figure 2. Absorption spectra of the (a) CdSe NCs and (b) CdS NPs capped with organic, MoS$_4^{2-}$, and WS$_4^{2-}$ ligands. (c) PL spectra of the organics-capped CdSe NCs and inorganic MoS$_4^{2-}$- and WS$_4^{2-}$-capped CdSe NCs after exposure to air and light for several days. (d) Fluorescence lifetime measurements of the CdSe NCs capped with organic, MoS$_4^{2-}$, and WS$_4^{2-}$ ligands. (e) Absorption and (f) PL spectra of MoS$_4^{2-}$-capped CdSe NCs under different air-flow bubbling reaction times (in the PL spectra, the dotted line is measured after exposure to UV irradiation and air in the absence of bubbling). The inset of (e) shows the scheme of the photo-oxidation treatment. In (f), the insets on the left and right sides show photographs of organics- and MoS$_4^{2-}$-capped CdSe NC solutions under UV irradiation and the fwhm of PL spectra of MoS$_4^{2-}$-capped CdSe NCs under air bubbling with different flowing times, respectively.
solvent for low charged ionic ligand-capped NCs. We further checked the colloidal stability of the NCs in the less polar solvents of FA (ε ≈ 106), DMF (ε ≈ 36), and DMSO (ε ≈ 47), and we found that MoS$_4^{2-}$- and WS$_4^{2-}$-capped NCs were able to maintain their colloidal stability for more than 1 month.

Optical properties of MoS$_4^{2-}$- and WS$_4^{2-}$-capped NCs were characterized by absorption and PL spectroscopy. The absorption spectra of the organics-capped CdSe NCs (Figure 2a) show a well-defined 1S$_{1/2}$(h)−1S(e) transition and other high-energy transitions. After ligand exchange with MoS$_4^{2-}$ and WS$_4^{2-}$ anions, their excitonic characteristics were well conserved, demonstrating no changes in their sizes and shapes, which is in agreement with the TEM and XRD results (Figures 1c−e and S2a). The increased absorption of the peak at 462 nm in MoS$_4^{2-}$-capped CdSe NCs can be attributed to the electronic coupling between the exciton states of CdSe NCs and MoS$_4^{2-}$ anions because MoS$_4^{2-}$ anions have a strong optical band at 468 nm, arising from 1t$_1$−2e* transition of a $T_d$ symmetry compound.33 Similarly, we observed increased absorption of peaks in CdS NPs capped with WS$_4^{2-}$ ligands at 380 nm and CdS NCs capped with MoS$_4^{2-}$ ligands at 465 nm (Figures 2b and S5a), which matches exactly with the optical transition of the WS$_4^{2-}$ and MoS$_4^{2-}$ anions (Figure S1), suggesting electronic coupling between the NCs and ligands. The PL of the MoS$_4^{2-}$- and WS$_4^{2-}$-capped CdSe NCs was quenched almost immediately after ligand exchange (Figure S6), consistent with previous reports on the characterization of all-inorganic NCs, due to the formation of multiple trap sites on their surfaces.12,16,18,19 To characterize the surface coverage of the ligands MoS$_4^{2-}$ and WS$_4^{2-}$ on NCs, elemental analyses of the CdSe NCs were conducted by inductively coupled plasma optical emission spectroscopy (ICP-OES). The atomic ratio of Cd/Mo in the 2.5 nm sized MoS$_4^{2-}$-capped CdSe NCs was about 8.39, revealing that around 18 MoS$_4^{2-}$ ions were bound to each CdSe NC. Thus, the estimated MoS$_4^{2-}$ surface coverage was about 12%, implying that 0.9 MoS$_4^{2-}$ ions occupied a unit area (nm$^2$) of the surface on average. This low surface coverage of ligands can be responsible for the quenched PL.16 The surface coverage of WS$_4^{2-}$ was found to be similar to that of the MoS$_4^{2-}$ ligands. In addition, we characterized the optical properties of Au NCs and did not observe a peak shift in the surface plasmon resonance (SPR) band transitions of the absorption spectra for either the organics- or MoS$_4^{2-}$-capped NCs (Figure S5b).

Inorganic capping ligands usually generate trap sites for nonradiative recombination of electrons and holes on the surfaces of semiconductor NCs due to their lower surface passivation than that of the organic ligands.12,16,18−20 In the current study, we found that the all-inorganic MoS$_4^{2-}$- and WS$_4^{2-}$-capped CdSe NCs exhibited strong PL properties after exposure to air and light for several days. The absorption spectra of these NCs (Figure S7) show a little broader excitonic transition, and their peak positions are shifted to 5−7 nm lower wavelengths, compared to that of organics-capped CdSe NCs, which indicates the reduction of the average size of NCs and broadening of the size distribution. The PL spectra of these NCs (Figure 2c) are a little broadened, and the peak positions are shifted by less than ~5 nm. Time-resolved photo-luminescence (TRPL) measurement of CdSe NCs (Figure 2d) reveals that the decay time of luminescence slightly decreases from 18 to 13−14 ns before and after ligand exchange,49 suggesting that the CdSe NCs underwent surface changes such as oxidation during exposure to air and light.
effective size and related blue shifts of the PL spectrum, the
tained peak position in the PL spectrum of MoS\textsubscript{4}\textsuperscript{2−} - and
WS\textsubscript{4}\textsuperscript{2−}-capped CdSe NCs during treatment suggests that these
ligands seemed to prevent the substantial oxidation of the CdSe
core.

To understand the oxidation behaviors of these NCs, X-ray
photoelectron spectroscopy (XPS) analysis was conducted on
MoS\textsubscript{4}\textsuperscript{2−}-capped CdSe NCs before and after the photo-oxidation
treatment (Figure 3). The XPS spectra of the NCs before the
oxidation show peaks of CdSe in the Se 3d region (Figure 3a)
and Cd 3d peaks (Figure S9a) in the Cd 3d region. Furthermore, Mo 3d peaks and the S 2s peak were clearly
detected in the XPS spectra (Figure 3b). These results reveal that MoS\textsubscript{4}\textsuperscript{2−} ligands were well bound to the surface atoms of CdSe NCs. In the Se 3p region (Figure S9b), the peaks corresponding to Se 3p and S 2p were overlapped over each other, making it difficult to index the peak related to S 2p. On the other hand, in the XPS spectrum of the photo-oxidized MoS\textsubscript{4}\textsuperscript{2−}-capped CdSe NCs, a new peak of SeO\textsubscript{2} appeared in the Se region (Figure 3c), whereas the peaks related to Cd\textsubscript{2}O\textsubscript{2} phases (Figure S9c) were not observed in the Cd region, which indicates that the surface of the CdSe core was slightly oxidized during the photo-oxidation treatment. In addition, new peaks related to molybdate (MoO\textsubscript{3}) in the Mo 3d region were detected with Mo 3d peaks and the S 2s peak (Figure 3d). Also, we clearly observed a shoulder peak associated with SO\textsubscript{3}\textsuperscript{2−} in the S 2p region (Figure S9d), which indicates that MoS\textsubscript{4}\textsuperscript{2−} ligands were partially oxidized during the photo-oxidation treatment. This partial oxidation was further supported by the negative ζ-potential of photo-oxidized MoS\textsubscript{4}\textsuperscript{2−}-capped CdSe NCs (Figure S10) because the fully oxidized MoS\textsubscript{4}\textsuperscript{2−} should be a neutral oxide phase. The fact that the peaks corresponding to the oxidized phases of Mo and S appeared after photo-oxidation suggests that thin MoS\textsubscript{O} layers were formed on the surface of CdSe by the photo-oxidation.

(NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}WS\textsubscript{4} compounds are known to be
easily decomposed thermally and photochemically: Brito et al.
reported that (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{3} can be decomposed to form MoS\textsubscript{2} at as low as 120 °C under an inert atmosphere, which finally forms MoS\textsubscript{2} at higher temperatures.\textsuperscript{41} Vogler et al. studied the photochemistry of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{3} and (NH\textsubscript{4})\textsubscript{2}WS\textsubscript{4} compounds and demonstrated that the MoS\textsubscript{4}\textsuperscript{2−} and WS\textsubscript{4}\textsuperscript{2−} anions become photochemically active in the presence of O\textsubscript{2}.
\textsuperscript{33} The light absorption by these compounds leads to an intramolecular ligand to metal charge transfer (LMCT)-type transition from sulfide to Mo and W. The LMCT transition of MS\textsubscript{4}\textsuperscript{2−} compounds undergoes a reductive elimination of S\textsubscript{2} to form very reactive intermediates of MS\textsubscript{4}\textsuperscript{2−}, which easily react with O\textsubscript{2} to generate metal sulfur oxide compounds. We also monitored the decomposition of MoS\textsubscript{4}\textsuperscript{2−} ligands during photo-oxidation treatment of (NH\textsubscript{4})\textsubscript{2}MoS\textsubscript{3} solution under UV irradiation in the air by absorption spectroscopy. As shown in Figure S11, the absorption band of MoS\textsubscript{4}\textsuperscript{2−} completely disappeared with photo-oxidation treatment for 12 h, where we could not observe any peaks related to the formation of impurity as byproducts such as S\textsubscript{2−} in the absorption spectrum. Therefore, the reactive intermediates of MoS\textsubscript{4}\textsuperscript{2−} or WS\textsubscript{4}\textsuperscript{2−} formed from MoS\textsubscript{4}\textsuperscript{2−} or WS\textsubscript{4}\textsuperscript{2−} on the surface of CdSe NCs by light absorption should undergo oxidation preferentially rather than the CdSe core, which can preserve the CdSe core against oxidation.

To further verify this oxidation mechanism, additional MoS\textsubscript{4}\textsuperscript{2−} anions were controllably mixed with a MoS\textsubscript{4}\textsuperscript{2−}-capped CdSe NCs solution, and they were treated under UV irradiation in air. With an increase of the amount of added MoS\textsubscript{4}\textsuperscript{2−} anions, the excitonic peaks in the absorption spectrum were progressively broadened (Figure 4a), indicating polydispersity due to the oxidation. Interestingly, the 1S peak position in the absorption spectrum was not shifted (the inset of Figure 4a), regardless of the amount of added MoS\textsubscript{4}\textsuperscript{2−} anions, which reveals that the effective size of CdSe NCs was maintained during the photo-oxidation. Furthermore, the PL peak positions were retained with the significant improvement of QY at higher amounts of added MoS\textsubscript{4}\textsuperscript{2−} anions (Figures 4b and S12). The fwhm of PL spectra of these NCs (the inset of Figure 4b) was progressively increased with the amount of added MoS\textsubscript{4}\textsuperscript{2−} anions, which is consistent with the absorption spectra. These results demonstrate that the excess MoS\textsubscript{4}\textsuperscript{2−} compounds in the NC solution were preferentially oxidized and some of them contributed to the formation of thicker oxide layers on the surface of CdSe NCs. Accordingly, the surface oxidation of the CdSe core was blocked by excess MoS\textsubscript{4}\textsuperscript{2−} compounds, which can be responsible for the fixed 1S peak position in the absorption spectrum of colloidal MoS\textsubscript{4}\textsuperscript{2−}-capped CdSe NCs with various MoS\textsubscript{4}\textsuperscript{2−} amounts. The peak broadening can be explained by the thicker surface layers of MoS\textsubscript{O} phases with higher amounts of additional MoS\textsubscript{4}\textsuperscript{2−} anions during the treatment because the formation of oxide layers could not be uniform for all NCs.

We also performed control experiments in which the photo-
oxidation treatment was conducted on CdSe NCs capped with Cl\textsuperscript{−} and S\textsuperscript{2−} inorganic ligands, which were extensively studied for NC capping. After UV irradiation in air atmosphere for 24 h, the peaks in the absorption spectra of Cl\textsuperscript{−}- and S\textsuperscript{2−}-capped CdSe NCs (Figure 4c) were significantly broadened and shifted to shorter and longer wavelengths, respectively. Furthermore, the absorbance of the 1S peak in the absorption spectrum of S\textsuperscript{2−}-capped CdSe NCs was significantly reduced with the red shift, and the second peak became remarkably enhanced. This can be attributed to the formation of a quasi-type-II CdSe@CdS core@shell structure, which has an electronic structure
where the core CdSe lowest unoccupied molecular orbital (LUMO) level is close to the shell CdS LUMO level. The formation of type-II states in core@shell nanostructures generally shows featureless absorption tails into longer wavelength regions due to carrier delocalization.42,43 The PL properties of both the Cl\(^-\) and S\(_2\)\(^-\)-capped CdSe NCs (Figure 4d) were improved by the treatment. However, the peaks in the PL spectra of Cl\(^-\) and S\(_2\)\(^-\)-capped CdSe NCs were shifted to shorter and longer wavelengths by more than 40 nm from that of the primary organics-capped NCs, similar to their absorption spectrum. On the other hand, the peaks in the absorption and PL spectra of MoS\(_4\)\(^-\)-capped CdSe NCs were slightly broadened; however, the peaks were not shifted. These contrasting behaviors of the optical properties can be explained by the oxidation of CdSe and the subsequent reaction of the ligands of Cl\(^-\) and S\(_2\)\(^-\). For instance, Bae et al. reported that chlorine (Cl\(_2\)) molecules etch the Se atoms on the surface of PbSe NCs and the Pb atoms react with Cl\(_2\) to form a thin passivation layer of PbCl\(_x\) on the surfaces of PbSe NCs.14 Etching by Cl\(_2\) leads to a decrease in the effective size of the PbSe NCs, and consequently, the peaks are shifted to shorter wavelengths in both the absorption and PL spectra. Schnitzenbaumer et al. reported that S\(_2\)\(^-\) ligands could generate a thin layer of CdS on CdTe QDs, which results in the
formation of a CdS shell around a core CdTe QD. This core/shell structure of the CdTe/CdS NCs shifts the peaks to longer wavelengths in the absorption spectrum. In a similar manner, in the present study, Cl− and S2− ligands can strongly affect the surface structure of CdSe NCs via chemical reactions, which are responsible for the substantial shifts in the peaks of the optical properties. On the other hand, MoS2- and WS2- ligands instead undergo oxidation to form stable oxide layers for passivation of the CdSe core surface rather than reacting with the CdSe core. These explanations can be further supported by improvement in the QY of MoS2- and WS2-capped CdSe NCs, which was estimated to be at least 50% higher than that of the Cl−- and S2−-capped NCs. Thus, our results provide the effectiveness of MoS2- and WS2- ligands for the enhancement of luminescent properties of all-inorganic CdSe NCs by selective oxidation.

Generally, the major benefit of using inorganic ligands for NCs is the improvement of charge transport in NC solids. In the current study, a field-effect transistor (FET) with back-gate geometry was fabricated in all-inorganic NC thin films. Among the various NCs studied in the current work, we chose the PbS NC for the charge-transport study because it is one of the most extensively studied nanoscale materials for electronic and optoelectronic device applications and its charge-transport properties depending on the surface ligands, electronic structures, and device structures are well established. The thin film of all-inorganic MoS4- capped PbS NCs was prepared by spin-coating of NC solution in NMF onto a doped silicon wafer with a 100 nm oxide layer and patterned source and drain Ti/Au electrodes with a gap spacing of 10 μm. This film was further annealed at 250 °C for 30 min. As shown in Figure 5a, the drain current (Id)−drain voltage (Vd) output and Id−gate voltage (Vg) transfer curves (Figure 5a) show p-type characteristics with small gate modulation, which is typically observed in heavily doped degenerate semiconductors.

To further study the charge transport of these NCs, we investigated the photoresponse of all-inorganic MoS4- capped PbS NC thin films because optoelectronics including photodetectors are the major application of PbS NCs. To investigate the photoresponse of MoS4- capped PbS NC thin films, the photocurrent−time response was measured in the dark and under illumination using a laser diode at 405 nm at a fixed light intensity (1.98 mW/cm2). As shown in Figure 5b, the photocurrent sharply increases under illumination due to the increased number of photoexcited charge carriers and decreases in the dark. Furthermore, this photocurrent modulation reproducibly responded to on−off cycles. The observed tails in on−off cycles may result from surface trap states that can capacitively store charge carriers.

As aforementioned, (NH4)2MoS4 and (NH4)2WS4 compounds are utilized as sources for the formation of MoS2 and WS2 phases because they easily decompose upon heat treatment and form those phases. The MoS4- and WS4- capped NCs synthesized in this work can be used as platforms for the preparation of 2D nanoscale MoS2 and WS2 structures on different materials. In this regard, we conducted experiments on the MoS4- and WS4- capped CdS NCs calcined at 500 °C under flowing H2S. The TEM images of calcined materials (Figure S13) clearly show the formation of nanoscale 2D materials grown along the [002] direction on CdS nanostructures. These 2D materials were predominantly double-layered MoS2 and WS2, and their length was less than 10 nm. These materials can be utilized as photocatalysts for the production of H2 from water splitting as the catalytically active sites on MoS2 and WS2 lie on the edges rather than basal planes. The tiny MoS2 and WS2 nanostructures formed on the NCs could provide multiple catalytically active sites due to a large number of exposed edges. Furthermore, well-designed NCs with appropriate electronic structures can create new synergistic properties through a combination of MoS4- and WS4- ligands.

In conclusion, we have shown the general applicability of molybdenum and tungsten sulfide molecular anions (MoS4− and WS4−) for functional capping of various inorganic colloidal NCs. These inorganic anions have been demonstrated to fulfill all expected functions that have been reported for other inorganic ligands, such as colloidal stability of the NCs in polar solvents and preservation of primary structural and electronic properties of the NCs. In particular, MoS4- and WS4- capped CdSe semiconductor NCs exhibited great enhancement of PL properties through photo-oxidation treatment. This treatment contributed to the preferential formation of stable MoS4O2 layers on the surface of CdSe NCs without affecting the electronic structure of the NCs, leading to an increase in QY by more than 50% without any notable peak shift, in contrast to Cl− and S2− ligands. Furthermore, we studied the charge transport of MoS4- capped PbS NCs by the fabrication of the FET and photodetector, which showed clear gate modulation and photoresponse. Finally, we explored the possibility to synthesize various nanoscale 2D materials of MoS2 and WS2 from MoS4- and WS4- capped NCs, which can provide catalytic platforms with designed electronic structures, combining the functions of nanoscale support and 2D catalysts with a large number of exposed edges. These transition-metal sulfide ligands can extend the list of inorganic ligands for NC capping and endow additional functionalities to the class of all-inorganic NCs. We believe that these ligands will be widely utilized for advancing the promising applications of NCs in the fields of optoelectronics, catalysis, electronics, and biomedical engineering.

ASSOCIATED CONTENT

Supporting Information

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Experimental section, additional absorption and PL spectra, XRD patterns, XPS spectra, FT-IR spectra, Optical section, additional absorption and PL spectra, XRD patterns, XPS spectra, FT-IR spectra, "potential, and TEM images (PDF)

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