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Self-assembly of Nanorod-like Architecture of CdTe Nanocrystals in Langmuir Monolayer of Bolaamphiphiles

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A novel fabrication of two-dimensional CdTe nanoarchitecture was developed through the interaction between bolaamphiphiles of 1,3-bis(hexadecyldimethylammonio)propane dibromide and the prepared negatively charged CdTe nanocrystals hydrosols by controlling the surface pressure of the monolayer. The formed amphiphiles/CdTe nanocrystals composite monolayer confirm that plenty of CdTe nanorod-like nanostructure with the lengths of roughly 100–300 nm and the widths of about 25-nm distribute in Langmuir layer by a self-assembly way at low surface pressure.

To generate fascinating and functional nanostructures and nanometer-scale patterning is a fundamental issue for further miniaturization of electronic components, optical detectors, chemical and biochemical sensors and devices, etc.[1,2] Many of these devices will require immobilization of nanoparticles in different assemblies on various substrates.[2] Assemblies of metallic and inorganic nanoparticles are well known to yield collective physical properties dependent on particle size, spacing, and higher-order structure.[3] In recent years, there has been considerable interest in assembling nanoscale building blocks into thin films using both novel building block compositions and assembling strategies because thin films of organized nanoparticles displayed promising characteristics for the fabrication of diversified nanodevices and electrically conductive films.[4–7] Through electrostatic interaction between the ionic head groups of amphiphiles and the charged nanoparticles hydrosol from subphase, monolayer and Langmuir–Blodgett (LB) technique, provide a important way in assembly nanoparticles into organized ultrathin film. In this communication, we present a simple, highly efficient method for stabilization of two-dimensional nanorod-like structures by spreading a kind of a bolaamphiphiles on CdTe aqueous hydrosol subphase. To the best of our knowledge, this may be the first report on self-assembly of nanorod-like architecture of CdTe nanocrystals on bolaamphiphiles monolayer.

Figure 1 shows TEM image of CdTe nanoparticle hydrosols. CdTe nanocrystals were synthesized in aqueous phase with the materials of $CdCl_2 \cdot 2H_2O$, $NaBH_4$, and tellurium powders using 3-mercaptopropionic acid (MPA) as stabilization reagent according to the method described in the Ref. 8 with a little modification. As-prepared CdTe nanocrystals are in definitely spherical form, and have a very narrow size distribution with an average diameter of approximate 5 nm. The synthetic CdTe particles coated with mercapto groups have negative-charged surface (as shown in Scheme 1). Consequently, CdTe nanocrystals are quite even throughout the aqueous medium because of the electrostatic repulsions from each other.

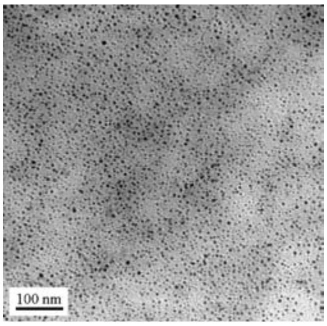
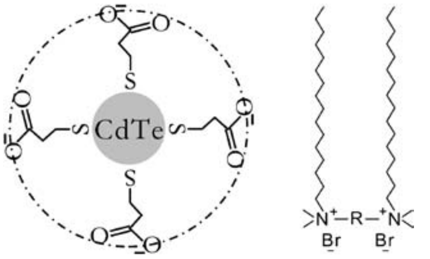


Figure 1. TEM image of CdTe nanocrystals.



Scheme 1. Surface-charged CdTe nanocrystal (left) and general structure of bolaamphiphiles of C_{16}–C_3–C_{16} (right).

Figure 2 shows the surface pressure–area isotherms (π–A isotherms) of 1,3-bis(hexadecyldimethylammonio)propane dibromide (C_3H_6-α, ω-$(C_{16}H_{33}N^+(CH_3)_2Br^-)_2$ (abbreviated as C_{16}–C_3–C_{16}, molecular structures shown as Scheme 1, 99%) monolayer on the subphase of ultrapure water and CdTe nanocrystal hydrosols. The bolaamphiphiles monolayer on CdTe nanocrystal hydrosols exhibits some exotic Langmuir behavior such as lower collapse pressure, a little peak at lower surface pressure of about 7 $mN \cdot m^{-1}$, and a following gentle increase of surface pressure other than sharp enhancement on water subphase. Since C_{16}–C_3–C_{16} has two cationic head groups and CdTe nanocrystals take negative charges, it is reasonable to regard that it is the electrostatic interaction between the two species that cause the distinct Langmuir behavior of the bolaform amphiphiles monolayer on CdTe hydrosols. Besides, in the presence of CdTe nanocrystals, the average area of C_{16}–C_3–C_{16}, extrapolated by the linear part of the isotherm is 0.28 nm^2 per molecule. This molecular area is much less than the result on pure water, which is 1.05 nm^2. Generally, nanoparticles on subphase will lead to larger mean molecular area of amphiphiles because nanoparticles move into Langmuir layer, inhabit there

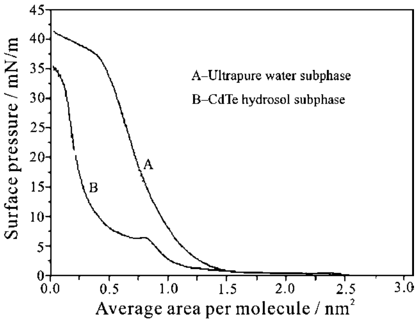


Figure 2. π–A isotherms of bolaamphiphiles on the subphase of ultrapure water (A), and 1.0×10^{-5} mol·L^{-1} CdTe nanocrystals hydrosol (B) at pH 8.

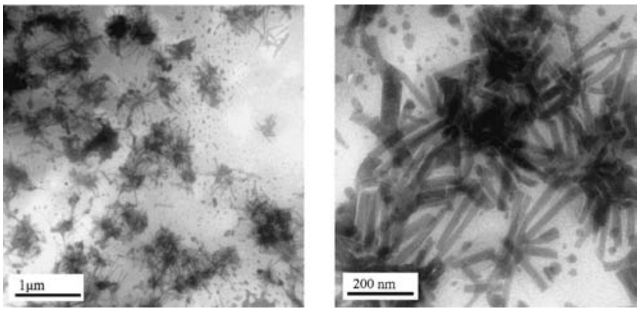


Figure 3. TEM images of patterned C_{16}–C_3–C_{16}/CdTe nanocrystals nanocomposite monolayer at 7 mN·m^{-1}.

and push away the amphiphiles.[9,10] Thus, the significant reduction of molecular area of bolaamphiphiles on CdTe hydrosols implies that there is some special complex of C_{16}–C_3–C_{16}/CdTe nanocrystals in the Langmuir layer, as we will discuss latterly.

The composite Langmuir film of the bolaamphiphiles and CdTe nanocrystals was deposited onto copper grids (100 mesh) coated with an amorphous carbon film by using subphase lowing method for TEM observation. Figure 3 shows TEM images of C_{16}–C_3–C_{16}/CdTe nanocrystals composite monolayer which was compressed to 7 mN·m^{-1}. Dispersive or unshaped CdTe nanocrystals could be seen in the Langmuir layer from the photograph. What is the most interesting is that plenty of nanorod-like architecture of CdTe nanocrystals with the lengths of roughly 100–300 nm and the widths of about 25 nm, distribute in C_{16}–C_3–C_{16} monolayer by a self-assembly way.

The mean area per molecule of bolaamphiphiles on CdTe nanocrystals hydrosol subphase is only about a quarter of that on water subphase. This Langmuir behavior should be explained by the particular assembly of CdTe nanocrystals with bolaform amphiphiles at air–water interface. Actually, through the interface or interactions between interfacial amphiphiles and various solutes from the subphase, many ordered nanopattern and some special architecture have been generated.[11–14] For instance, Liu et al.[12] designed a series of achiral cationic bolaamphiphiles, and found the supramolecular chirality of the TPPS–bolaamphiphiles system. The surface of CdTe nanocrystals takes negative charge, which have strong interaction with the positively charged heads of bolaamphiphiles. And the surface area of CdTe nanocrystals is much bigger than the average molecular area of C_{16}–C_3–C_{16}. In this case, CdTe nanocrystals on subphase transfer into monolayer of bolaamphiphiles, and then they are adsorbed fully in their surface by C_{16}–C_3–C_{16} other than only pushing aside the amphiphiles. Considerable C_{16}–C_3–C_{16} molecules taking up the surface of CdTe nanocrystal is equivalent in great reduction of virtual amount of amphiphiles in the monolayer. It should be pointed out that the total surface area of each spherical CdTe nanoparticle is happened to four times larger than a circle with equal radius. If the arrangements of C_{16}–C_3–C_{16} on the surface of CdTe nanoparticles are as compact as the ones on water, the complexes of CdTe nanocrystals with bolaamphiphiles would lead to three-fourths decrease in molecular area of bolaamphiphiles. This assumption matches exactly the results from the π–A isotherms. The complexes, then probably aggregate each other by the line tension among the long hydrophobic portions of the bolaamphiphiles, to form particular nanoarchitecture at the air–liquid interface.

In conclusion, we present a simple, highly efficient method for fabrication of two-dimensional nanostructures, specifically, self-assembly of nanorod-like architecture of CdTe nanocrystals in bolaamphiphiles monolayer of 1,3-bis(hexadecyldimethylammonio)propane dibromide. This finding is significant because it offers the prospect of assembling novel nanoscale architectures at the interface.

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