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In-Situ Synthesis of Semiconductor Nanocrystals at the Surface of Tubular J-Aggregates

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Supporting Information

1. Materials and Methods

Preparation of nanotubular J-aggregates. The amphiphilic cyanine dye derivative 3,3'-bis(2-sulfopropyl)-5,5',6,6'-tetrachloro-1,1'-dioctylbenzimidacarbocyanine (C8S3, $M_w = 902.8$ g mol^{-1}, Fig. 1a) was obtained as a sodium salt (FEW Chemicals, Germany) and used as received. A stock solution of C8S3 (2.92 mM) was prepared by dissolving C8S3 powder in pure methanol (≥99.9% GC, Sigma-Aldrich). A volume of 130 mL of the C8S3 stock solution was added to 500 mL of ultrapure H_2O, slightly shaking by hand to ensure complete mixing. An immediate color change from clear orange to deep pink was observed, indicating the formation of double-walled nanotubular C8S3 aggregates. The solution was stored in the dark for 24 h before adding another 500 mL of ultrapure H_2O to stabilize the aggregation process, resulting in a final dye concentration of 3.36×10^{-4} M. Solutions of J-aggregate nanotubes were stored in the dark and used within three days of preparation.

Preparation of semiconductor nanocrystal at the surface of J-aggregate. In a typical process, 6.68 μL of 100 mM $Cd(NO_3)_2$ (cadmium nitrate tetrahydrate, ≥99.0%, Sigma-Aldrich) solution was added to 400 μL C8S3 J-aggregate solution (3.36×10^{-4} M). The solution was stored for 0.5 h in the dark. Then 33.4 μL of 100 mM TAA (thioacetamide, ACS reagent, ≥99.0%, Sigma-Aldrich) and 12 μL of 10 mM NH_4OH (ammonium hydroxide, ammonia 25%, J.T.Baker) were added and stored for another 23.5 h in the dark. The final concentrations of $Cd(NO_3)_2$, TAA and NH_4OH are 1.64×10^{-3} M, 8.4×10^{-3} M and 3.0×10^{-4} M, respectively. To prepare CdS nanocrystals with different thickness, the concentration of TAA and NH_4OH were varied. When the TAA/NH_4OH concentration was 5.04 mM/0.18 mM, 16.8 mM/0.6 mM, and 33.6 mM/1.2 mM, the diameter of J-aggregate/CdS nanohybrids was 21 nm, 46 nm, and 100 nm, respectively.

$Zn(NO_3)_2$ (zinc nitrate hexahydrate, reagent grade, 98%, Sigma-Aldrich) and $Ni(NO_3)_2$ (nickel(II) nitrate hexahydrate, ≥98.5%, Sigma-Aldrich) were used as precursors to prepare ZnS and NiS nanocrystals.

Absorption spectra. Absorption spectra of the solutions were taken with a double-beam UV-vis spectrometer (Shimadzu UV-2101PC, Duisburg, Germany) in a 0.2 mm demountable quartz cell from Hellmar GmbH.

Fluorescence spectra. Fluorescence spectra of the solutions were taken with a fluorescence spectrometer (JASCO FP 6500) in a 0.2 mm quartz cell (Hellma) with an excitation wavelength of 380 nm (nanohybrid I). It comes with built-in light-source (Xe-lamp UXL-159, 150W), two grating-monochromators with variable slit-width and detector.

Cryogenic Transmission Electron Microscopy (Cryo-TEM). Droplets of the solution (5 µL) were applied to carbon film covered 200 mesh grids (1 µm hole diameter, R1/4 batch of Quantifoil Micro Tools GmbH, Jena, Germany), which had been hydrophilized before use by plasma process. Supernatant fluid was removed by Vitrobot Mark IV (FEI Company, Eindhoven, Netherlands) until an ultrathin layer of the sample solution was obtained spanning the holes of the carbon film. The samples were immediately vitrified by propelling the grids into liquid ethane at its freezing point (90 K). Frozen samples were transferred into a JEOL JEM2100 (JEOL, Eching, Germany) using a Gatan 914 high-tilt cryo-transfer holder and Gatan work station (Gatan, Munich, Germany). Microscopy was carried out at a 94 K sample temperature using the microscope's low-dose protocol at an accelerating voltage of 200 kV (LaB6-illumination). The defocus was chosen to be approximately 2 μm to create sufficient phase contrast for imaging. Image analysis was performed with Image J software[i].

High Resolution Transmission Electron Microscopy (HRTEM). High resolution transmission electron microscopy (TEM) was performed on a JEOL JEM2200FS operating at 200 kV. Droplets of the solution (5 μL) were applied to carbon film covered 200 mesh grids (Quantifoil Micro Tools GmbH, Jena, Germany), which was hydrophilized before use by simply storing the grids over a water bath for a day. The supernatant fluid was removed with a filter paper until an ultra-thin layer of the sample solution was obtained on the carbon film. Image analysis was performed with Image J software.

2. Cryo-TEM image and line scan analysis of J-aggregate/CdS nanohybrids.

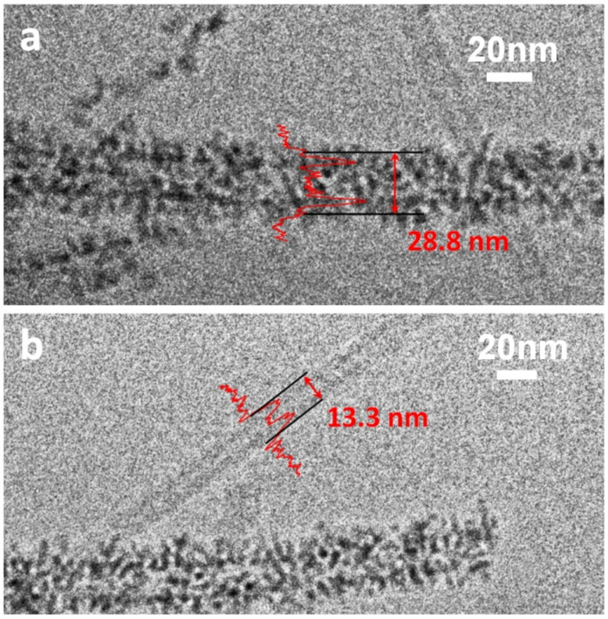

Figure S1. Cryo-TEM images and line scans of (a) CdS nanocrystals decorated J-aggregate nanotubes with a width of 28.8 nm, and (b) J-aggregate with a width of 13.3 nm.

Experimentally, line scans are taken from the cryo-TEM images as gray value profiles along a line perpendicular to an aggregate, see Fig. S1. In order to reduce the noise the width of the line was increased to more than 100 pixels, which corresponds roughly to a length of 10 nm. Typical line scans are shown in the Fig. S2 - S5 and in Fig. 2. The line scans show features that allow the conclusion that J-aggregates are covered by a thin “hard” shell of CdS nanocrystals and a more blurred shell of loosely bound particles. This can be confirmed by a simple model described belowed.

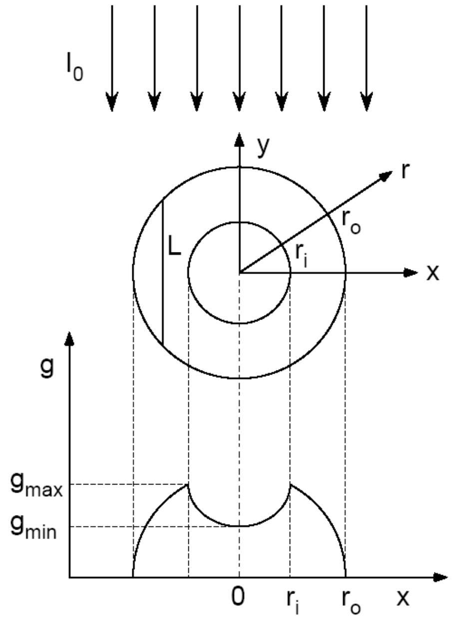

Figure S2. Scheme of relationship between the gray value of the image and the transmitted intensity.

As shown in Fig. S2, the cryo-TEM images provide transmission contrast images where the transmitted intensity depends on the mass density and thickness of the objects. If we neglect any effects of the phase of the transmitted electrons (usually described by the contrast-transfer function) and assume that all objects are of identical and homogeneous density the intensity is completely defined by the geometry of the observed objects. We also assume a linear relationship between the gray value of the image and the transmitted intensity. For these assumptions, the gray value g is proportional to the length L the electron has passed through the sample.

Assuming structures of cylindrical symmetry, transmission profiles allow reconstruction of the radial density distribution $\rho(r)$ of the object. We consider a homogeneous tube with outer diameter $2r_o$ and inner diameter $2r_i$. The density profile *g(x)* is then proportional to the length *L* in *y*-direction across the tube. Assuming a density of 1 we obtain:

For $x < r_i$:

$$g(x) = 2\int_{y_i}^{y_o} dy = 2\left(\sqrt{r_o^2 - x^2} - \sqrt{r_i^2 - x^2}\right),$$

for $r_i \le x \le r_o$:

$$g(x) = 2\int_{0}^{y_o} dy = 2\sqrt{r_o^2 - x^2}.$$

A tube causes a U-shaped density profile as shown on the left. It is important to note that the inner diameter of the tube is obtained from the distance between the peaks, while the outer diameter is defined by the zero-values of the curve.

The formalism above is used to “fit” the scan profiles taken from various images at different tubes. A model is built using two tubes, one describing an inner layer that corresponds to a thin shell of CdS nanocrystals (with inner and outer radii *Rsh_i* and *Rsh_a*), and a layer of CdS particles with lower density (with inner and outer radii *Rdif_i* and *Rdif_a*). The radii and the relative intensities were “fitted” manually to obtain a reasonable fit of the scan with the model. Below, several samples are shown and the results are listed in Table S1.

Although the experimental data are influenced by noise (also due to the small number of particles within the scan area), the qualitative shape of the line scans can be reproduced quite well. Also the radii obtained are very consistent. The description of the C8S3/CdS hybrids by such a double tube model therefore seems to be reasonable.

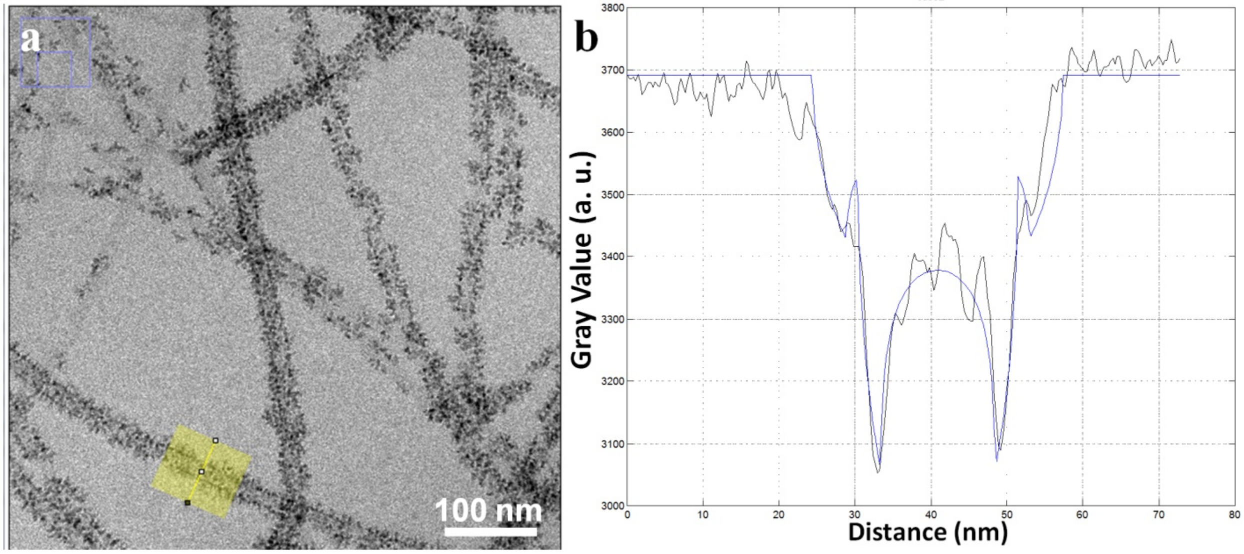

Figure S3. Sample # CdS 1: (a) Cryo-TEM image and (b) line scan profile.

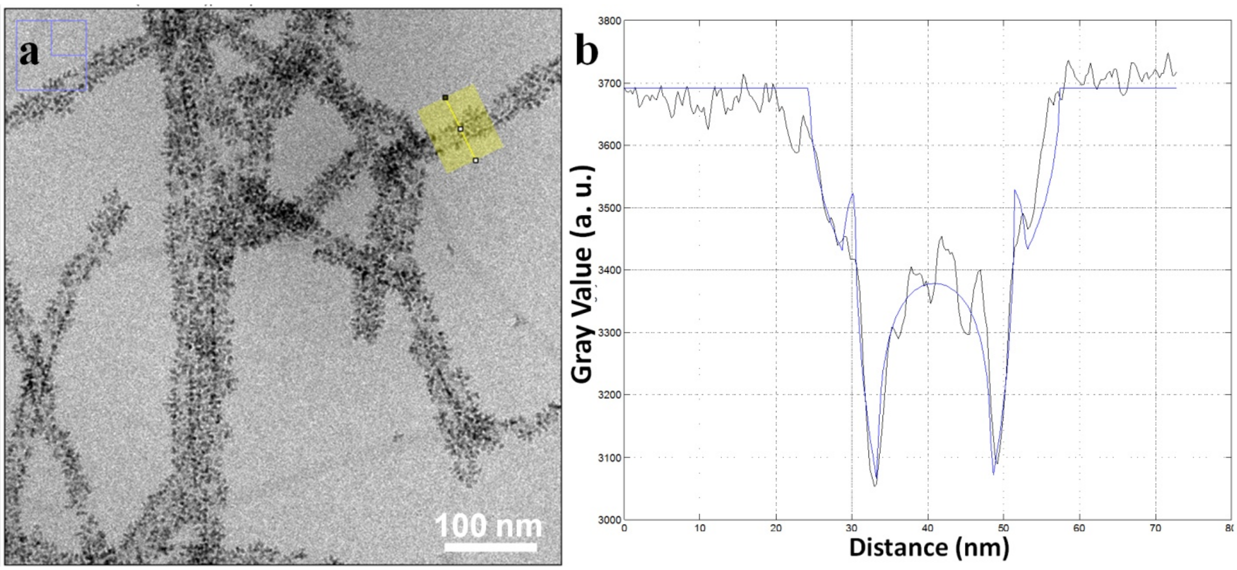

Figure S4. Sample # CdS 2: (a) Cryo-TEM image and (b) line scan profile.

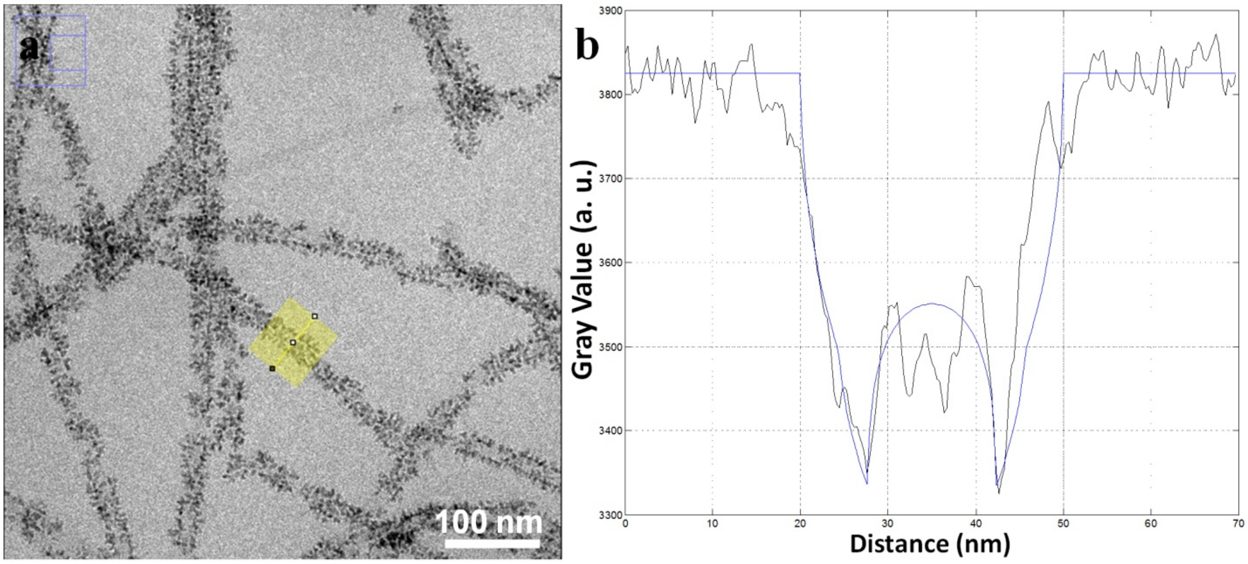

Figure S5. Sample # CdS 3: (a) Cryo-TEM image and (b) line scan profile.

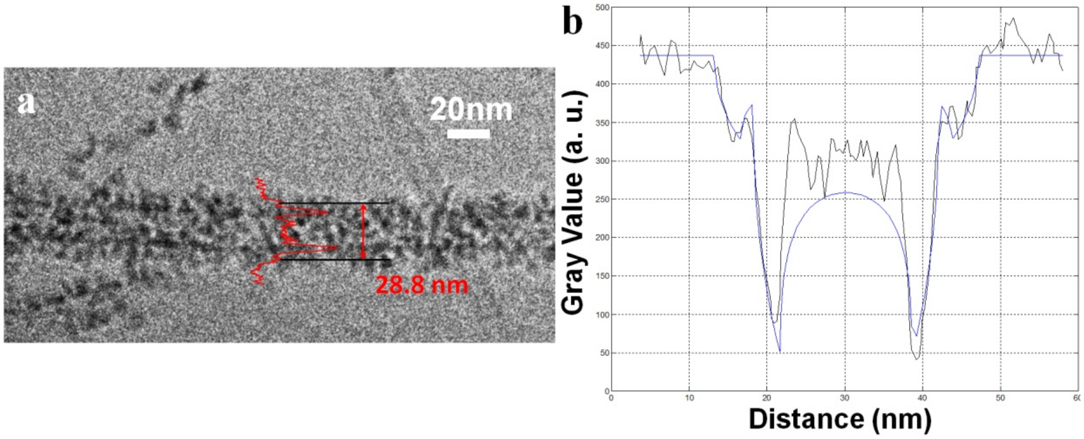

Figure S6. Sample # CdS F1: (a) Cryo-TEM image and (b) line scan profile.

Table S1: Summary of the values for the fitted models shown above. All lengths are in nm. Rsh is the inner hard shell, Rdif the diffuse outer layer of particles.

Sample	**Cds 1**	**CdS 2**	**CdS 3**	**F1**
Rsh_i / nm	7.65	7.5	7.34	8.5
Rsh_a / nm	10.5	10.5	10.6	12.0
Rdif_i / nm	11.95	12	10.6	13.5
Rdif_a / nm	17.0	16.5	15	17.0

3. Calculation of mean CdS coverage on J-aggregates:

Assume in 1 μL solution:

solution volume: 1E-6 L

C8S3 concentration: 0.000336 mol/L

N_A: 6.022045E+23 /mol

C8S3 molecular number in 1 μL solution:

C8S3 concentration* solution volume* NA = 2.02341E+14 /**μL**

J-aggregate molecules per nm length: 90 /nm

the total length of J-aggregates in 1 uL solution: 2.24823E+12 nm

Cd^{2+} concentration: 0.00168 mol/L

CdS Mol weight: 144.48 g/mol

Zinc Blende CdS QD Density at 300K: 4870000 g/m3[ii]

total CdS volume in 1μL:

Cd^{2+} concentration* solution volume* CdS Mol weight/ Zinc Blende CdS QD Density at 300K = 4.98411E-14 m^3

CdS nanoparticle radius: 1.6E-09 m

CdS nanoparticle volume: (4/3*pi*r3) = 1.71573E-26 m^3

CdS nanoparticle number in 1 ul solution: 2.90496E+12

Considering the cover density like the sketch:

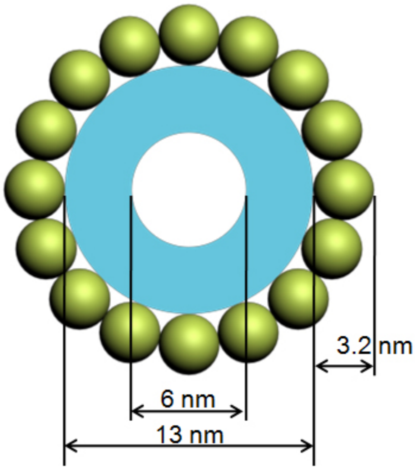

Figure S7. Sketch of parameters of CdS nanoparticle decorated J-aggregate hybrid.

As shown in Fig. S7: 16 CdS nanoparticles cover 3.2 nm nanotube

or calculate by perimeter:

pi* (13+3.2)/3.2= 15.9 (perimeter of hexadecagon is bigger than circle, so, assume 16)

So, numbers of CdS nanoparticles per nm length: 5 /nm

the total coverage length of CdS nanoparticles in 1 ml solution: 5.80992E+14 nm

compare to the total length of J-aggregate nanotubes in 1 ml solution: 2.24823E+12 nm

CdS nanoparticles coverage: 25.8 %

4. Size distribution of CdS nanocrystals on the surface of J-aggregate.

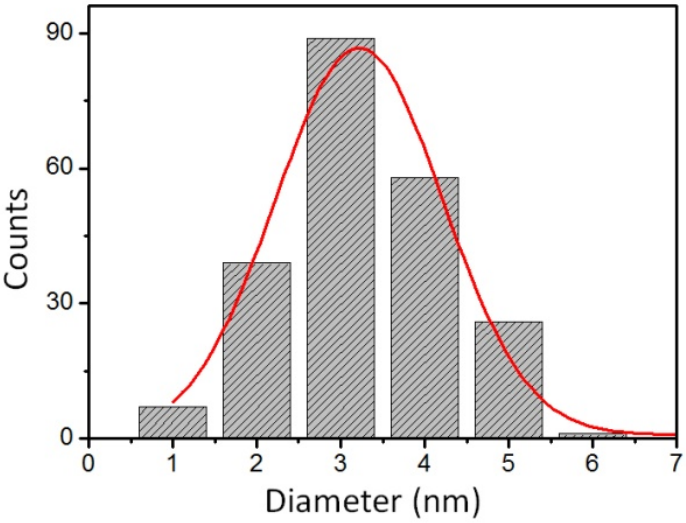

Figure S8. Size distribution of CdS nanocrystals acquired by HRTEM yields an average diameter of d = 3.2 nm.

5. EDXS analysis of J-aggregate/CdS nanohybrids.

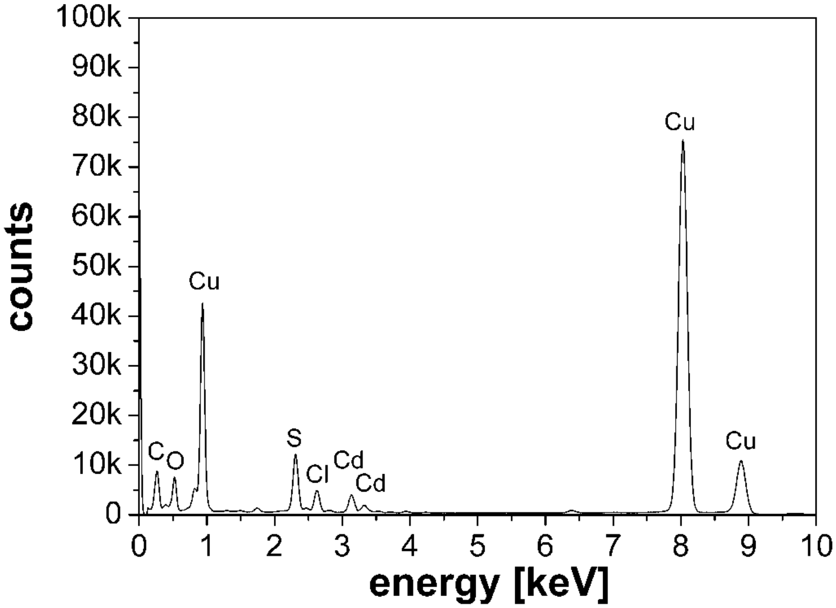

Figure S9. EDXS analysis of J-aggregate/CdS nanohybrids confirming the presence of Cd and S elements. The Cu and C energy peaks are from carbon-coated TEM copper grids used for the EDXS measurement. The other element peaks (i.e., carbon, oxygen, and chloride) presumably come from C8S3 molecules.

6. Electron diffraction pattern analysis of J-aggregate/CdS nanohybrids.

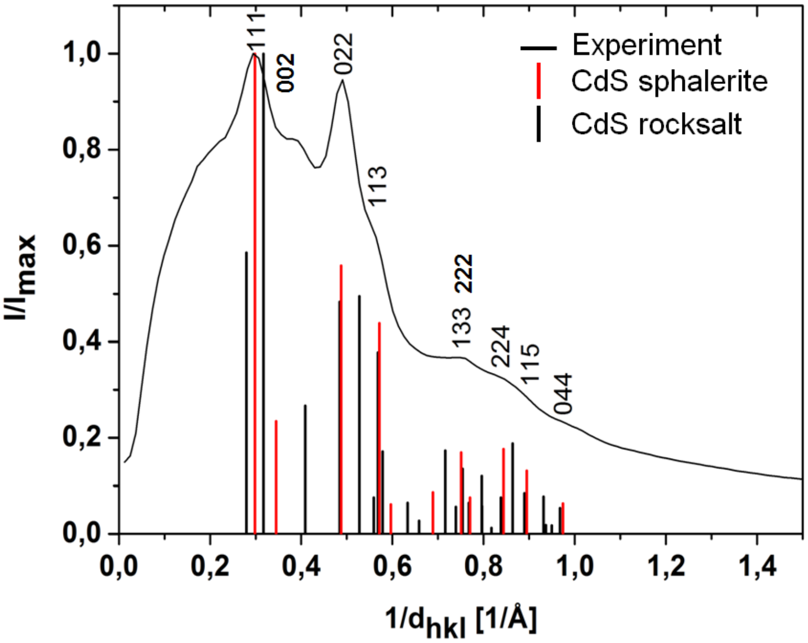

Figure S10. Line scan of transmission electron diffraction pattern of CdS nanocrystals showing as-prepared CdS nanoparticles are sphalerite crystal.

7. Cryo-TEM images and line scans of J-aggregate/ZnS and J-aggregate/NiS nanohybrids.

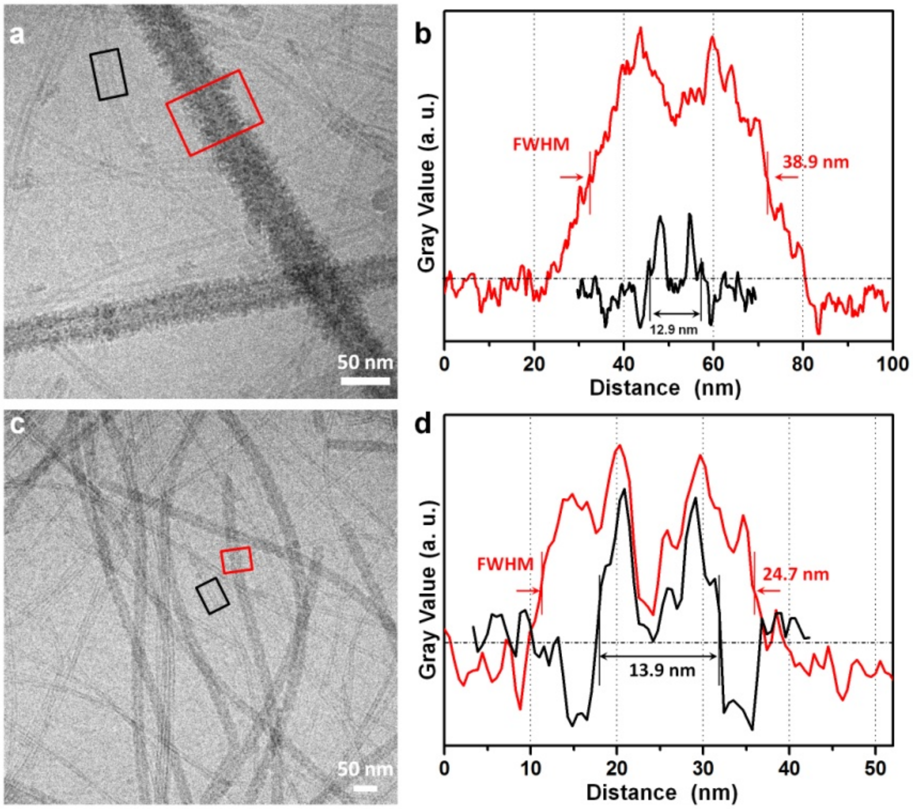

Figure S11. Cryo-TEM images of nanohybrids consisting of (a) ZnS and (c) NiS nanocrystals decorated on the outer surface of C8S3 J-aggregate nanotubes. (b) Line scans across (b) ZnS and (d) NiS-decorated J-aggregates (red) and bare J-aggregate nanotubes (black) showing the FWHM diameters of nanohybrid are around 38.9 nm and 25.1 nm, respectively.

8. Electron diffraction pattern analysis of J-aggregate/ZnS nanohybrids.

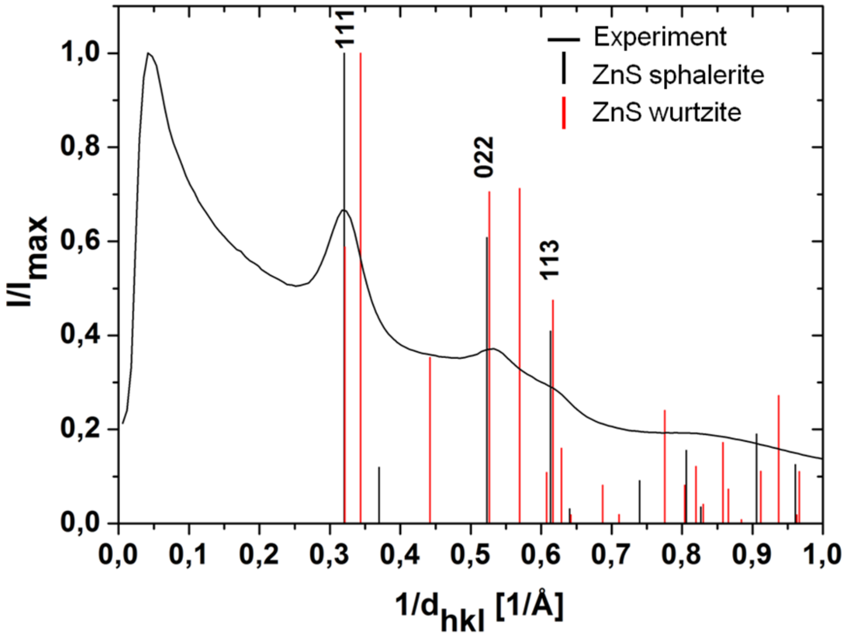

Figure S12. Line scan of transmission electron diffraction pattern of ZnS nanocrystals showing the as-prepared ZnS nanoparticles are sphalerite crystal.

9. Electron diffraction pattern analysis of J-aggregate/NiS nanohybrids.

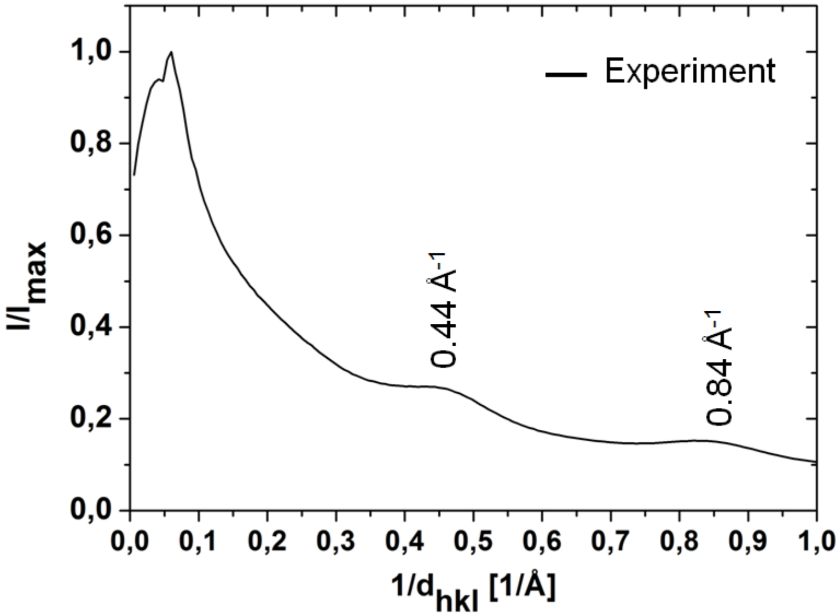

Figure S13. Line scan of transmission electron diffraction pattern of NiS nanocrystals. Only two weak and broad reflections at around 0.44 Å^{-1} and 0.84 Å^{-1} are visible, which do not allow a reliable analysis.

10. EDXS analysis of J-aggregate/ZnS nanohybrids.

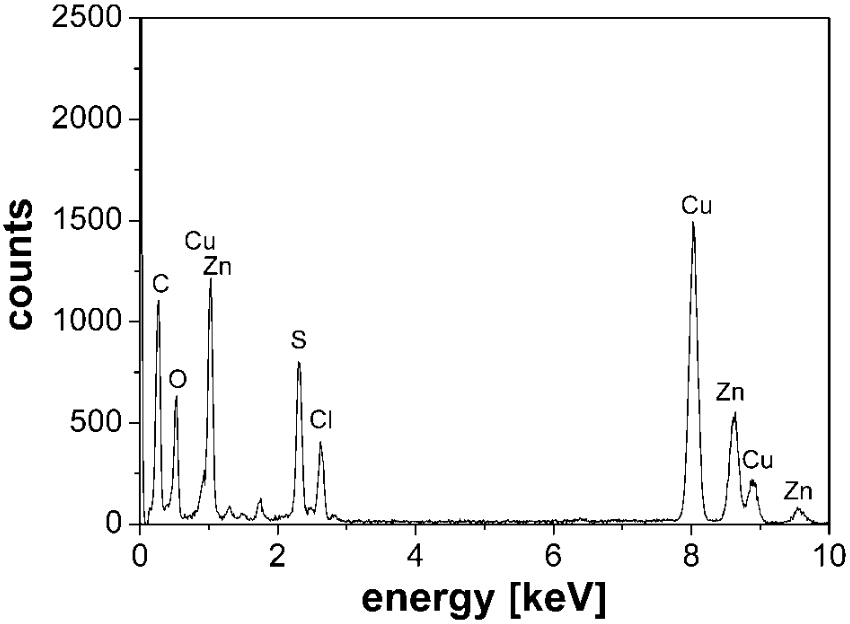

Figure S14. EDXS spectra show the presence of Zn and S elements. The Cu and C energy peaks originate from carbon-coated TEM copper grids used for the EDXS measurement. The other element peaks (i.e., carbon, oxygen, and chloride) presumably come from C8S3 molecules.

11. EDXS analysis of J-aggregate/NiS nanohybrids.

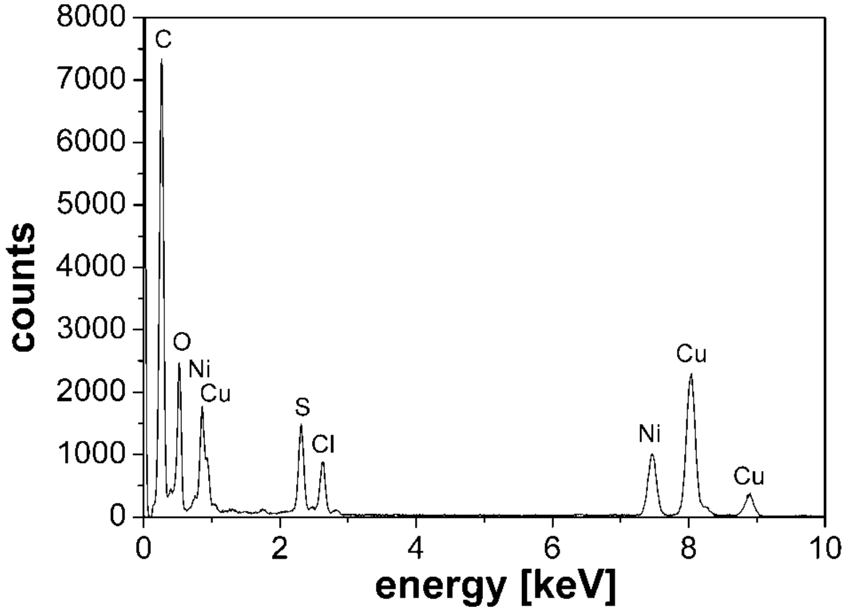

Figure S15. EDXS spectrum shows the presence of Ni and S elements. The Cu and C energy peaks originate from carbon-coated TEM copper grids used for the EDXS measurement. The other element peaks (i.e., carbon, oxygen, and chloride) presumably come from C8S3 molecules.

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[i] Rasband, W.S., ImageJ, U. S. National Institutes of Health, Bethesda, Maryland, USA, http://imagej.nih.gov/ij/, 1997-2012.

[ii] http://www.semiconductors.co.uk/propiivi5410.htm#CdS,CdSe,CdTe