Supplementary Information

Analysis and characterization of iron pyrite nanocrystals and nanocrystalline thin films derived from bromide anion synthesis

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1. Band gap calculation for FeS_2 NC film

Thickness of FeS_2 NC film is used to convert optical absorbance to absorption coefficient (α). Then a graph of $(\alpha h\nu)^2$ vs. $h\nu$ is used to extract the direct band gap of ~1.3 eV and a graph of $(\alpha h)^{1/2}$ vs. $h\nu$ is used to extract the indirect band gap of ~0.95 eV as shown in Figure 1a and 1b.

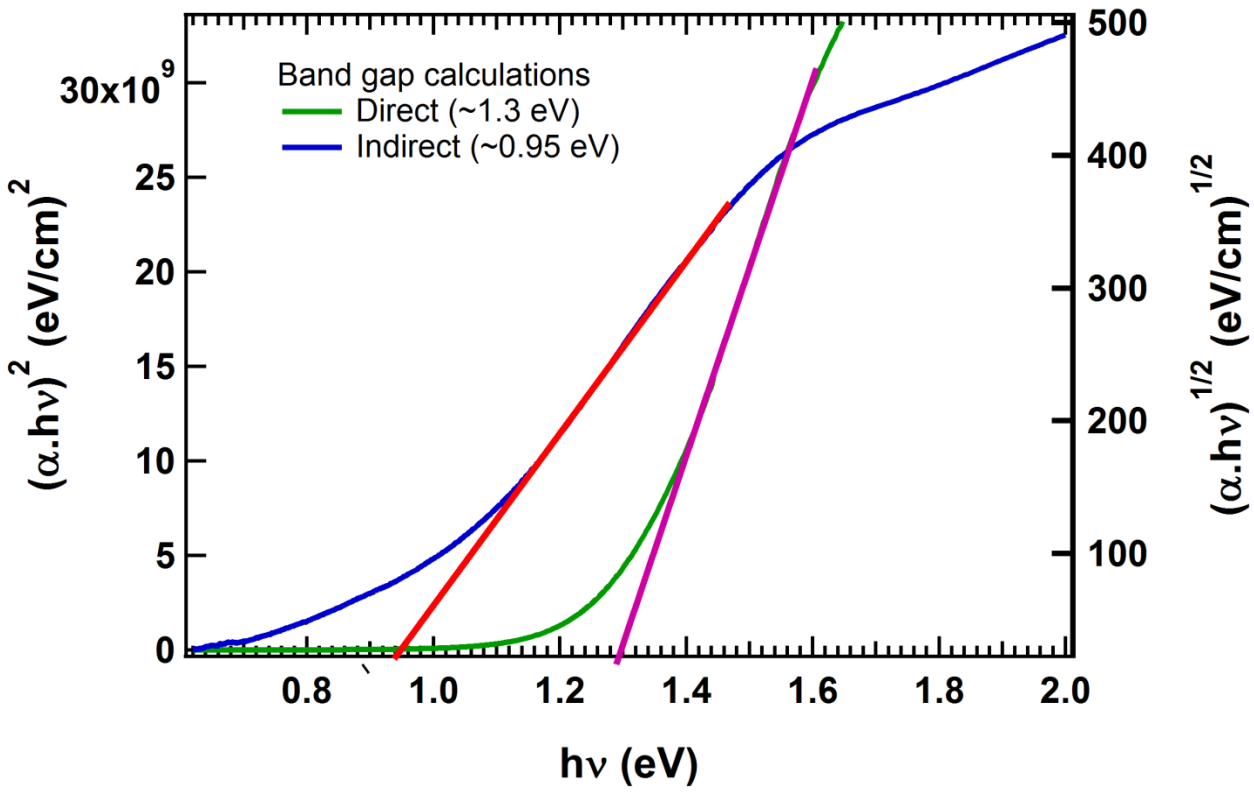

Figure S1. Band gap of FeS_2 NC capped with TOPO: (green) direct band gap calculation and (blue) indirect band gap calculation.

2. FeS_2 NC films before and after hydrazine treatment

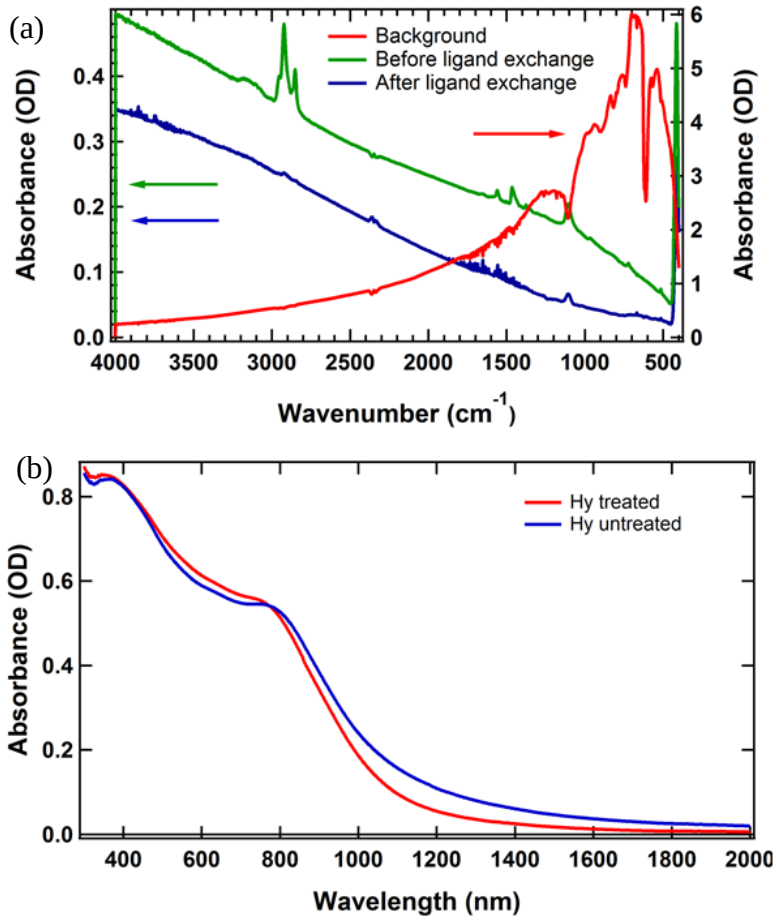

Figure S2. (a) Absorbance spectra of as synthesized and hydrazine treated FeS_2 NCs taken from FTIR measurement. Red spectra show background spectra for single crystal silicon substrate; (b) Absorbance spectra of FeS_2 thin films, prepared on soda-lime glass substrate, before and after hydrazine treatment. These spectra were calculated using transmission and reflection spectra taken from spectrophotometer.

3. Size distribution of FeS_2 NCs

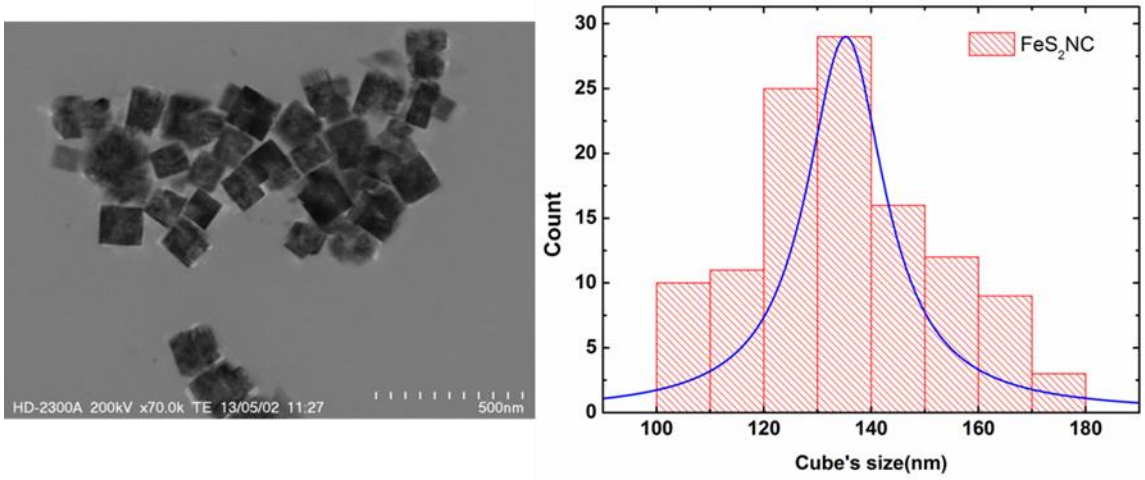

Figure S3. Size distribution of the FeS_2 NCs synthesized with TOPO/OLA combination. Size distribution was calculated using TEM images and imagej software with the help of origin software. The average size of these NCs is 133 ± 17.8 nm.

4. Oleylamine and 1,2-hexanediol doped FeS_2 NCs

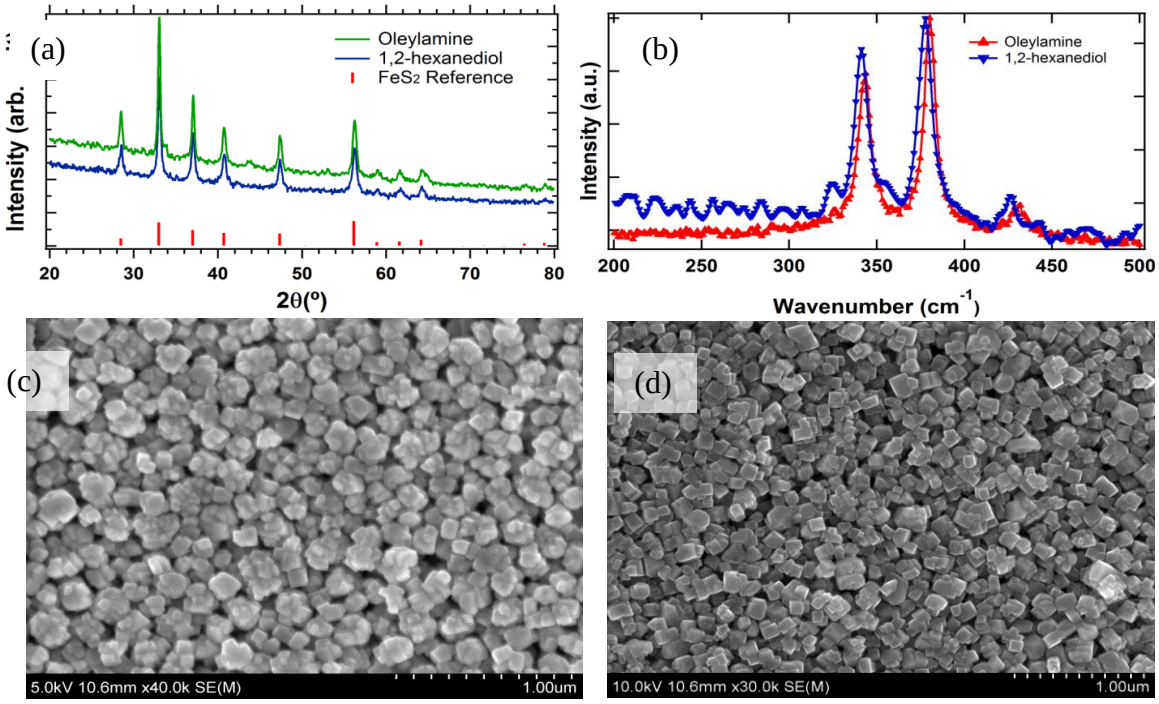

Figure S4. (a) XRD pattern of oleylamine (OLA) and 1,2-hexanediol capped FeS_2 NCs, (b) Raman spectra of phonon vibrations of FeS_2 for OLA capped and 1,2-hexanediol capped NCs, (c) SEM images for 1,2-hexanediol capped NCs and (d) SEM image for OLA capped FeS_2 NCs.

5. Sintering of FeS_2 NC films

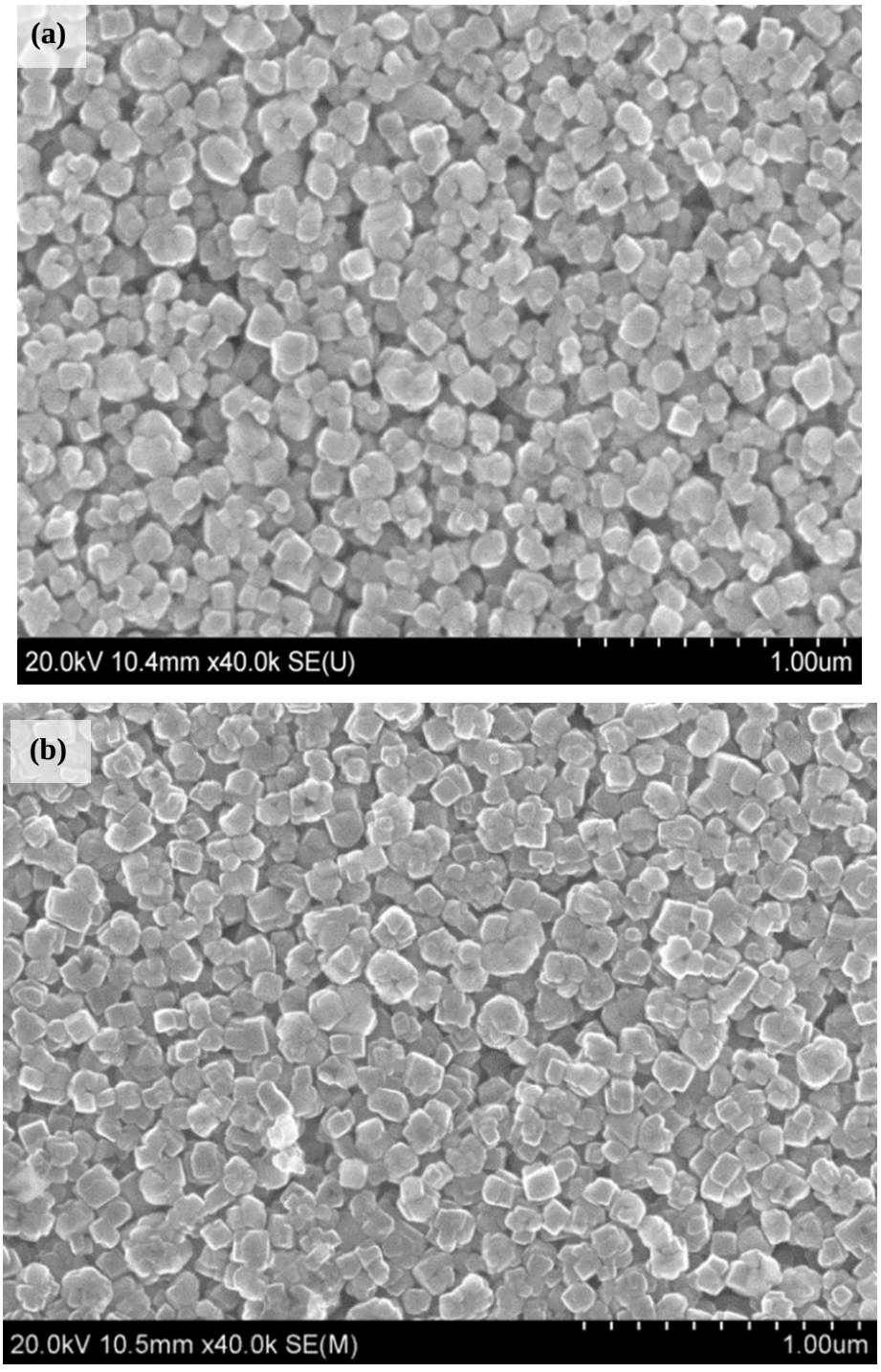

Figure S5. Characterization of FeS_2 NC films deposited by LbL drop-cast method using NC of size ~70 nm: (a) an as-deposited film and (b) a film hydrazine treated and annealed at 540 ^{0}C for 3 hours.

6. **Calculation of FWHM and grain size of the NC films**

Using igor procedure software Gaussian fit was applied to the peak corresponding to (200) direction. Equation used for this purpose was $f(x) = y_0 + A\exp\left\{-\left(\frac{x - x_0}{width}\right)^2\right\}$. After fitting the peak, the software provides magnitudes of fitting parameters y_0, A, x_0 and width. The FWHM is calculated using a relation $FWHM(\beta) = 2\sqrt{2\ln 2}\sigma$, where σ is the standard deviation and is calculated by $\sigma = \frac{width}{\sqrt{2}}$. Similarly, to calculate grain size Scherrer equation $\tau = \frac{K\lambda}{\beta\cos\theta}$ is used. In this equation, τ is grain size of the crystallites, K is a dimensionless constant, shape factor, with a value ~0.9, β is FWHM and θ is the Bragg angle.

7. Performance of thin film solar cells made from FeS2 NC films as absorber layer

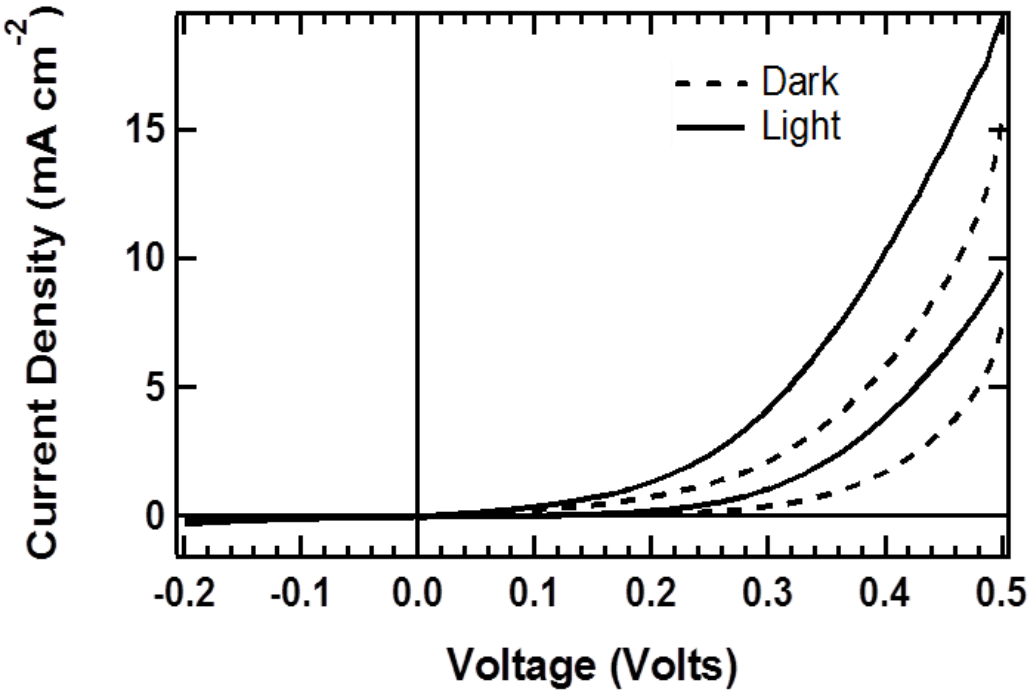

Figure S6. Current voltage characteristics for ITO/CdS/FeS_2/Ag device structure. The thickness of ITO, CdS, FeS_2 and Ag were respectively ~150 nm, ~100 nm, ~500 nm and ~100 nm. Thin film of CdS was deposited by RF magnetron sputtering method and Ag by thermal evaporator.

8. Work function measurement of FeS_2 NC films before and after hydrazine treatment

Two samples were prepared to measure the work function of nanocrystalline iron pyrite thin films. The first film was prepared from as-synthesized FeS_2 NCs without further treatment; the second film was prepared by treating the NC film, during the film formation, to remove the organic capping ligand (trioctylphosphine oxide, TOPO). Both films were deposited onto TEC 15 (Pilkington, N.A.) glass substrates and the thickness of each NC film is ~500 nm. For the work function measurement, ultraviolet photoelectron spectroscopy (UPS) was used. For UPS measurement, He I ($\hbar\omega$ = 21.22 eV) gas discharge lamp was used as an excitation source with sample bias of −10 V for secondary electron cutoff region. Figure S7 and S8 show binding energy spectra from UPS measurement with linear and semilogarithmic scale of intensity. The UPS measurement can allow us to get Fermi energy level and valence band maximum (VBM) position of semiconductor versus vacuum level. Usually, the secondary cut-off (SECO) region is used when determining the Fermi energy level and near the Fermi level (E_F=0) region is used for getting the VBM with linear intensity plot scale. We used semilogarithmic plot method instead to measure VBM, which gives more accurate value when determine VBM of semiconductor having small band gap such as quantum dots.[1]

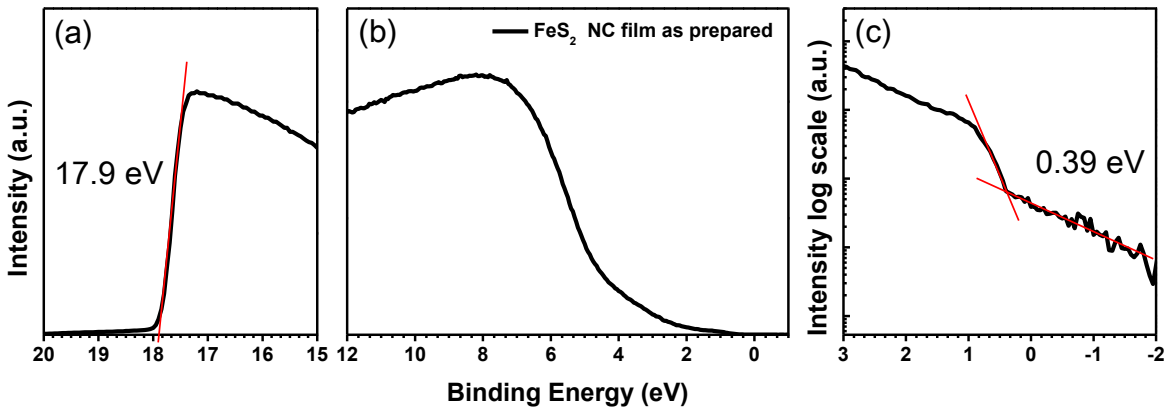

Figure S7. The binding energy spectra of FeS_2 NC film as prepared with secondary cutoff (SECO) regions (a) and near the Fermi level region in linear scale (b) and semilogarithmic scale of intensities.

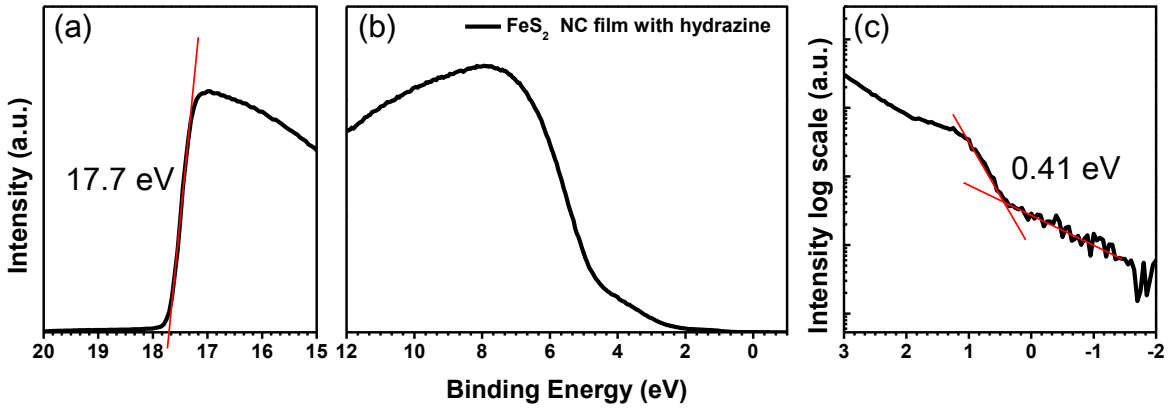

Figure S8. The binding energy spectra of FeS_2 NC film after hydrazine treatment with secondary cutoff (SECO) regions (a) and near the Fermi level region in linear scale (b) and semilogarithmic scale of intensities.

Figure S7(a) and S8(a) show that the secondary cut offs are at 17.9 eV for as-synthesized NC film and 17.7 eV for treated NC film respectively. Using these cut offs, we get the Fermi energy position at 3.3 eV and at 3.5 eV for as-synthesized NC film and treated NC film respectively. Figure S7(c) and Figure S8(c) are enlarged from Figure S7(b) and Figure S8(b) respectively to determine VBM at 0.39 eV and 0.41 eV from Fermi energy level for as-synthesized NC film and treated NC film respectively.

References:

[1] T. G. Kim, H. Choi, S. Jeong, J. W. Kim, The Journal of Physical Chemistry C 2014, 118, 27884.