Iron Pyrite Nanocrystal Inks for Low-cost Photovoltaics: Surface and Material Design

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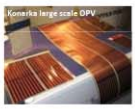
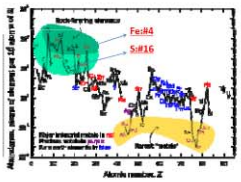
Research Motivation





Iron pyrite: Fool's gold for photovoltaics

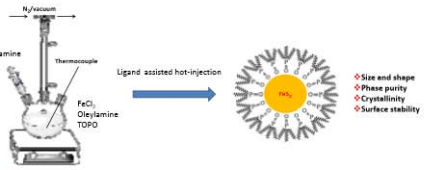
Promising:

- One of the most natural abundant semiconductor
- High absorption of light
- Band gap of 0.95 eV
- Low cost nanocrystal inks for future large scale printable solar cells

Current Problems:

- Low efficiency and photoresponce resulted from high dark current and low open circuit voltage (V_{oc})
- High density of surface defects and highly conductive impurity phase (such as FeS)
- Surface stability

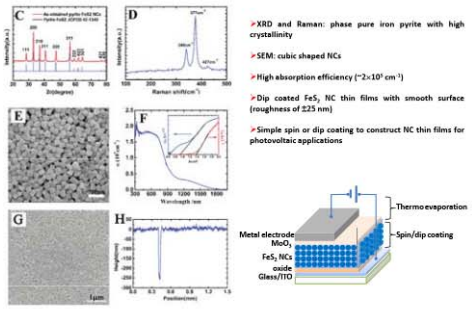
Proposed Mechanism



- Strong ligand protection with the P=O group for high crystallinity and surface stability of the NCs

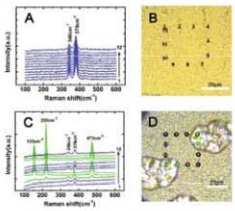
- Alloyed $Zn_xFe_{1-x}S_2$ NCs for band gap broadening and defect elimination
- Difficulties: Miscibility problem due to the size difference of Zn^{2+} (0.74 Å) and Fe^{2+} (0.61 Å)
  Large band-gap bowing effects predicted by calculation

Material Characterization and Device Fabrication

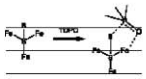


- XRD and Raman: phase pure iron pyrite with high crystallinity
- SEM: cubic shaped NCs
- High absorption efficiency ($\sim 2\times10^5$ cm^{-1})
- Dip coated FeS_2 NC thin films with smooth surface (roughness of ±25 nm)
- Simple spin or dip coating to construct NC thin films for photovoltaic applications

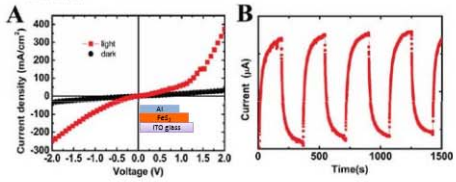
Increased Stability and Photoresponse by Ligand



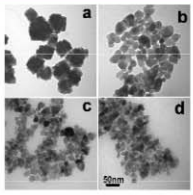
- With TOPO: stable over 1 year
- Without TOPO: surface decomposition to FeS and S as indicated by Raman mapping of the stored NC films



- The first photoresponsive pyrite NC thin film with on/off ratio of 12 from the TOPO protected FeS_2 NCs



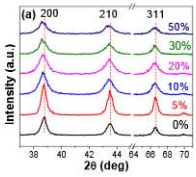
Alloyed $Zn_xFe_{1-x}S_2$ Nanocrystals

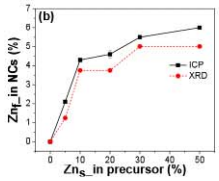


- NC size decreases with increased zinc ratio: more lattice distortion and strain to be released to the NC surface
- XRD peak shift with zinc incorporation resulted from from lattice parameter enlargement

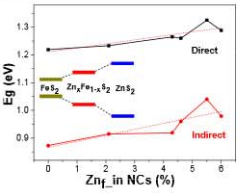
$$\frac{\Delta d}{d} = \frac{1}{\tan(\theta)}\Delta\theta$$

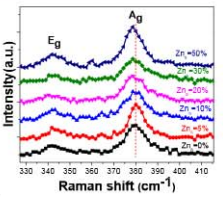
- Zn at% calculated from XRD shift and measured using ICP-AES
- 6 at% is the highest reported Zn incorporation percentage reported to date alloyed into iron pyrite

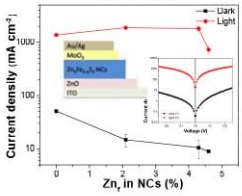




Band Gap Broadening and Dark Current Reduction







- Band gap enlargement with increased zinc alloying level in contrast to theoretical calculations
- Red shift of Ag mode in Raman indicates the increase of the S-S force constant in accord with the shortening of the bond and thus a more stable surface
- Optimized device structure and decreased dark current enable large increase of on/off ratio
- An increased band gap of the semiconductor gives lower density of thermally activated free charges and thus lower dark current

Conclusions

- We have synthesized uniform, phase pure, and air stable pyrite FeS_2 NCs.
- With TOPO as a surfactant in the reaction mixture, the pyrite FeS_2 NC films show excellent stability in air, which is also the first pyrite NC film show excellent optoelectronic properties for efficient photovoltaic application.
- Zinc alloying of iron pyrite NCs was investigated for band gap broadening. Improved alloying level up to 6 at% was achieved with comprehensive consideration of precursor ratio, capping ligands, and temperature.
- The band gap of the $Zn_xFe_{1-x}S_2$ NCs increases with increasing zinc alloying level and no band gap bowing was observed.
- Shortening of the S-S bond observed by Raman spectroscopy is expected to further improve the stability of iron pyrite.
- Increased photoresponse with zinc alloying was achieved in the $Zn_xFe_{1-x}S_2$ NC devices resulted from reduced dark current that was related to eliminated defect states.

References

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Acknowledgements

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