

High Performance Nanostructured Spectrally Selective Coating

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Project No: DE-EE0005802

**Project Title: Low Cost High Performance Nanostructured
Spectrally Selective Coating**

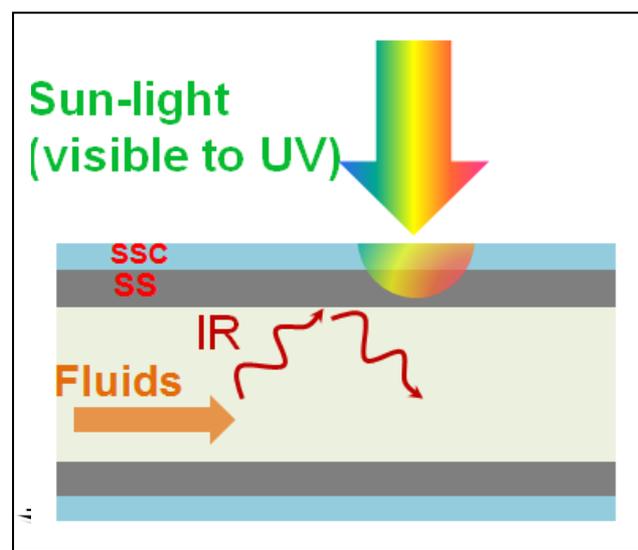
Project Period: 8/1/12 – 7/31/14

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San Diego)**

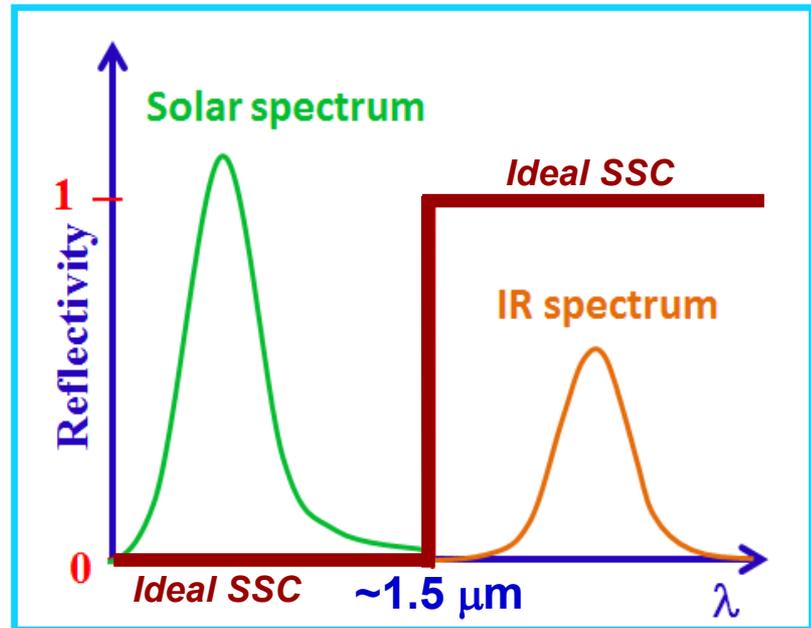
An ideal SSC would possess the following characteristics:

- (a) High spectral absorptivity α_S (>97%) in the solar spectrum (0.3-1.5 μm).
 - (b) Low spectral emissivity e_{IR} (<3%) in the IR spectrum (from $\sim 2 \mu\text{m}$ to 15 μm) corresponding to the blackbody radiation of the surface temperature of solar receivers.
 - (c) Excellent durability at elevated temperature ($\geq 750 \text{ }^\circ\text{C}$) in air and with humidity.
 - (d) Low cost, including inexpensive starting materials and scalable coating processes.
- Bandgap-adjusted semiconductor with optical cut-off wavelength of $\sim 1.5 \mu\text{m}$.

(a)

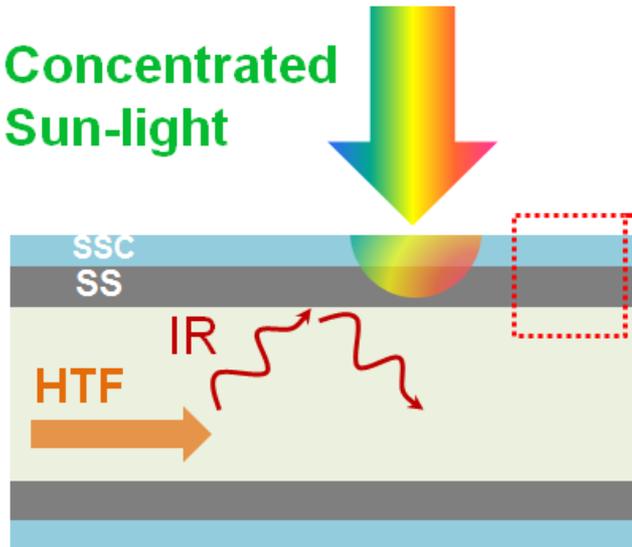


(b)

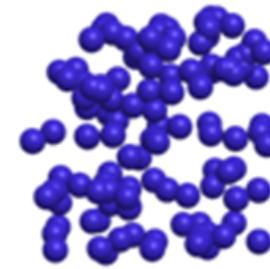


(a)

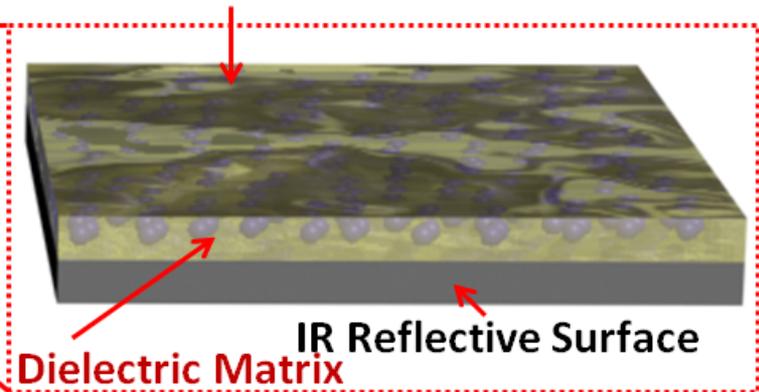
Concentrated Sun-light



(b)

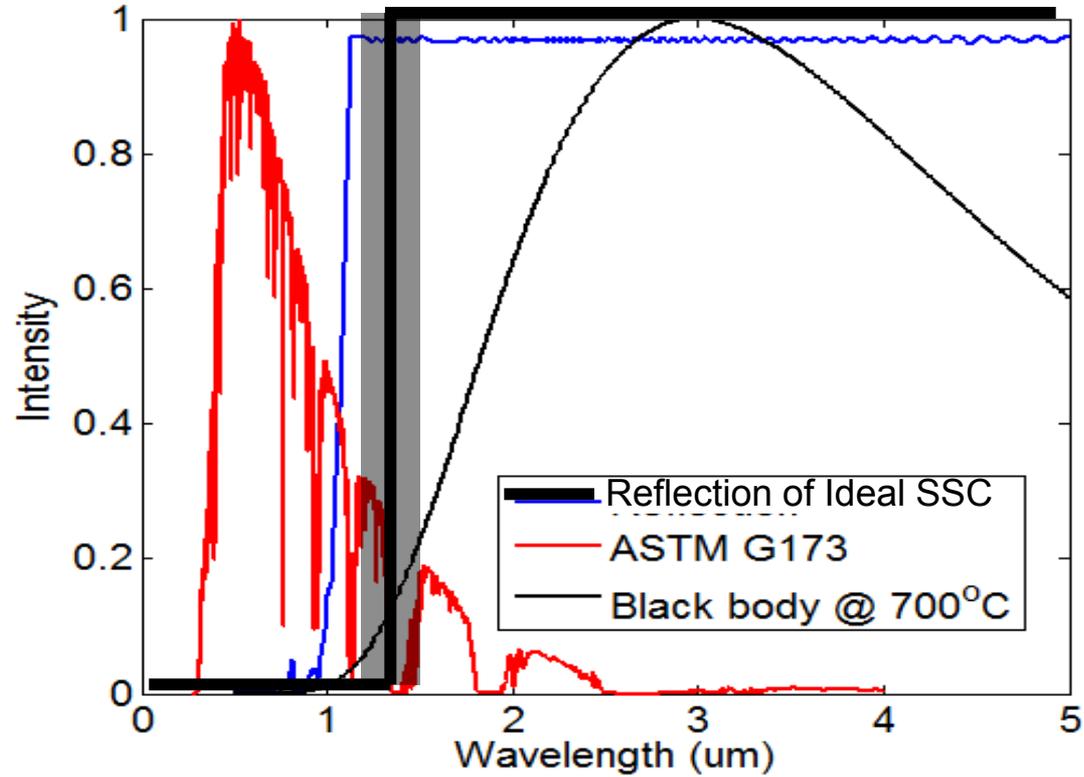


Nanoparticles



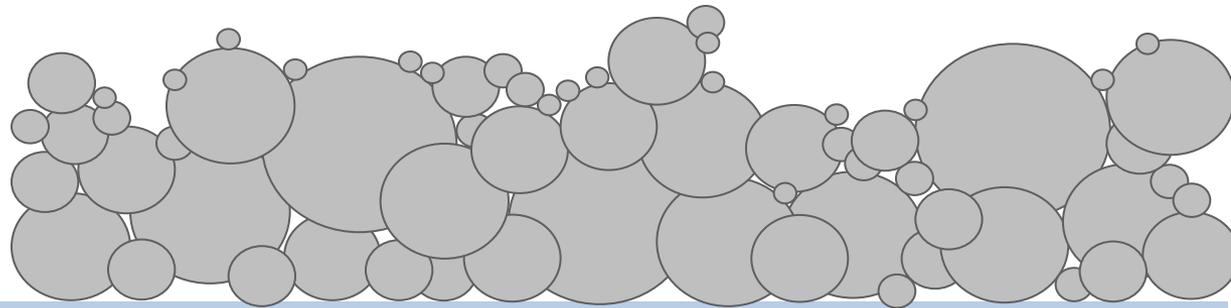
Overall schematic of the proposed spectral selective coating (SSC). (a)) A solar absorber with stainless steel (or Inconel) tube coated with SSC. The performance and durability of the SSC has significant impact on the efficiency and O&M cost of absorbers and the whole CSP systems. (b) SSC with semiconductor nanoparticles embedded in a dielectric ceramic matrix.

Ideal SSC for CSP

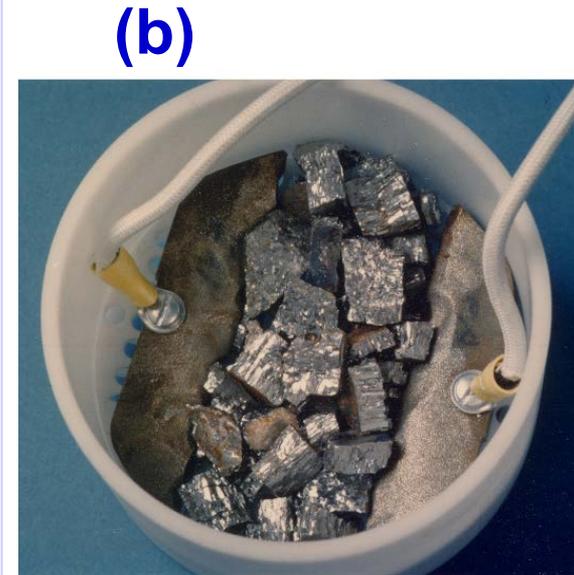
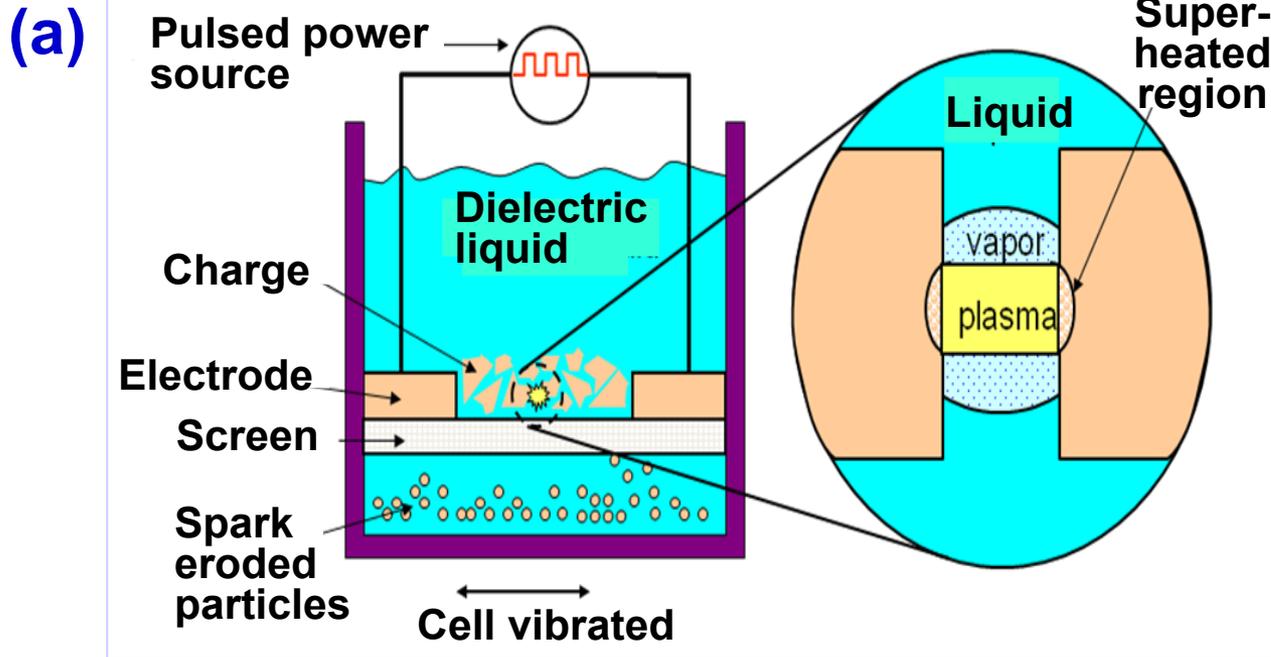


Our Strategy for High Performance SSC

- **Multi-Scale Nanostructured Surface** → No separate anti-reflection layer, enhance absorptivity by light scattering
- **Powder (+ dielectric)** → Amenable to spray coating
- **Semiconductor absorber** → desirable spectral selectivity (tunable cut-off wavelength in SiGe and other semiconductors)
- **Highly reflective metal surface** → high IR reflectivity

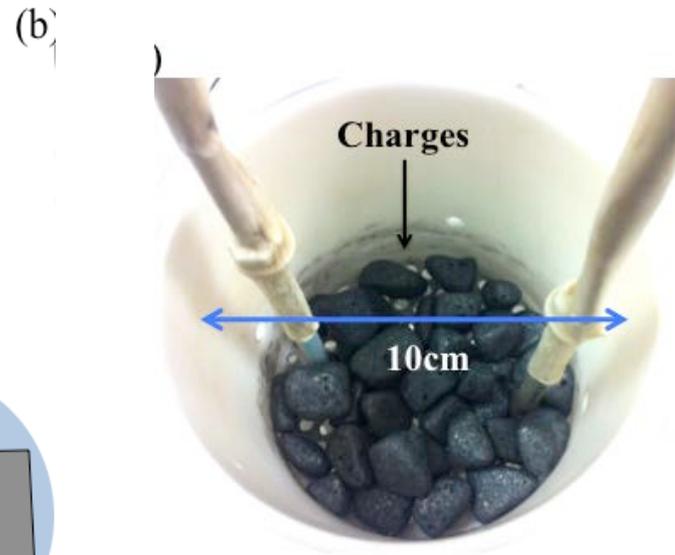
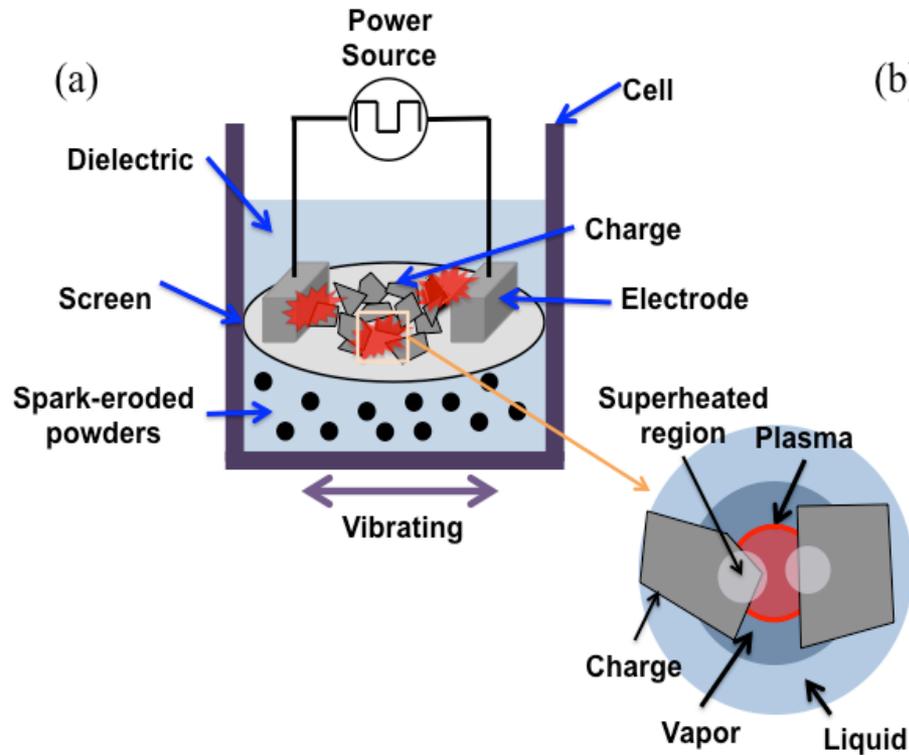


Substrate (Stainless steel
or Inconel)



Schematic illustration of spark erosion method for fabricating nano particles of semiconductor alloy. (b) Semiconductor material charges in a shaker pot container cell for spark erosion process.

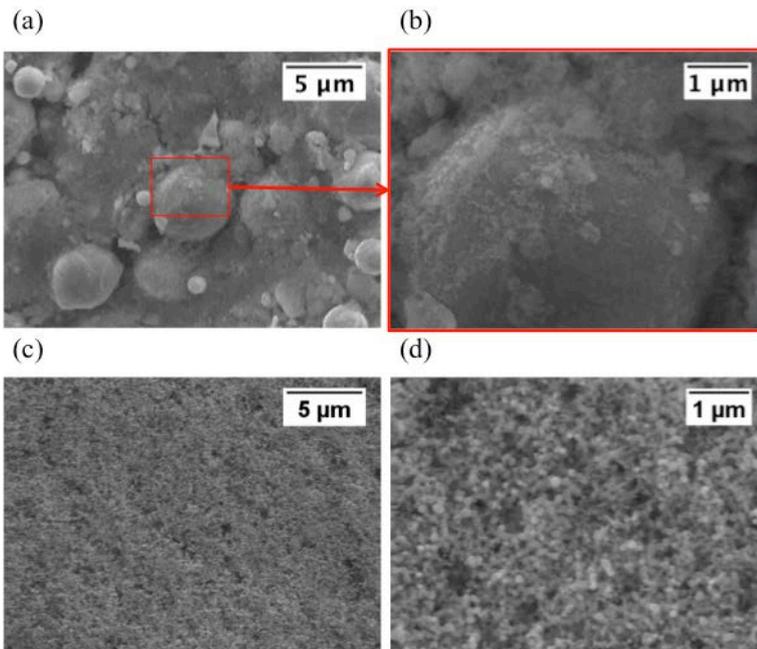
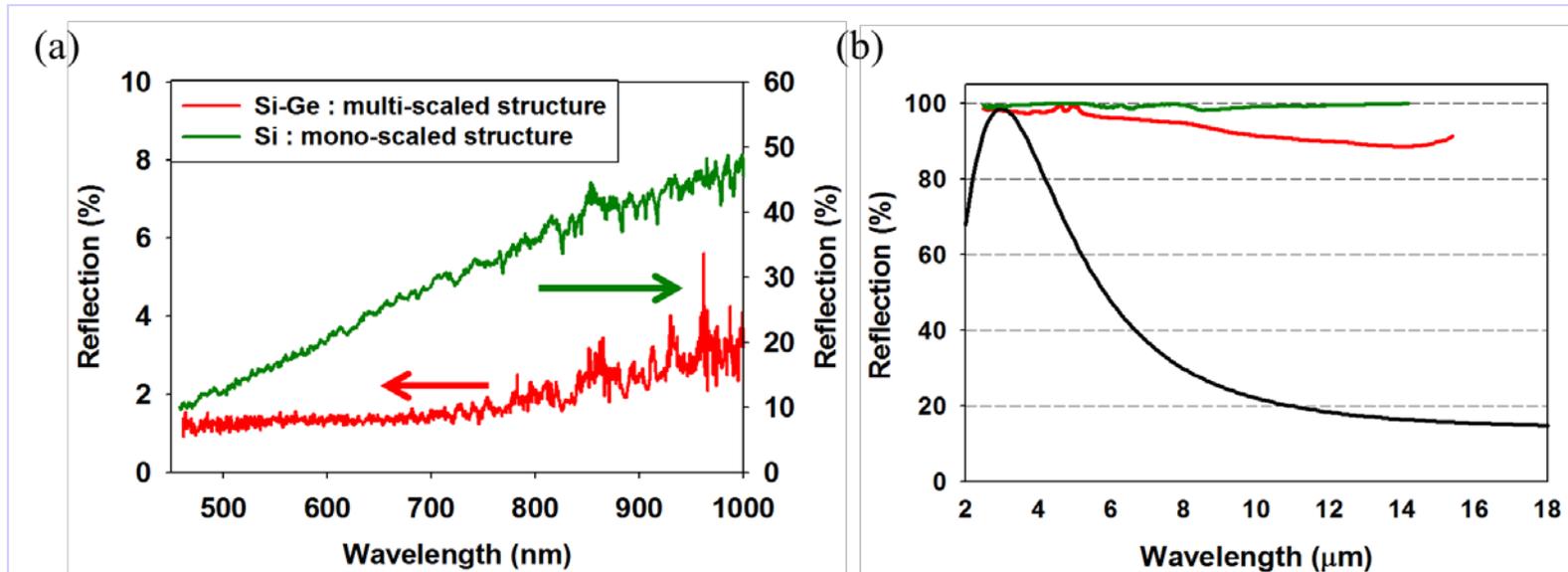
Spark-Erosion Process for High Yield Powder Fabrication



Spark Erosion Process has the following merits:

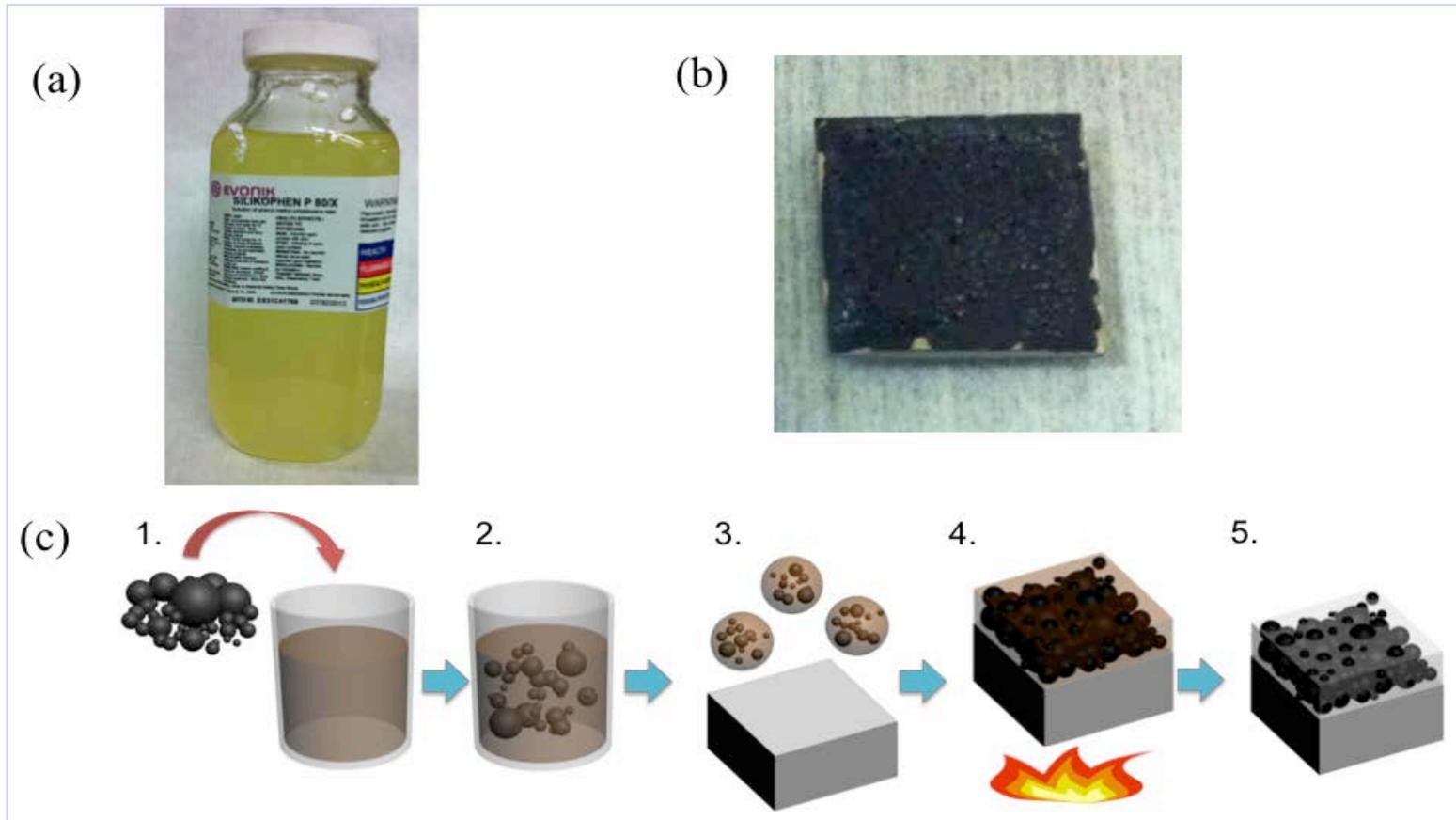
- High Yield
- Low Energy Consumption
- Versatile (works for virtually all the semiconductors and metals)
- Results in 'multi-scale' particles (next slide)
- Useful for making powders for SSC layer paste

Multi-scale vs. Mono-scale Structures

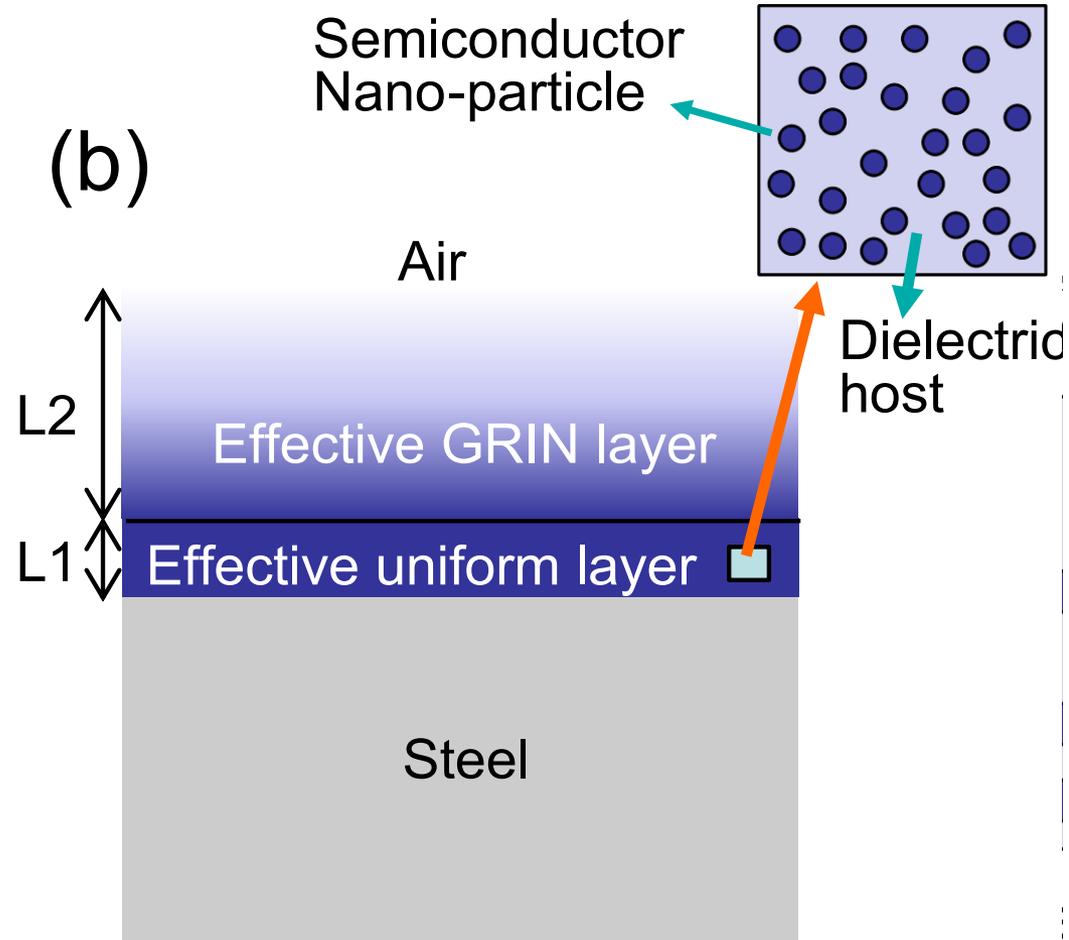
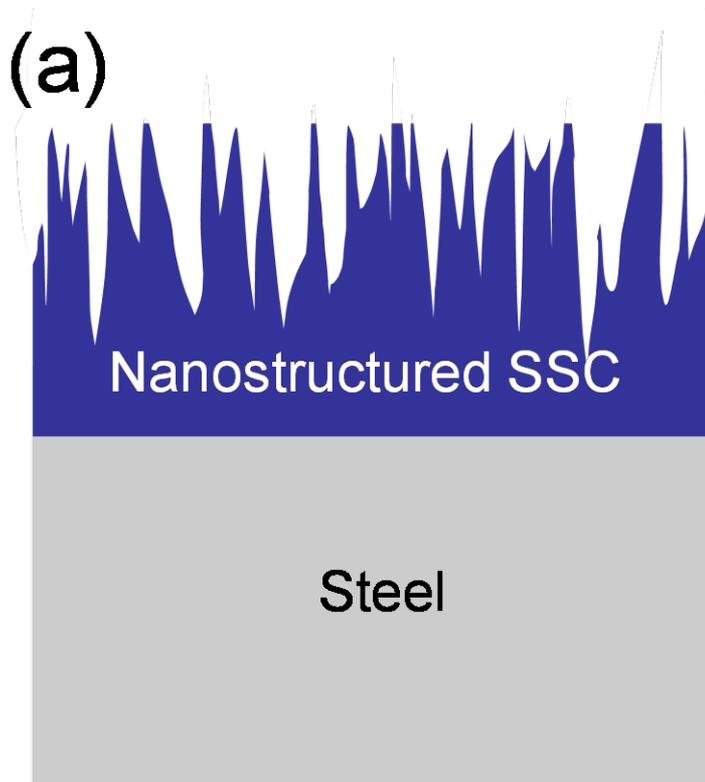


‘Multi-scale’ particles clearly show much better light absorption

Coating Process Development



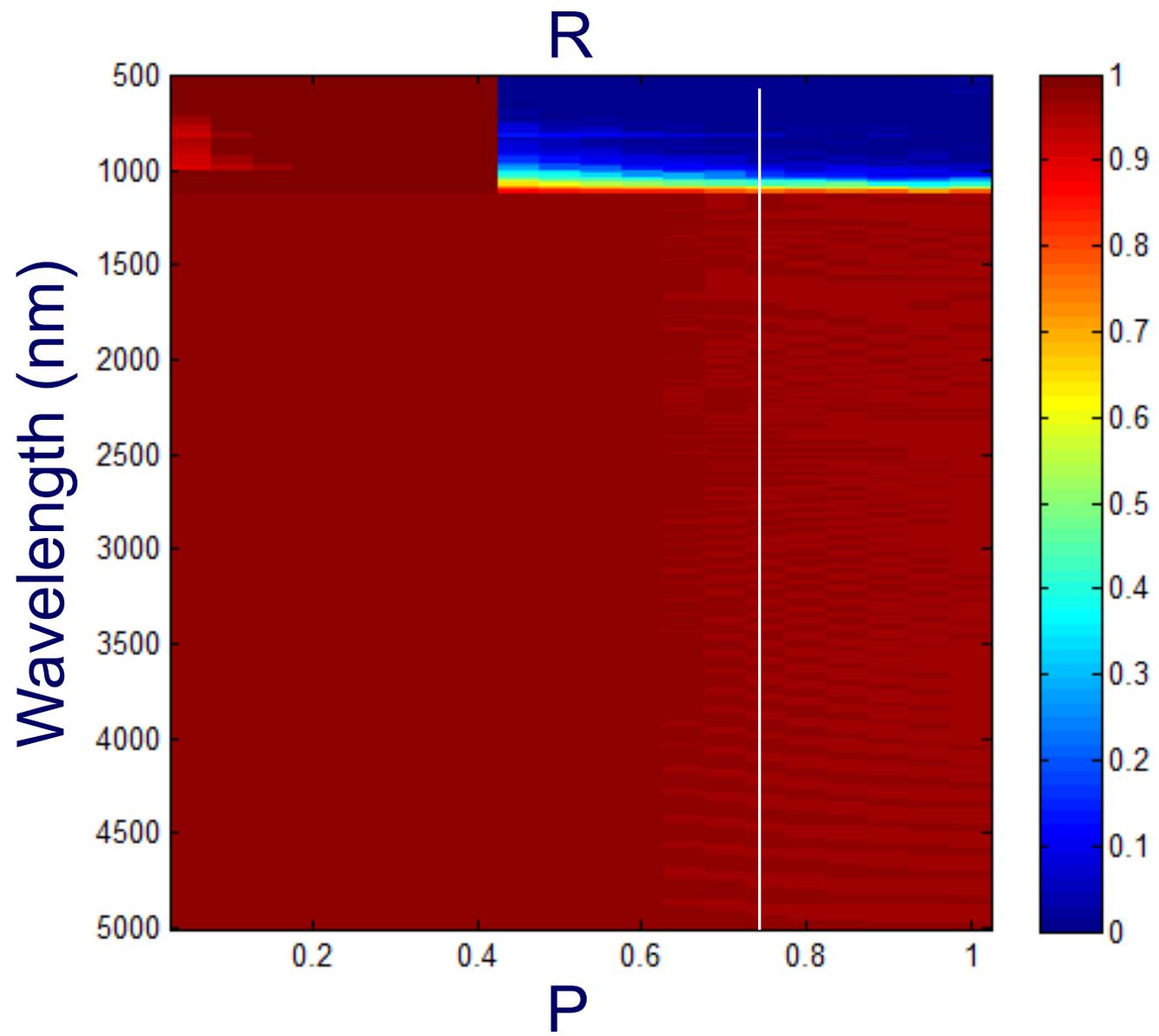
Coating of SSC with silicone resin: (a) high temperature silicone resin (b) the as-coated SiGe SSC sample (c) coating processes: 1, mixing SiGe powders with the silicone resin; 2, stirring the mixture; 3, drop casting onto targeted substrates; 4, baking; 5, the resultant particles-in-dielectric-matrix structure.



Optical modeling system. The nanostructured SSC in (a) is modeled by a multilayer system schematically shown in (b). The effective materials properties of each layers can be described by the effective media theory when the particle size is much smaller compared to the operation wavelengths.

Simulated reflectance from the SSC layer vs incident wavelength and the volumetric filling ratio of the nanoparticles p is shown on the right.

- The materials of the nanoparticles and the dielectric host are Si and SiO₂ in this specific calculation. The SSC layer shows sharp contrast change when the Si filling ratio is greater than 42%. The cut-off wavelength of the reflectance is around 1.1 μ m, which is aligned well with the bandgap of Si.**
- The detailed reflectance data is shown on the right along with spectrum and the blackbody radiation spectrum at 700 °C, when the Si filling ratio is 75% (i.e. $p=0.75$). Based on these calculation results, the solar absorptivity α is around 99% and the IR emissivity ϵ is about 4%.**
- It was found that the overall high performance is achieved by three major factors:**
 - (1) The surface texture of the nanocomposite materials, i.e. the effective GRIN layer. This layer acts as a perfect light trapping layer or anti-reflection layer when the texture size is subwavelength at visible frequencies (typically < 300nm).**
 - (2) An appropriate nanoparticle material and filling ratio. These are the key parameters to tune the cut-off wavelength in the reflectance.**
 - (3) Flat metal layer to improve the reflectance at IR wavelengths. The surface roughness should be deep-subwavelength at IR frequencies (typically <100nm) to reduce the absorption due to surface light trapping.**

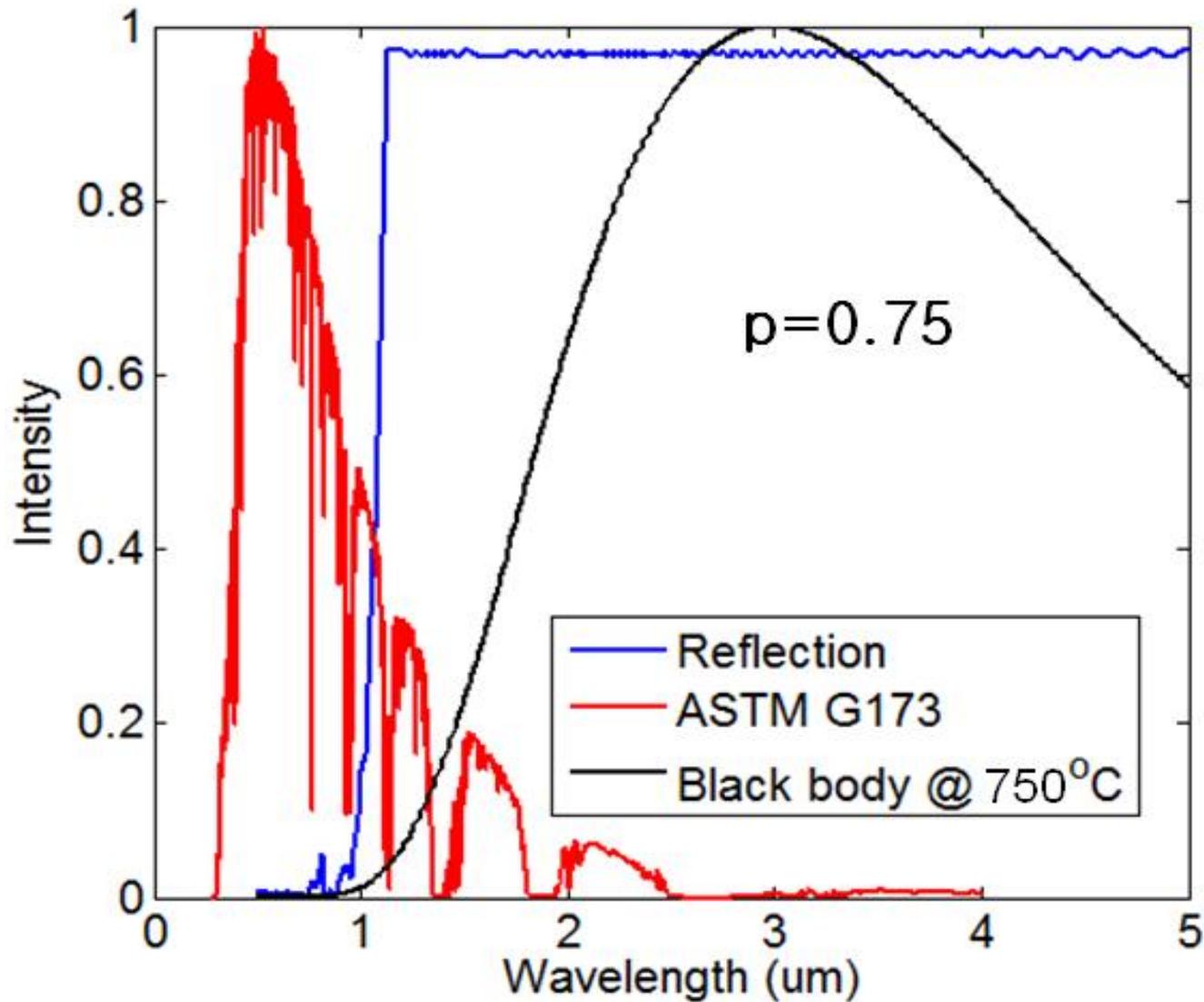


--- Preliminary measurements of optical absorption of SiGe nanoparticle SSC coating indicate low reflectivity (1-4%) across the entire visible to near-IR spectrum.

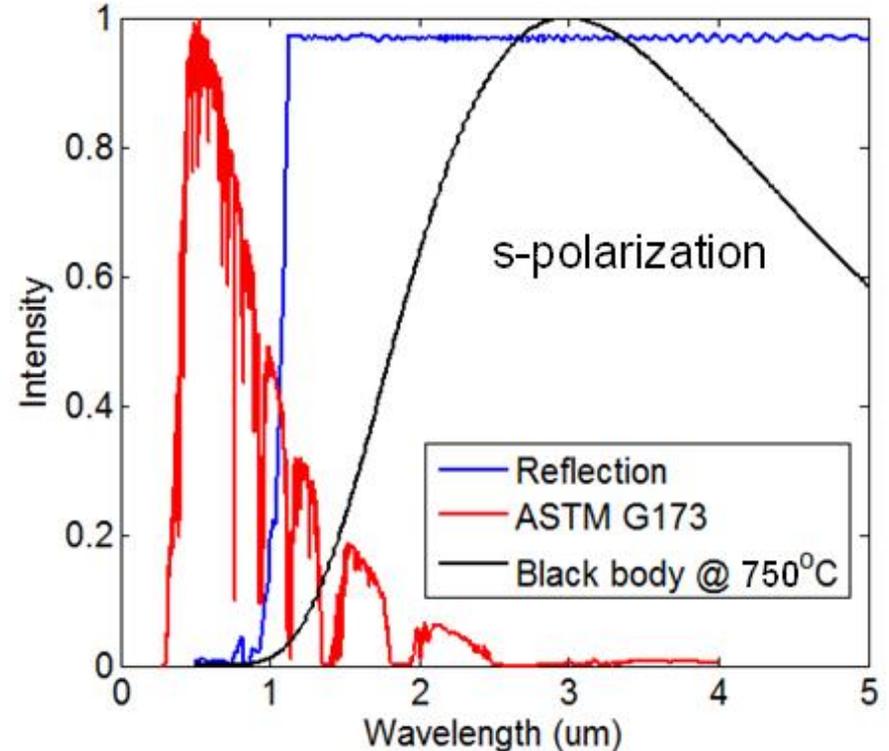
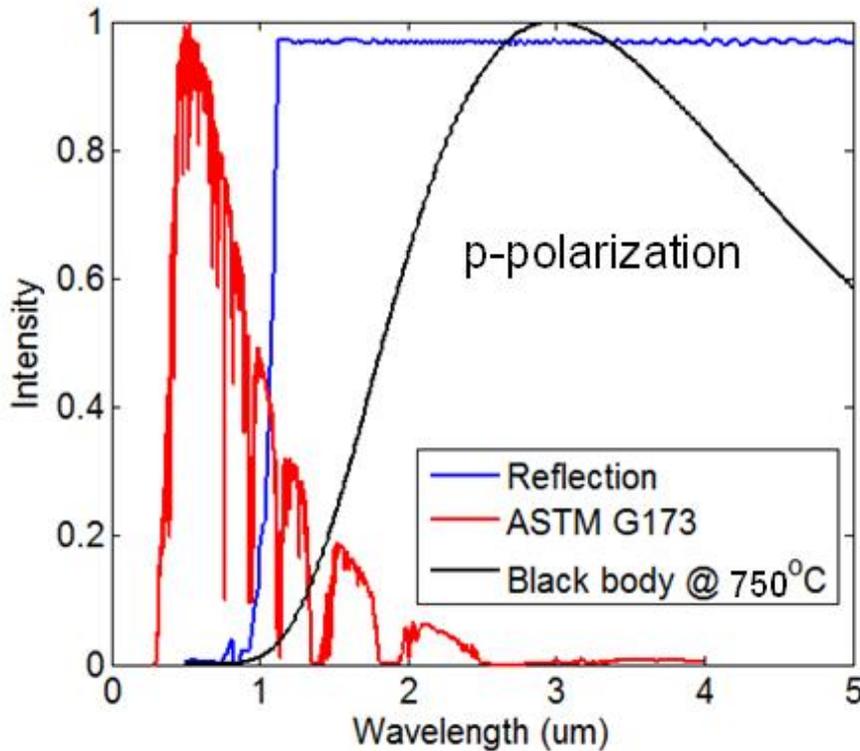
---- Due to the micro/nano scale roughness and high optical absorption of the coating layer.

--- The roughened surface effectively traps visible light, leading to extremely low reflection, such that there is no need for any additional AR coating.

--- Also tested the optical performance for SiGe SSC layer at IR frequencies, which showed excellent reflection (>96%) around the peak blackbody radiation wavelengths at 700°C (~3 μm), which is the result of the low absorption coefficient when the light energy is below the semiconductor bandgap (~1.04 eV or 1.2 μm for $\text{Si}_{0.8}\text{Ge}_{0.2}$). Without much optimization, the results ($\alpha_s \sim 96 - 99\%$, $\varepsilon_{\text{IR}} \sim 1 - 4\%$) prove the excellent performance from the proposed semiconductor nanoparticles based on SSC layers, as expected from our simulations.

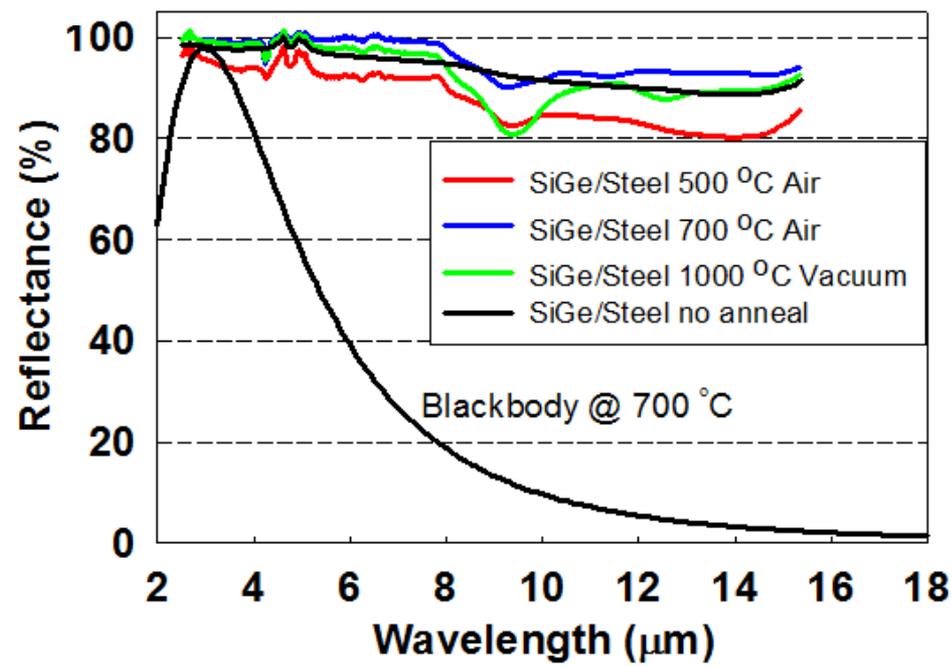
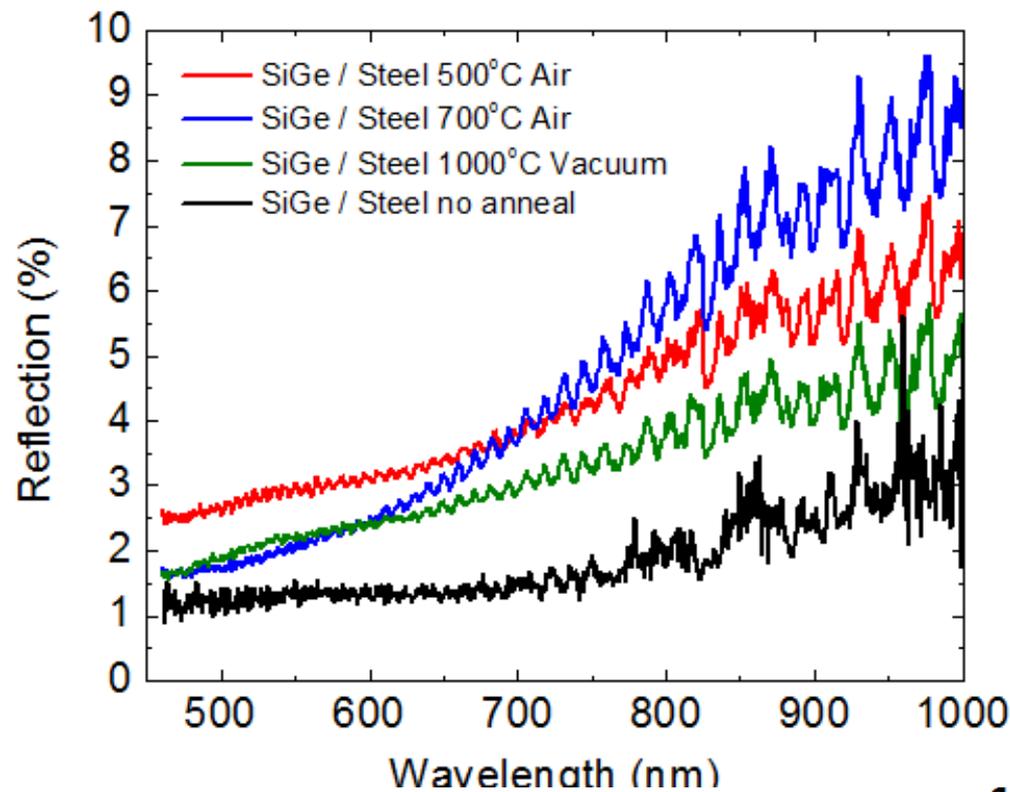


***Reflectance data when
 p is equal to 0.75***



polarization. The incident angle is 30 degrees.

Calculated reflectance dependence on the incident angle for both polarizations. The polarization and the incident angle do not affect the reflectance much, which also proves the robustness of the proposed SSC layer.



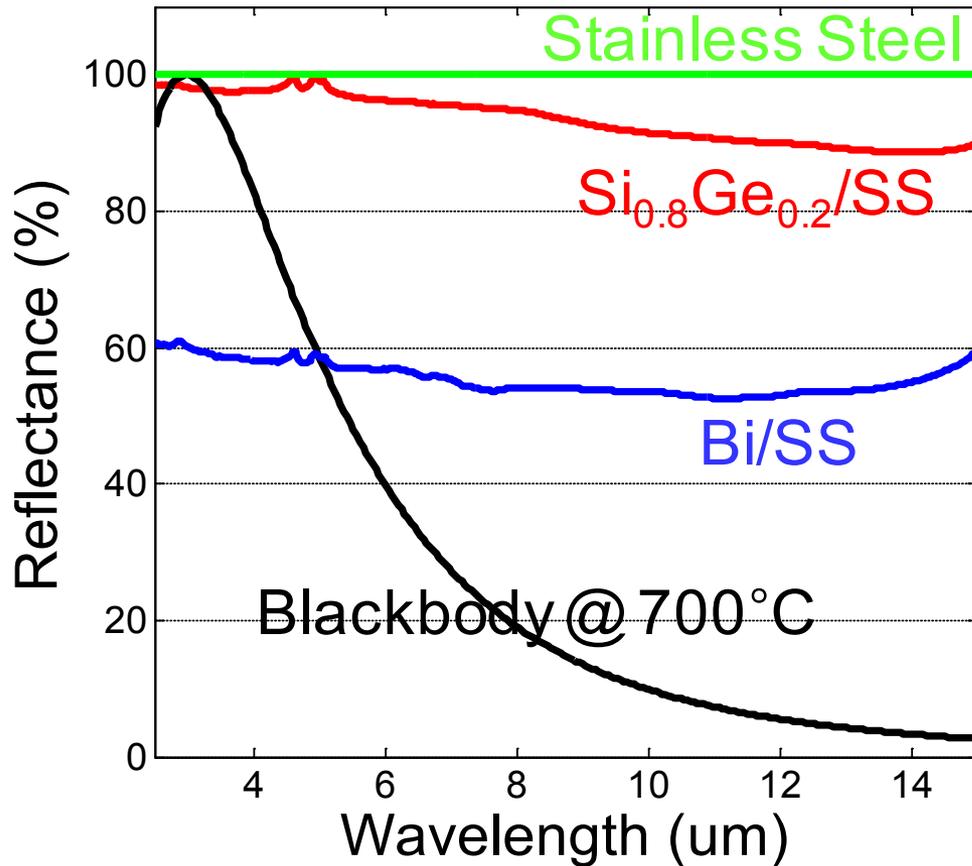


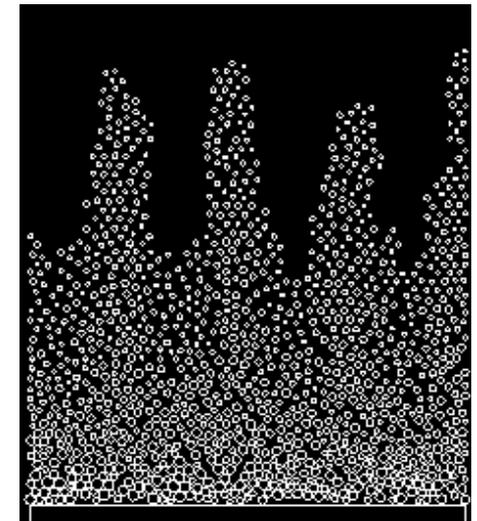
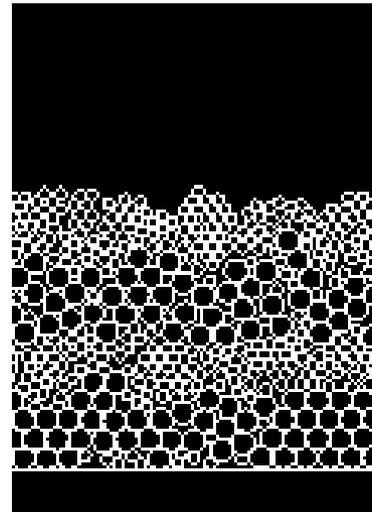
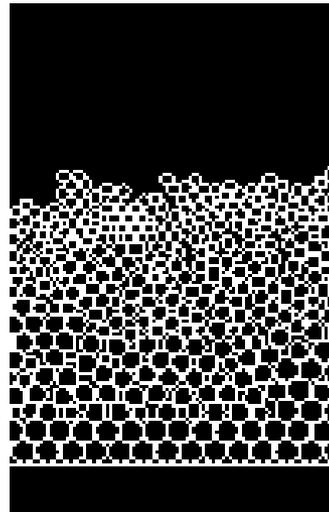
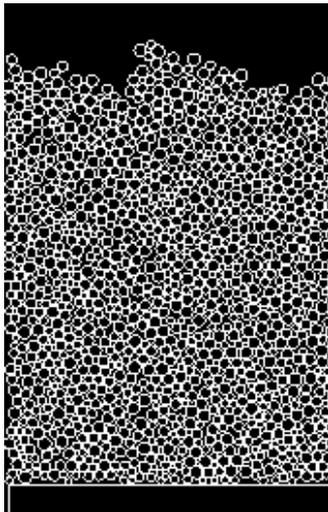
Figure 11: IR reflectance (2.5-15 mm) for various samples at IR frequencies. SiGe shows 96-99 % reflectance from 2.5-8 μm , close to that of the stainless steel substrate. The high IR reflectance is caused by the transparency of SiGe to light with energy less than its band gap (1.2 μm). As a control, metal NPs (Bi) show a much lower IR reflectance

Microstructure Consideration

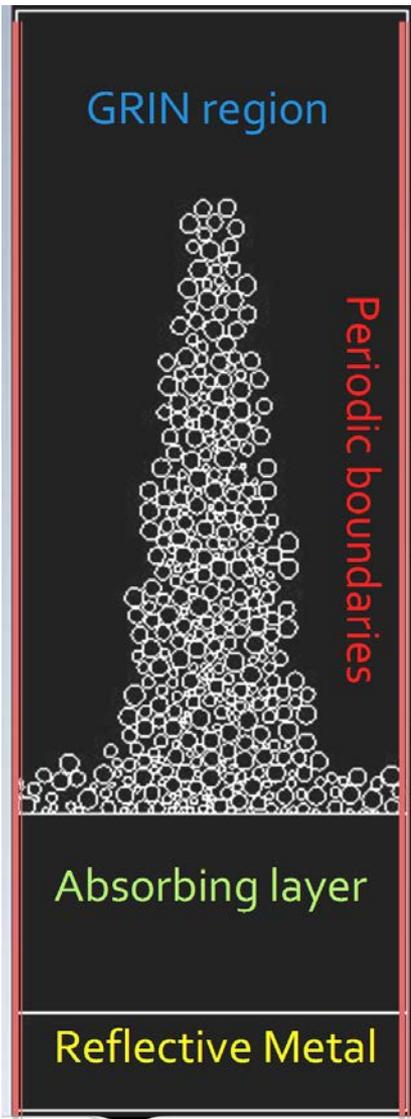
COMSOL® Multiphysics simulations: finite element modeling which considers interfacial and geometrical effects

2D simulations provide guiding insight into underlying light trapping mechanisms while greatly reducing computational times

3D simulations will be needed in the future



Basic Comsol Simulation Setup

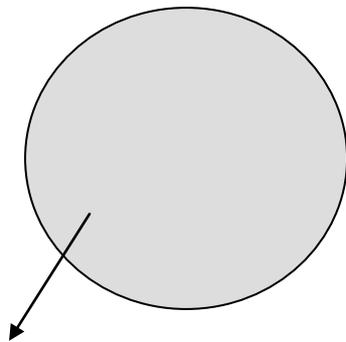


- **Periodic boundaries represent an infinitely repeating structure**
- **GRIN region with Si nanoparticles**
- **Absorbing layer mimics the absorption properties of Si over 20 μm of thickness (exaggerated extinction coefficient). This is purely for reduction of needed computation time. Previous results have confirmed that this 1 μm layer behaves identically to a 20 μm layer of 'regular' silicon.**

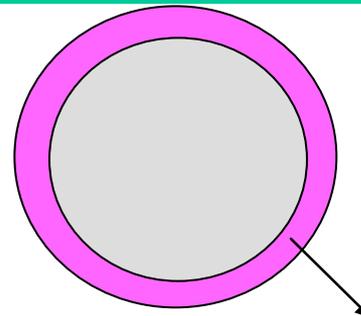
• SSC layer nanoparticles

- Bandgap adjusted semiconductor nanoparticles for high absorptivity combined with low IR emission
- However, for 750°C operation in air (such as for solar tower application), the nanoparticles in the SSC layer have to be oxidation resistant for many months/years.
- Semiconductors are not known to be strongly oxidation resistant.
- Surface coating via core-shell structuring desired.

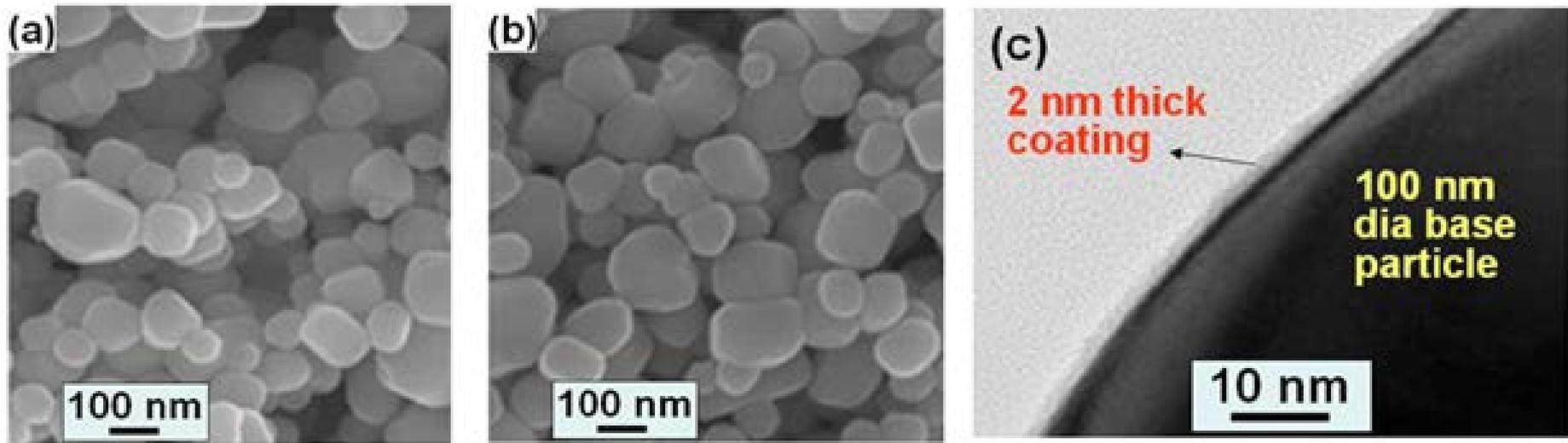
Ceramic coating on SiGe nanoparticles



Spark eroded, 50 – 200 nm size SiGe nanoparticles



Ceramic shell around SiGe nanoparticles



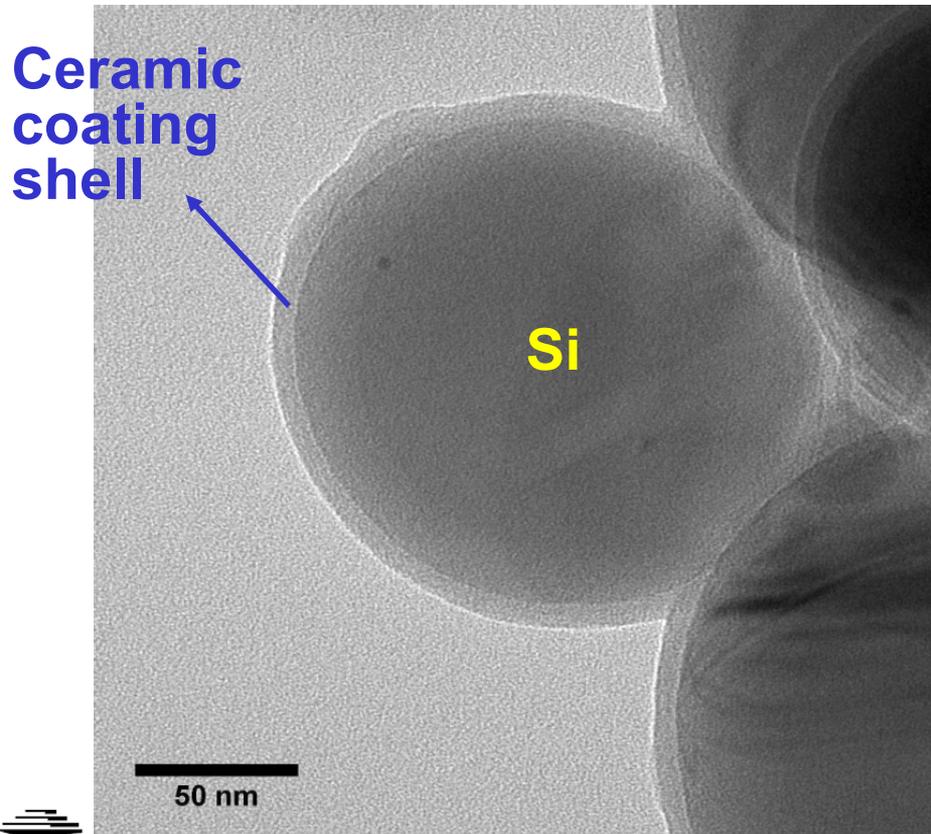
Example protective coating with thin ceramic layer. SEM images of Ti Nanoparticles, before (a) and after (b) the monolayer Al₂O₃ coating by relatively simple, organic-inorganic sol-gel synthesis technique. (c) TEM image of the 2nm thick coating.

Synthesized Core-Shell NanoParticles

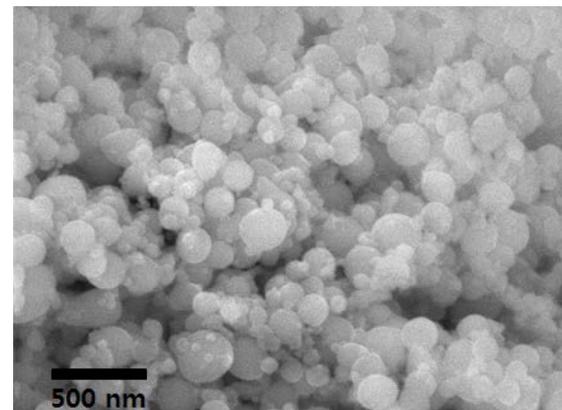
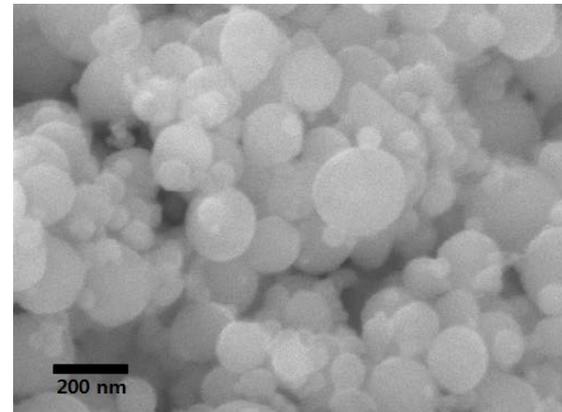
--- Core = Si or Si-Ge (APS ~ 100 nm)

--- Shell = 5~15 nm thick conformal ceramic coating)

TEM Image



SEM Image



ThermoGravimetric Analysis (TGA) at 900°C/6 hr for ceramic-shell-coated Si NPs vs. bare Si NPs (avg particle size ~100 nm)

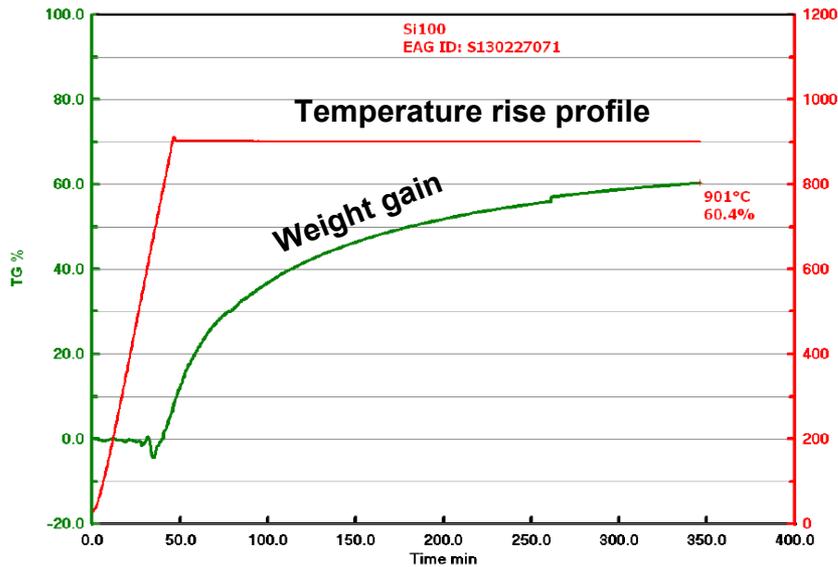


Fig. 1. TGA profile of Si NPs in pure oxygen atmosphere at 900°C.

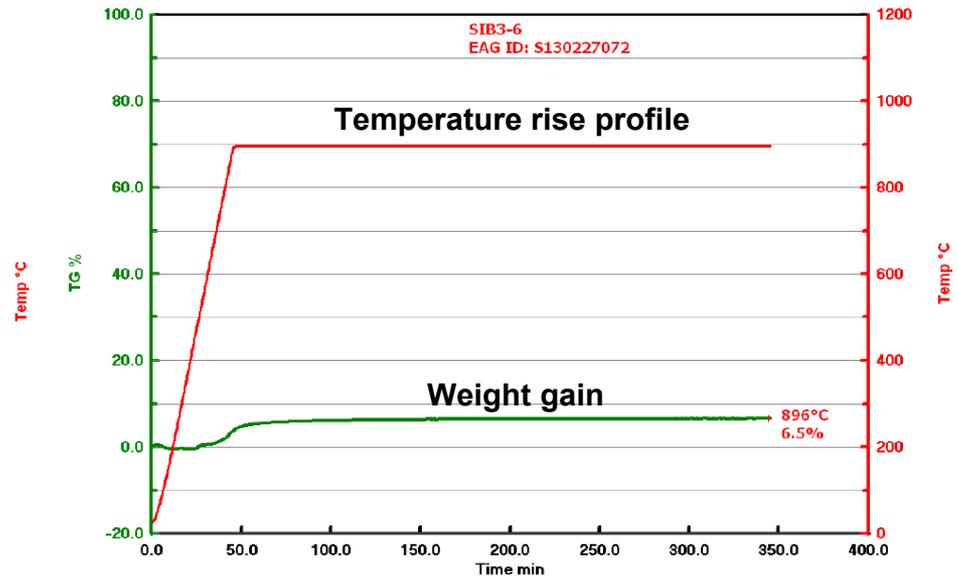


Fig. 2 TGA profile of ceramic-coated Si NPs in pure O₂ atmosphere at 900°C.

- This accelerated oxidation test in O₂ by TGA analysis indicates that ceramic-shell coated Si NPs exhibit a much higher resistance to thermal oxidation than bare Si NPs.
- Core shell Si particles: **+6.5 wt% wt gain** vs. bare Si : **+60.4 wt% wt gain**.
- Even this 6.5% weight gain for the core-shell structure occurs essentially only during the initial stage exposure to 900°C, followed by very little oxidation afterwards. Therefore, this 6.5% weight gain may be due to i) Non-uniform coating of the shell for some particles that tend to oxidize away and contribute to most of the observed weight gain, or ii) there might be some phase transformation that essentially stops the additional oxidation after the initial heating. Further analysis in progress.

Summary and Outlook

The research team at UCSD is working to demonstrate a nanoparticle-based coating that can achieve an effective solar absorptance greater than 97% and an effective infrared emittance lower than 5% at 750 °C. This could enable high thermal conversion efficiencies and increased temperature ranges for heat-transfer fluids ($\geq 650^{\circ}\text{C}$).

The goals of this project are to:

- i) Fabricate semiconductor nanoparticles and spray-coat them onto an absorber metal surface,**
- ii) Model and characterize optical and thermal properties, such as solar absorptance and infrared emittance,**
- iii) Achieve high-temperature durability by using modified semiconductor nanoparticles having ceramic protective coating layer.**