Volume phase transition in SWNT/PNIPAM hybrid microgels triggered by photo-thermal conversion under NIR-laser irradiation

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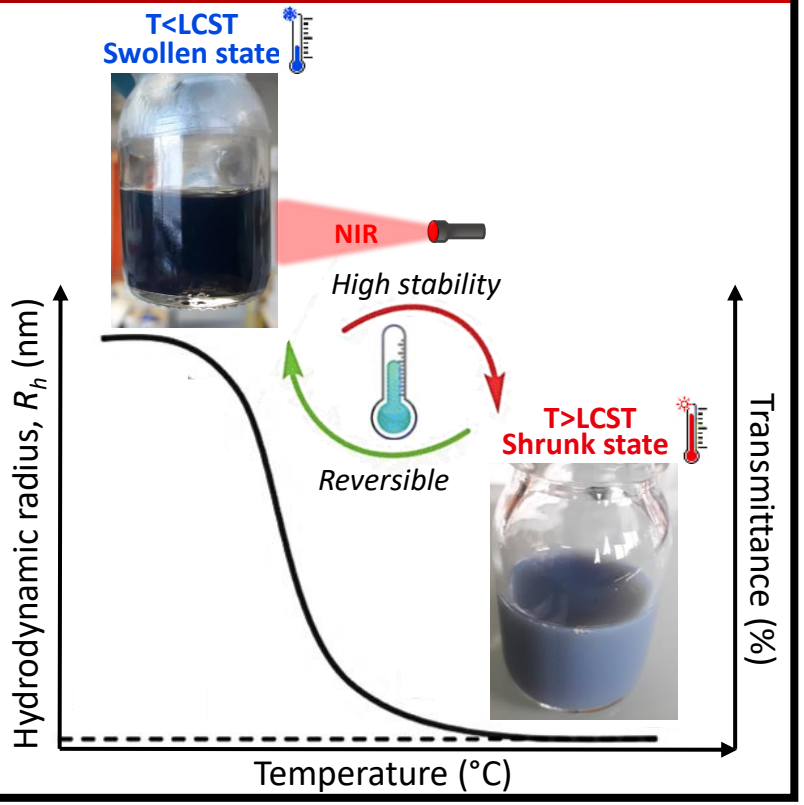
Abstract

Here we describe the preparation of hybrid microgels based on poly(*N*-isopropylacrylamide) (PNIPAM) and single-walled carbon nanotubes (SWNT) through non-covalent functionalization. The nanoparticles show a volume phase transition (VPT), which can be promoted by direct heating or by resonant photo-thermal conversion of semiconducting SWNTs in the near-infrared (NIR). The photoluminescence (PL) can be used to monitor the VPT thanks to a redshift observed when crossing the lower critical solution temperature (LCST).



Motivation

Some gels can exhibit a shape-change when submitted to environmental modifications, like PNIPAM, a known thermo-responsive polymer. SWNT show absorption bands in the NIR and can be used as a molecular heater to trigger the transition.

Objective

To design a hybrid material based on SWNT/PNIPAM in order to take advantage of the non-radiative relaxation process of excited SWNT by NIR irradiation to promote the VPT of PNIPAM through an efficient photo-thermal conversion.

Introduction

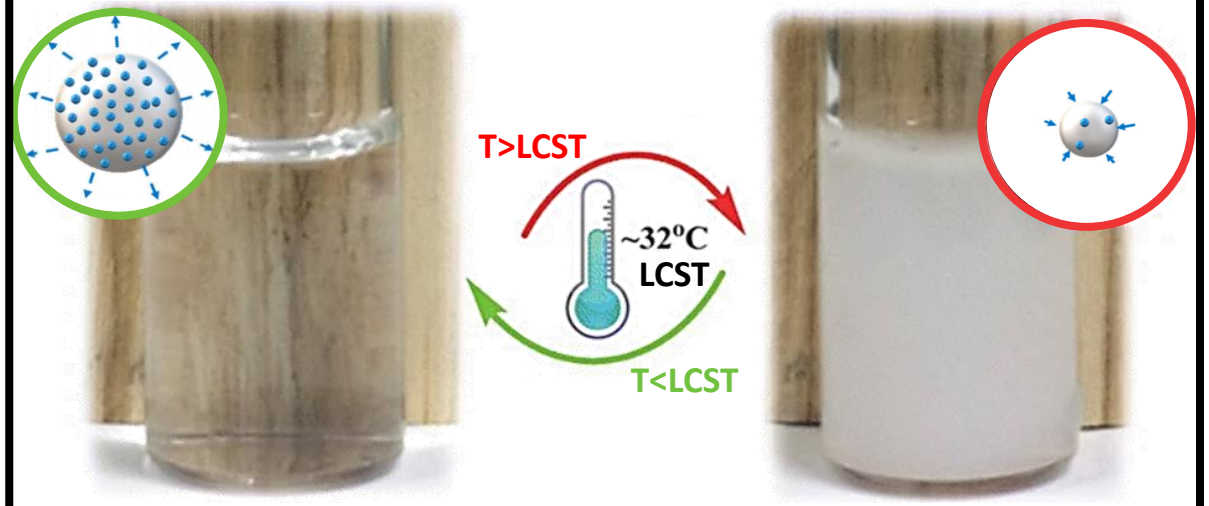


Figure 1. Schematic diagram of phase-transition behavior of PNIPAM. [Edited from: 1]

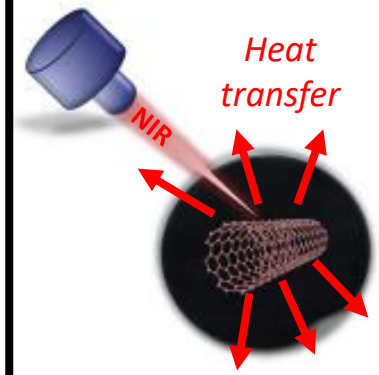


Figure 2. Schematic representation of photo-thermal heating by SWNT.

Linear chains of PNIPAM are water soluble at room temperature but undergo a reversible coil-to-globule transition at a LCST close to 32°C due to their dehydration and subsequent collapse into compact globules. [1-2] We have used this common material to design photo-responsive microgels based on SWNT. Carbon nanotubes can be used as a photon antenna with an adequate wavelength to locally heat the gel and promote the VPT through photothermal conversion. [3-4]

Synthesis of hybrid microgels

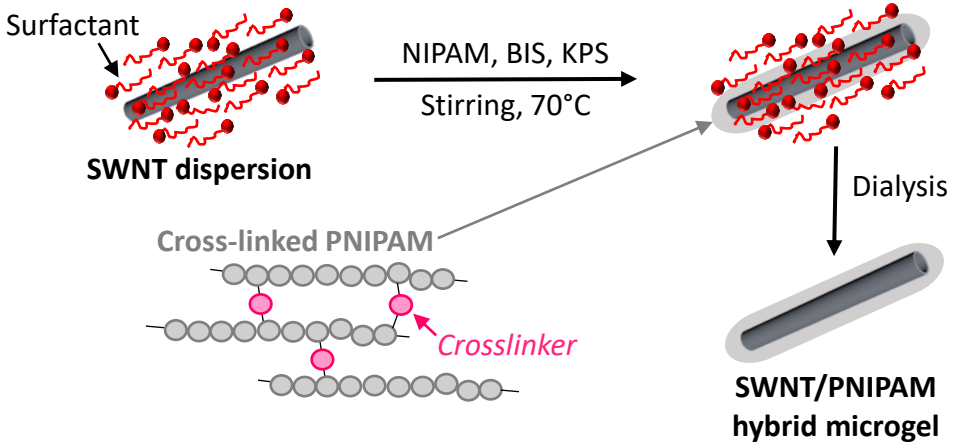


Figure 3. Schematic illustration showing the synthesis of PNIPAM/SWNTs hybrid microgels.

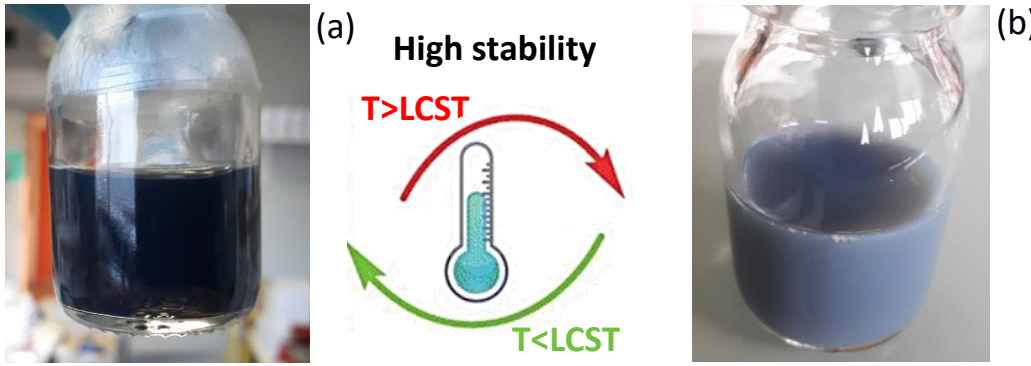


Figure 4. Phase transition behaviour of aqueous SWNT/PNIPAM hybrid microgels solution: (a) T<LCST and (b) T>LCST. By heating, the solution becomes opaque by shrinkage of the polymer without visible aggregation. The shrunk microgels return to the swollen state though cool down to room temperature.

Results and discussion

Morphology

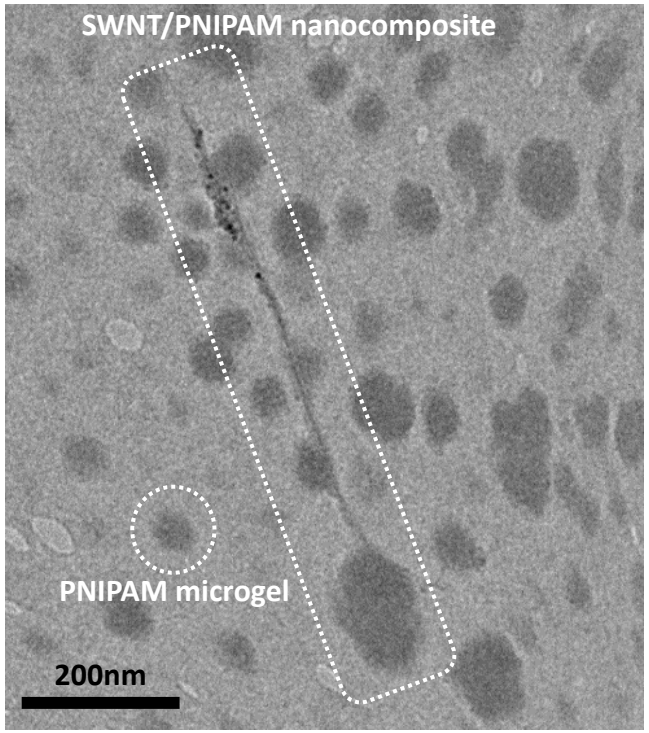


Figure 5. Transmission electron microscopy (TEM) picture of SWNT/PNIPAM hybrid microgels particles.

SWNT/PNIPAM nanocomposites has been obtained.

Thermal behavior

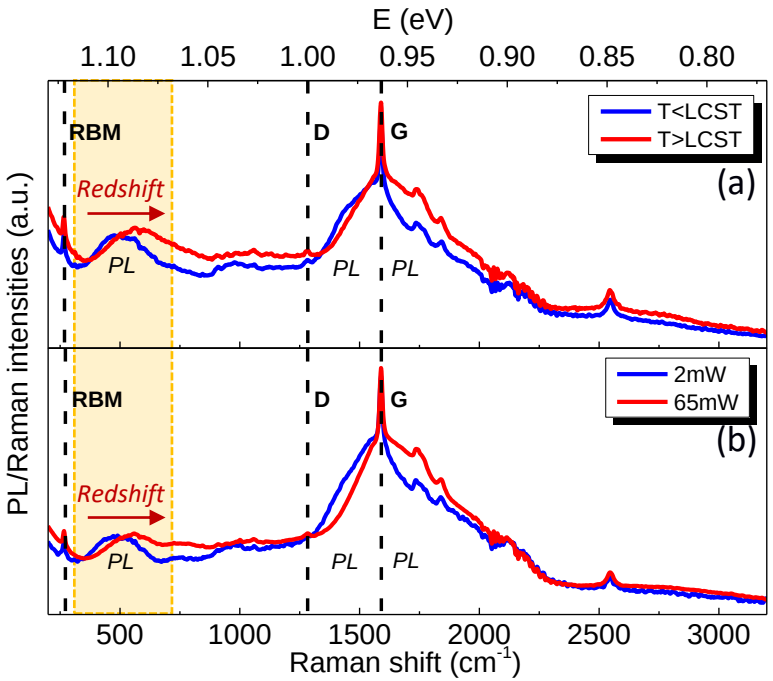
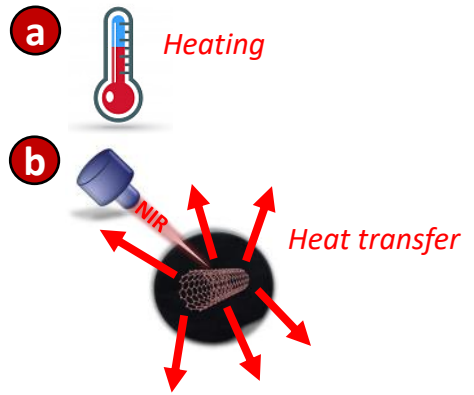


Figure 6. Comparison of coupled PL/Raman spectra (E_{laser} = 1.17eV, λ_{exc} = 1064nm) of SWNT/PNIPAM hybrid microgels below and above the LCST of PNIPAM (a) and as a function of the laser power (b). Raman signatures, labelled RBM, D and G, are superimposed to broader PL bands.

1) VPT promoted by:



2) PL signal can be used to monitor the VPT:

- Redshift observed when crossing the LCST.

Conclusions

- Smart SWNT/PNIPAM nanocomposites have been prepared through a non-covalent functionalization technique.
- SWNT/PNIPAM hybrid microgels are stable in water and show a volume phase transition, which can be promoted either by direct heating or by excitation of the resonant absorption of semiconducting SWNT in the NIR.
- The photoluminescence signal of semiconducting SWNT is modulated at the phase transition and therefore can be used to monitor the VPT under irradiation.

References

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