Thermosensitive Au-PNIPA Yolk–Shell Nanoparticles with Tunable Selectivity for Catalysis

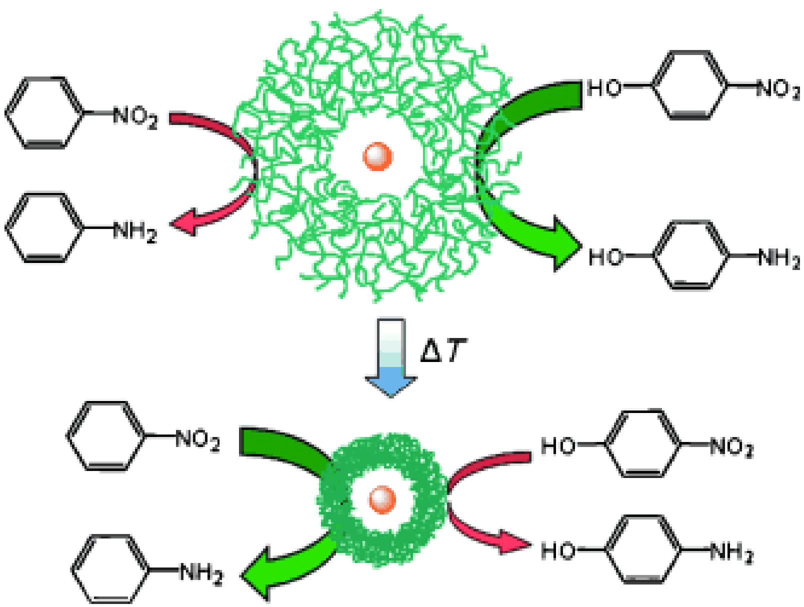
Shuang Wu, Joachim Dzubiella, Julian Kaiser, Markus Drechsler, Xuhong Guo,Matthias Ballauff, and Yan Lu*

State-Key Laboratory of Chemical Engineering, East China University of Science and Technology, 200237 Shanghai (China)

F-I2 Soft Matter and Functional Materials, Helmholtz-Zentrum Berlin fr Materialien und Energie,14109 Berlin (Germany)

Institut fr Physik, Humboldt-Universitt zu Berlin, 12489 Berlin (Germany)

Makromolekulare Chemie II, University of Bayreuth, 95440 Bayreuth (Germany)



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Ammu Mathew

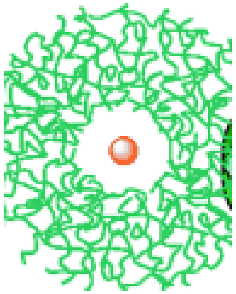
Introduction

- free NPs in Catalysis – aggregation, difficult to handle
- Thermosensitive microgels - smart carrier systems - react on external stimuli

Ex: thermosensitive polystyrene (PS)-poly(N-isopropylacrylamide)(PNIPA)

- The catalytic activity of immobilized metal nanoparticles can be tuned by the swelling and shrinking of the microgels.
- Yolk shell structure - consist of a single metal nanoparticle within an inorganic or polymeric shell

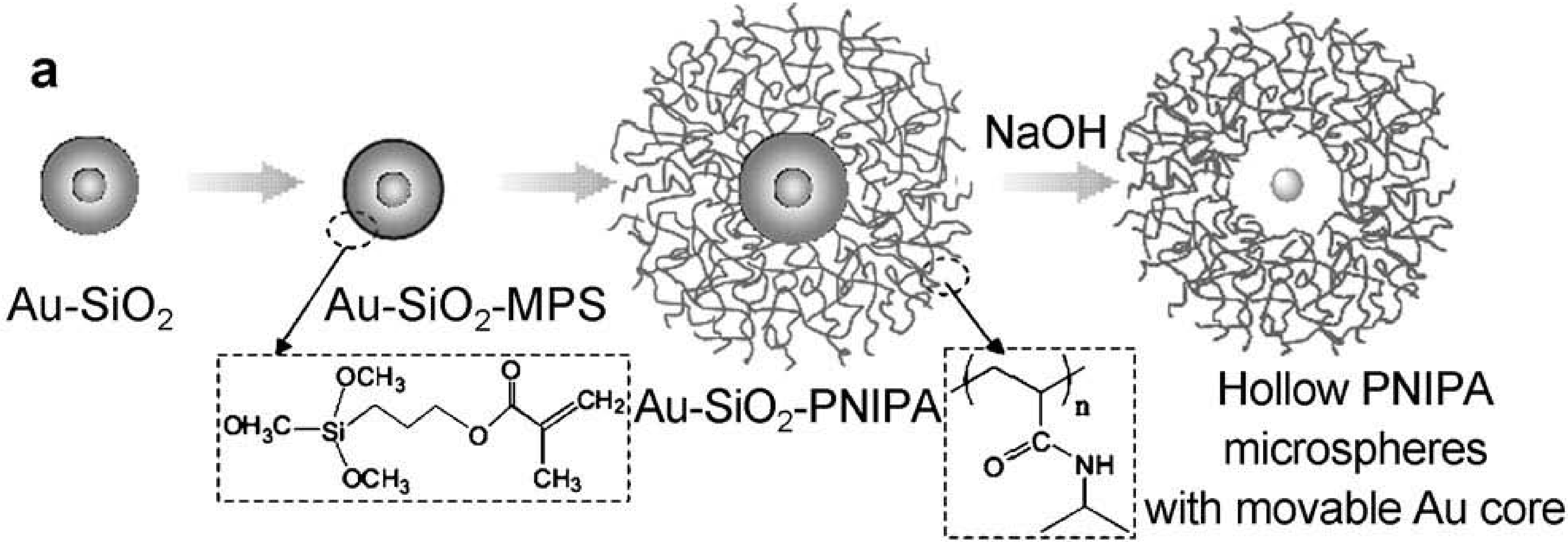
*Prevents aggregation
*Free surface of Au NP compared to Au@PNIPA core-shell system
*Permeability of shell can be tuned

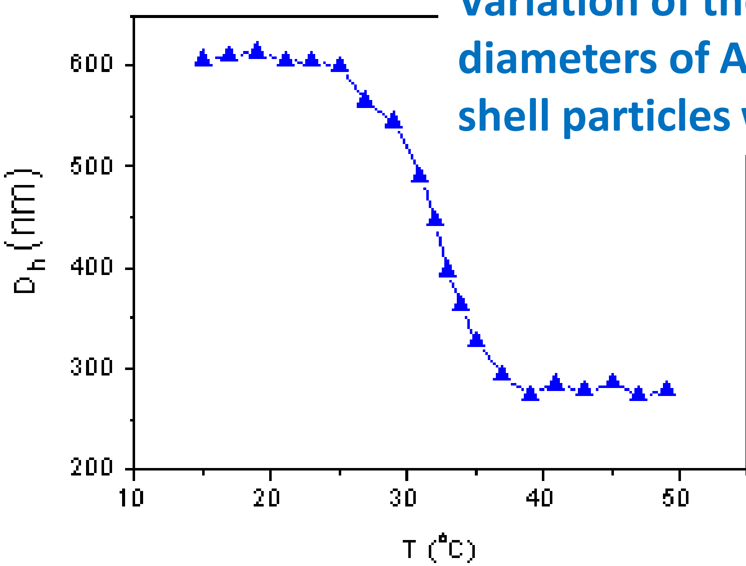


In this paper

- A thermosensitive yolk–shell system that uses temperature as a trigger for the reaction.
- A single Au nanoparticle is encapsulated in a hollow thermosensitive PNIPA shell.
- Reduction of hydrophilic 4-nitrophenol and hydrophobic nitrobenzene by sodium borohydride using this catalyst is demonstrated.
- Combination of these reactions was used to study the selectivity of the catalyst.
- The selectivity of the enclosed metal nanoparticles can be tuned by temperature.

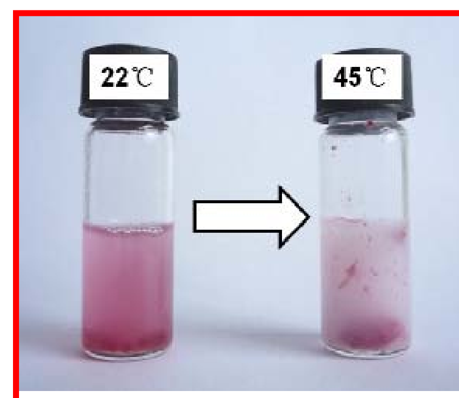
Illustration of the generation of Au-PNIPA yolk–shell composite particles

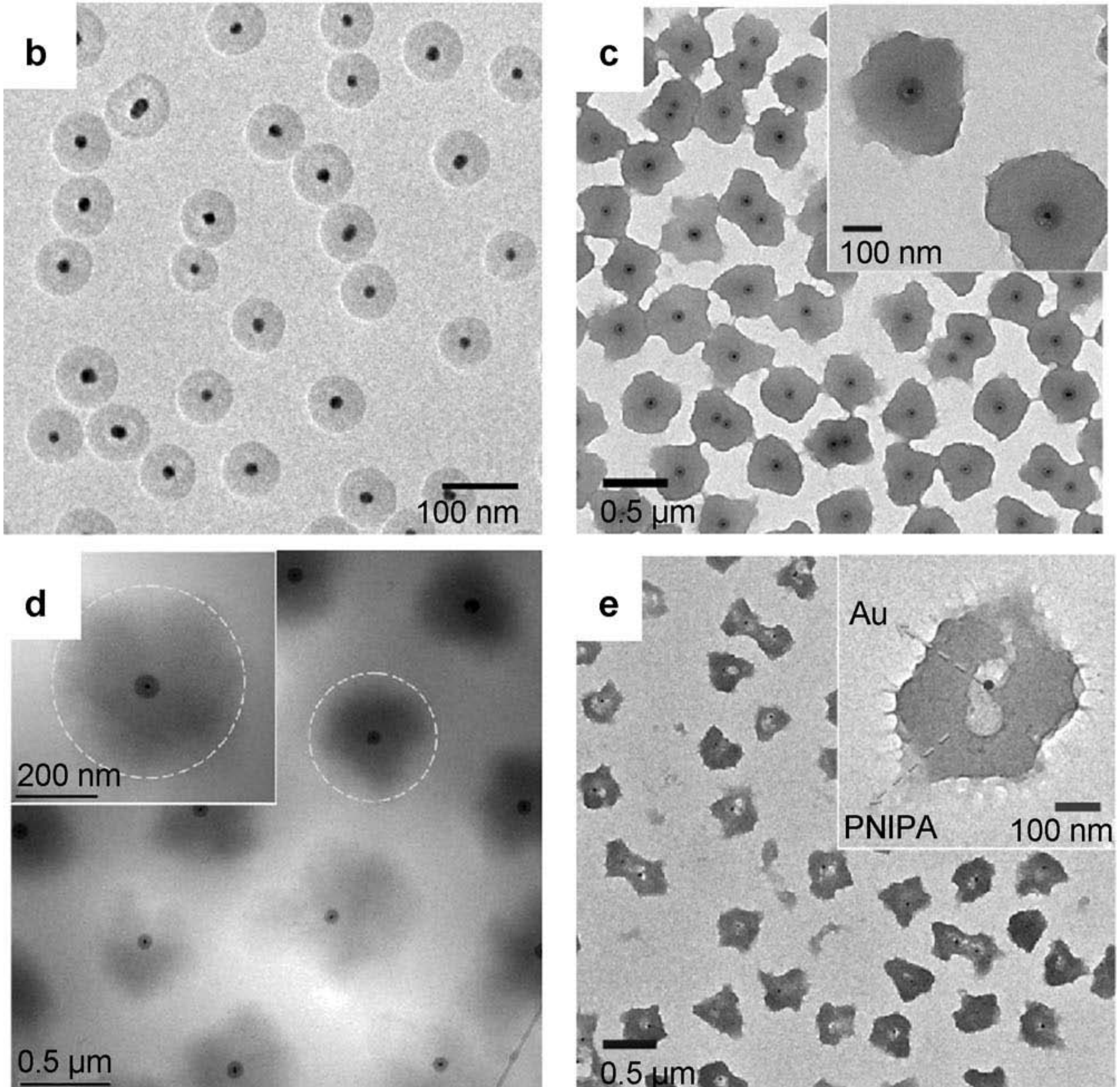




Variation of the hydrodynamic diameters of Au-PNIPA yolk-shell particles with temperature

Without MPS surface-modification



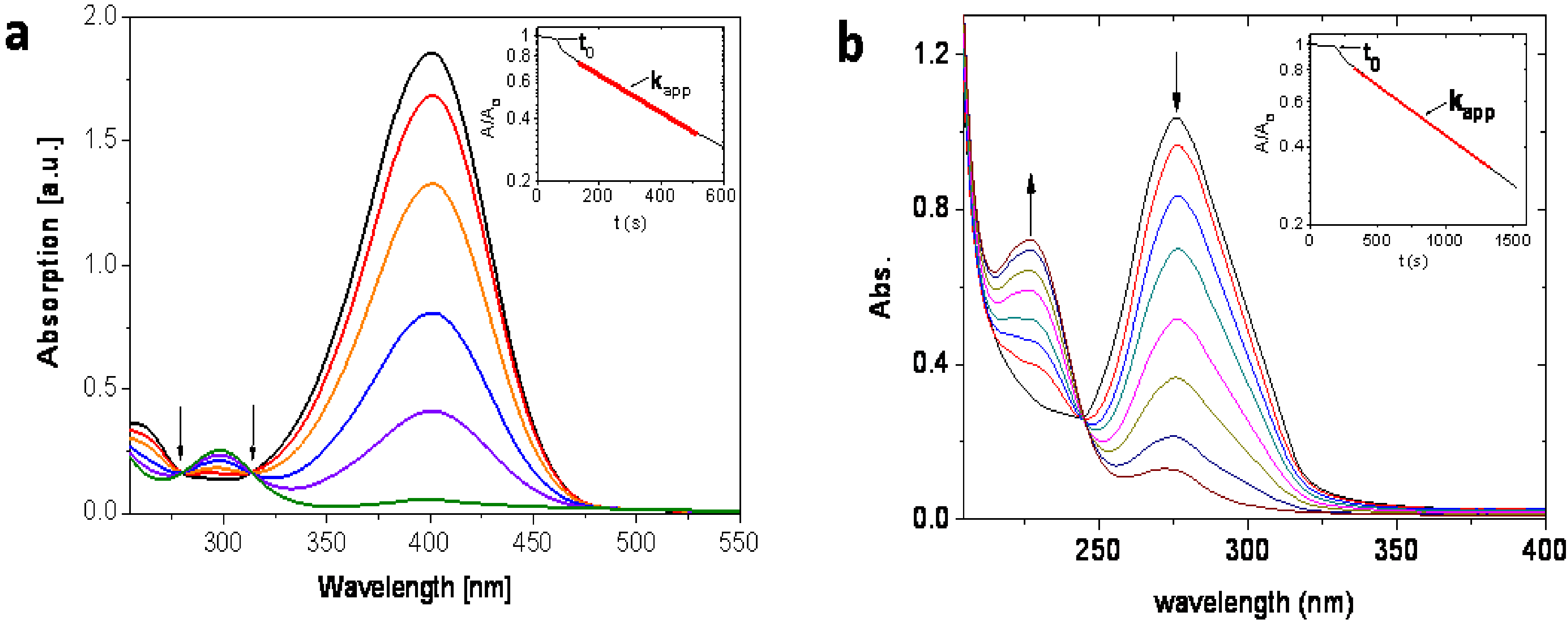


TEM images of
b) Au-SiO2 core–shell nanoparticles

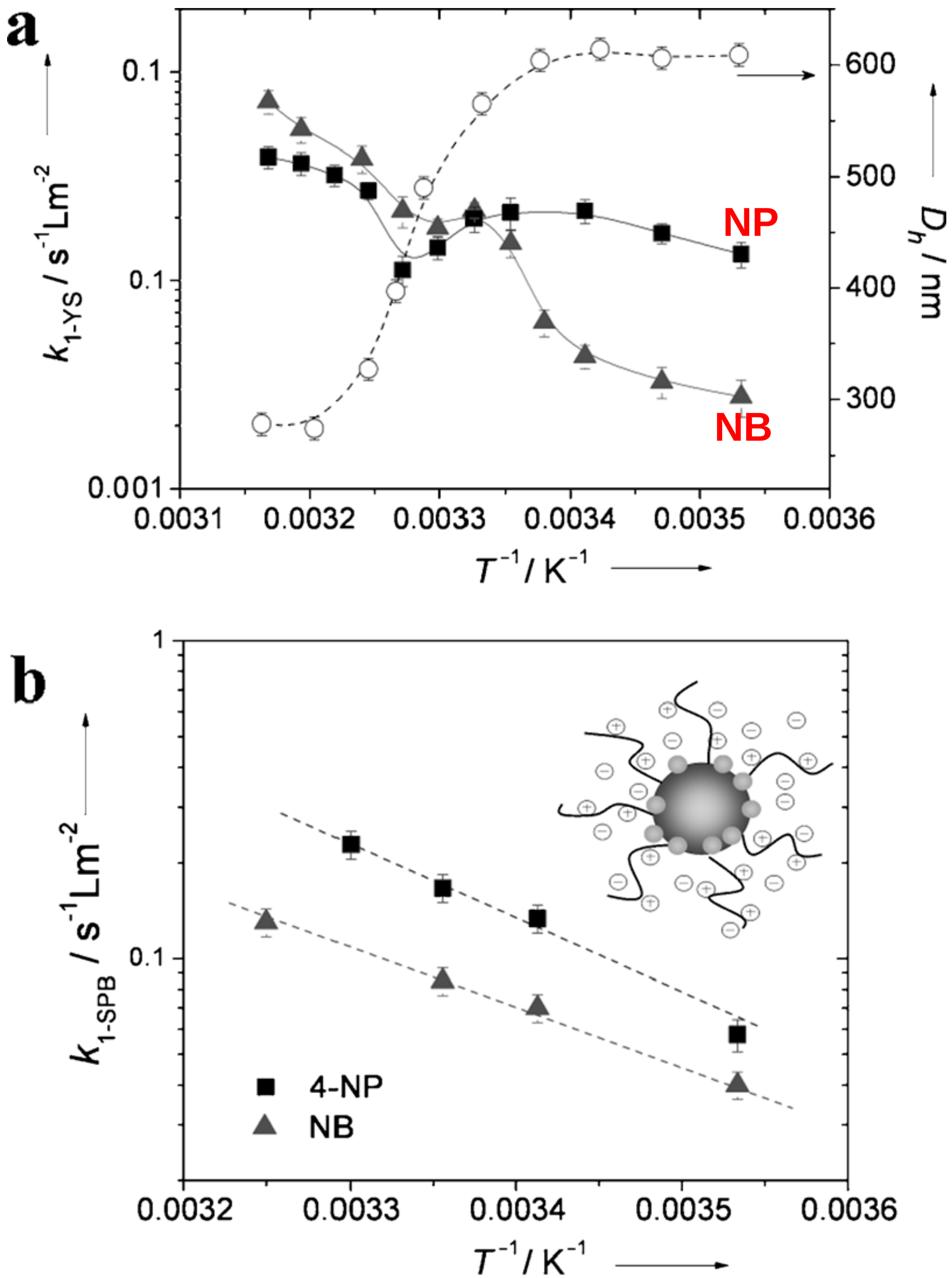
c) Au-SiO2-PNIPA trilayer composites

d) Cryo-TEM image of Au-SiO2-PNIPA composites

e) TEM image of Au-PNIPA yolk–shell particles after the removal of silica



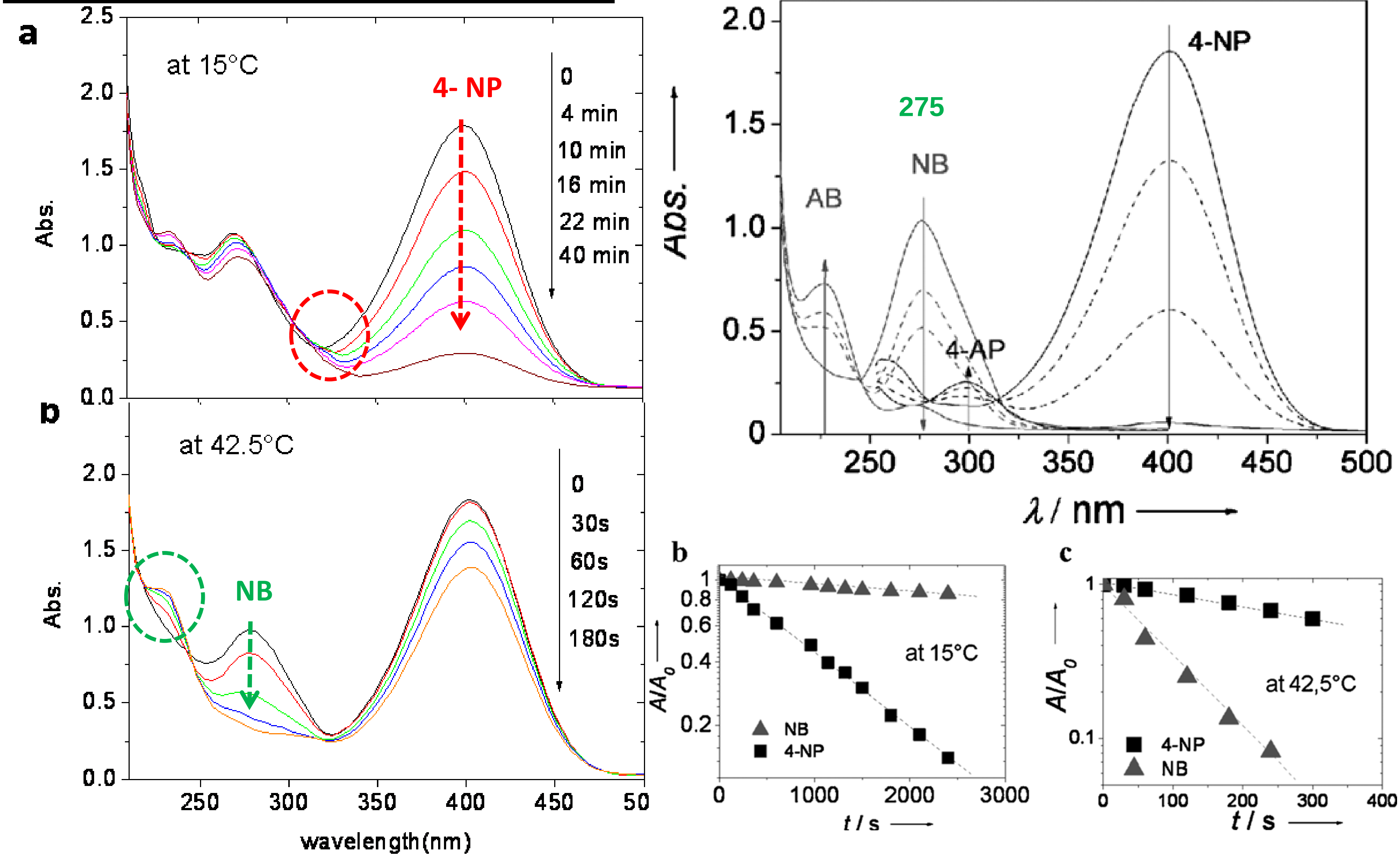
UV-vis absorption spectra of (a) 4-nitrophenol and (b) nitrobenzene reduced by sodium borohydride using Au-PNIPA yolk-shell particles as catalyst. The insets show typical time dependence of the absorption of (a) 4-nitrophenolate ions at 400 nm and (b) nitrobenzene at 275 nm.



Arrhenius plots of the reaction rate constant k_1
a) in the yolk–shell carriers (this work)and
b) in non thermosensitive spherical polyelectrolyte brushes (SPB).

rectangles: reduction of 4-NP;
triangles: reduction of NB;
open circles: hydrodynamic diameter (Dh) of Au-PNIPA yolk–shell particles.

Selectivity test: mixture of NB and 4-NP



Competitive reduction of 4-nitrophenol (4-NP) and nitrobenzene(NB) by $NaBH_4$ using Au-PNIPA yolk–shell catalyst.

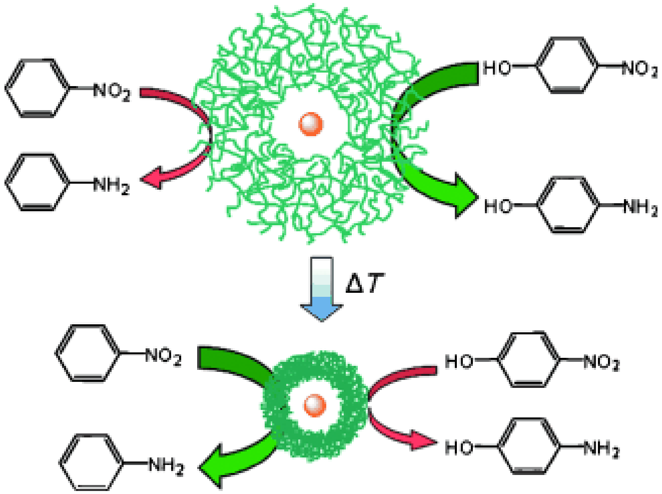
a) UV/Vis absorption spectra as the function of the degree of conversion. b, c) Kinetic analysis of the competitive reduction. The reduced absorptions of 4-NP and NB ofthe mixture is plotted against time t at b) 15 8C and c) 42.5 8C.

Summary

• In conclusion, an inorganic–organic hybrid yolk–shell nanostructure that contains a metallic Au nanoparticle as the core and thermosensitive microgel PNIPA as the shell is introduced.

• This hybrid is an effective catalyst for the reduction of 4-nitrophenol and nitrobenzene in aqueous solution.

•Temperature can be used as a trigger to enhance the selectivity of the catalysis for a given substrate: 4-NP reacts much faster at low temperature, while the reduction of NB is preferred at higher temperature.



• This selectivity is even enhanced in mixtures of 4-NP and NB.

• Yolk–shell systems have a great potential to tailor the catalytic activity and selectivity of metal nanoparticles toward a given reaction.

Thank you