

# Rational design of Au@PNIPAM core-shell nanoreactors with tunable selectivity for catalysis

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Gold nanoparticles have been extensively studied in the last decades due to their catalytic properties, which significantly differ from the bulk metal [1]. Since the free nanoparticles tend to aggregate and are difficult to handle in catalytic applications, stimuli-responsive polymer coatings have been developed to encapsulate and stabilize the nanoparticles [2,3]. The polymer coating not only prevents particles from aggregation but also controls the catalytic activity and selectivity by changing the local environment for the reactants. Thus, the catalytic rate can be flexibly tuned and switched by parameters such as temperature [3,4], ionic strength or pH.

In this work we report the synthesis of thermosensitive core-shell nanoreactors, composed of a polystyrene core, embedded in a poly(N-isopropylacrylamide) (PNIPAM) network in which the gold nanoparticles are immobilized. We demonstrate that the catalytic activity of the gold nanoparticles can be tuned by the volume transition within the polymer shell by using the catalytic reduction of 4-nitrophenol as a model reaction [3,5]. More importantly, we show that the catalytic selectivity of the system can be tuned by temperature as is shown by the competitive reduction of the hydrophilic 4-nitrophenol and the hydrophobic nitrobenzene by borohydride [3,4]. We qualitatively and quantitatively describe the catalytic rates in the stimuli-responsive nanoreactors by using a theoretical framework that extends concepts from the Debye-Smoluchowski theory of diffusion [4].

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