Microwave, Photo- and Thermally Responsive PNIPAm-Gold Nanoparticle Microgels

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Recently considerable attention has been given to gold nanoparticles (AuNP) in the emerging field of nanomedicine, where research into the delivery, release and targeting of pharmaceutical, diagnostic and therapeutic species (drugs) by inorganic/organic hybrid nanoparticles is at the fore-front of research in nanomedicine[1]. A number of methods have been developed to incorporate gold nanoparticles and various polymer molecules. Combining the intelligent sensitivity of a *stimuli*-responsive polymer with an inorganic metal nanoparticle results in hybrid composite microgels with attractive synergistic properties. Depending on the nature of inorganic metal incorporated as nanoparticles, such as Au, Cu, Fe and Ag, specific functionality can be realized for potential applications in micro/nano sensors or microreactors, nano-electric devices[2], in photothermal ablation of cancer tumors[3] and in perspective drug delivery and release applications.[4]

The goal of this study was to develop a robust technique to synthesize a hybrid composite core-shell microgel that can be activated in a controlled manner by visible light *and* microwave radiation to release the liquid contained in the cores. To achieve this goal, we incorporated gold AuNP into a polymer matrix comprised of NIPAm copolymerized with a hydrophilic monomer, acrylamide (Am), which has been shown to increase the LCST[8]. The monomer ratios are adjusted to obtain a LCST closer to the physiological conditions (37°C) specifically required for drug, protein, gene or cell delivery and release applications.

Recently we reported a simple one-step liquid-liquid dispersion technique to synthesize reversibly swellable, magnetic nanoparticles-embedded polymer microcapsules[5]. In the present method, we utilized this liquid-liquid dispersion principle5 in a system of 3 immiscible liquids to prepare PNIPAm-*co*-AM core-shell microcapsules loaded with AuNP. The spontaneous encapsulation of the core-shell droplet morphology to form a double oil-in-water-in-oil (o/w/o) emulsion is facilitated by the control of the interfacial energy balance between the aqueous phase (in which a water-soluble drug can be dissolved), the monomer phase and the continuous phase. The core-shell morphology was developed in situ and fixed by photopolymerization by using a new microarray technique.

Our results demonstrated the development for the first time to the best of the authors' knowledge, AuNP/PNIPAm hybrid core-shell microcapsules and microgels that can be actuated by visible light *and/or* microwave radiation (≤1250 nm) *and/or* temperature. These results are significant firstly, because the microarray technique is rapid and robust and can be scaled up relatively easily for producing commercial quantities of AuNP/PNIPAm-*co*-Am microcapsules and microgels and secondly, because the liquid core of the polymer microcapsule can be released by activation by a range of electromagnetic radiation or temperature.

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