Hydrogel-Coated Gold Nanoparticles

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INTRODUCTION

Colloidal metal nanoparticles are currently drawing the attention of scientists due to their unique optical and electrical properties as well as their biocompatible characteristics.[1] In their ability to absorb and/or scatter light, metal nanoparticles such as platinum, silver, copper, and gold can be superior in many ways to molecule-based chromophores.[2] Gold nanoparticles are particular useful in optical absorption/scattering applications due to their strong optical responses and their biocompatible nature. One recent area of our research focuses on the development of discrete hydrogel-coated gold nanoparticles that respond structurally to photolytically induced changes in temperature and/or pH.

Hydrogel polymers are used in many areas, including catalysis, chemical separations, and drug delivery.[3] Hydrogels can be grown and dispersed in water as colloidal particles with a cross-linked polymer framework, which can undergo reversible volume changes as a function of the pH and/or the lower critical solution temperature (LCST).[4] These hydrogel-based nanoparticles are used in a variety of applications, such as controlled reversible flocculation, enhanced oil recovery, and the uptake and release of heavy metals.[5]

Due to its exceptional biocompatibility, the uncrosslinked homopolymer poly(N-isopropylacrylamide) (NIPAM) has been a particularly well-studied thermo-sensitive hydrogel. This material, however, enjoys limited applications because of a fixed LCST of 32 °C.[6] Colloidal NIPAM hydrogels swell and de-swell at this temperature upon cooling and heating, respectively. Scientists have sought to overcome this limitation by adding acrylic acid (AAc) into the NIPAM homopolymer backbone, which can shift the LCST of the copolymer anywhere from 32 to 60 °C.[7] This material also exhibits a completely reversible swelling-collapsing behavior in response to changes in temperature and/or pH. We report here the use of surfactant-free emulsion polymerization (SFEP)[8] to encapsulate gold nanoparticles with NIPAM-co-AAc hydrogel polymers. We describe the preparation and characterization of these hydrogel-coated gold nanoparticles, which have been designed to serve as discrete thermo-responsive nanopellets that can be thermally activated by exposure to light (via exploitation of the strong plasmon absorption of the gold nanoparticle core).

EXPERIMENTAL SECTION

Materials. The N-isopropylacrylamide (NIPAM) monomer was purchased from Acros (99%) and recrystallized in hexane. Acrylic acid (AAc, Acros, 99.5%) monomer, N,N`-methylenebisacrylamide (BIS, Acros, 96%), potassium hydroxide (EM Sciences, 85%), nitric acid (EM Sciences, 70%), ammonium persulfate (APS, EM Sciences, 98%), trisodium citrate (EM Sciences, 99%), hydrogen tetrachloroaurate (Strem, Au 99.9%) and oleic acid (OA, J. T. Baker) were all used as received from the indicated suppliers. Water used in all reactions was purified to a resistance of 18 MΩ using an Academy Milli-Q Water System (Millipore Corporation) and filtered through a 0.22 μm filter.

Preparation of Gold Nanoparticle Cores and Hydrogel-Coated Gold Nanoparticles. Colloidal gold nanoparticles were prepared by citrate reduction, where the amount of citrate can be used to dictate the nanoparticle diameter as described elsewhere.[9] In this work, the diameters of the gold nanoparticles were ~60 nm as judged by dynamic light scattering (DLS), field emission scanning electron microscopy (FE-SEM), and transmission electron microscopy (TEM). The gold nanoparticles were diluted with 0.001M potassium carbonate solution to inhibit aggregation at room temperature and to give a final ultraviolet-visible (UV-vis) absorption maximum of ~0.3 a.u. at 530 nm.

Using SFEP in aqueous media, the hydrogel-coated gold nanoparticles were prepared under argon in a 500 mL three-necked round-bottomed flask equipped with a reflux condenser. Oleic acid (0.00174 mL; 3×10^{-5} mol) was added to the gold colloid solution and stirred for 45 min and then placed in an ultrasonic bath for 15 min. An approximately 94:6 wt% ratio of NIPAM (0.1 g; 4.4×10^{-3} mol):AAc (0.0072 g; 5×10^{-4} mol) and cross-linker BIS (0.003 g; 1×10^{-4} mol) were then added, and the mixture was stirred for 15 min to give homogeneity. The solution was heated to 70 °C in an oil bath, and then APS (0.0048 g; 1×10^{-4} mol) was quickly added to initiate the polymerization. The reaction was allowed to proceed for ~14 h at rt. The solution was then filtered through a 1 μm membrane to remove any micron-sized impurities. The filtered solution was centrifuged at 3500 rpm for 1 h at rt with an RC-3B Refrigerated Centrifuge (Sorvall Instruments). Afterward, the top layer was decanted to remove any unreacted materials or water-soluble side products. The purified hydrogel-coated gold nanoparticles were then diluted with Milli-Q water and stored at rt for subsequent analyses.

Characterization of Gold Nanoparticles and Hydrogel-Coated Gold Nanoparticles. Given their ready availability, we focused our initial characterization studies on gold nanoparticle cores with ~60 nm diameters and hydrogel-coated composites with ~100-250 nm diameters. We employed a Cary 50 Scan UV-vis optical spectrometer (wavelengths 400-1100 nm) with Cary Win UV software to characterize the optical properties of the bare gold nanoparticles and the hydrogel-coated gold nanoparticles. For these studies, the bare gold nanoparticles were diluted with Milli-Q water, and the hydrogel-coated gold nanoparticles were analyzed as prepared above (i.e., without further dilution). Analysis of nanoparticle size and morphology by FE-SEM was performed using a JSM 6330F (JEOL) instrument operating at 15 kV. In order to collect the FE-SEM images, the nanoparticle samples were sputter coated with a carbon film (25 nm thick) to give homogeneous electron distributions. For the DLS studies, an ALV-5000 Multiple Tau Digital Correlation instrument operating at a light source wavelength of 514.5 nm and a fixed scattering angle of 90° was used to measure nanoparticle size. These measurements were conducted at dilute concentrations (~5×10^5 particles/mL) and with precise control over the temperature (25 °C), given the known temperature-dependence of the hydrogel structure.

RESULTS AND DISCUSSION

Hydrogel-coated gold nanoparticles were prepared by SFEP at 70 °C in aqueous solution. The procedure was found to be most convenient at this temperature because all starting materials were soluble under aqueous conditions. With inadequate stirring, temperature, or monomer concentration, phase separation was readily observed. However, in the absence of phase separation, we were able to prepare stable hydrogel coatings (~20-90 nm thick) on gold nanoparticle cores (~60 nm diameters). In these initial studies, we have found that the thinner hydrogel coatings can be produced more reliably than the thicker ones (vide infra). UV-vis absorption spectra of the bare and hydrogel-coated gold nanoparticles are shown on Figure 1. For the bare gold nanoparticles, the spectra show a maximum absorption band at 530-540 nm arising from the gold plasmon. For the hydrogel-coated gold nanoparticles, the gold plasmon band decreases in intensity when the thickness of the hydrogel coating increases because the refractive index of the hydrogel co-polymer shell is different from that of water and that of the gold nanoparticle core. This behavior is consistent with Mie scattering theory for core/shell particles.[10]

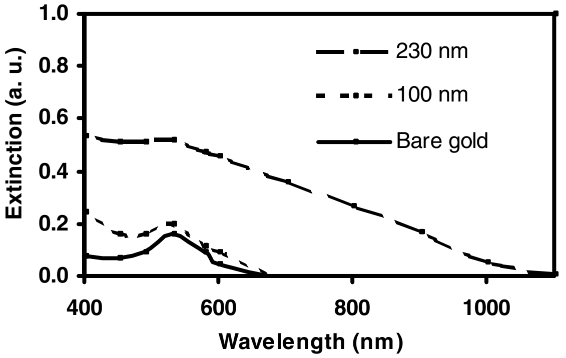
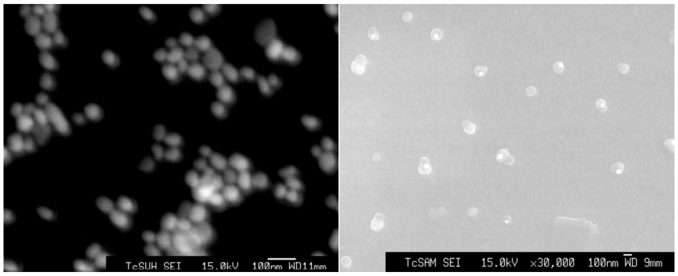
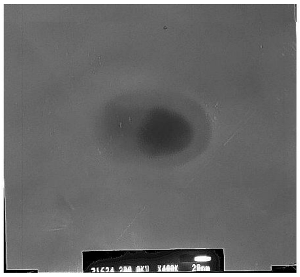


Figure 1. UV-visible spectra of bare gold (bottom trace) and hydrogel-coated gold nanoparticles at neutral pH (top traces).



(b) Hydrogel-coated gold nanoparticles (~230 nm)



(c) Hydrogel-coated gold nanoparticles (~230 nm)

Figure 2. FE-SEM (a-b) and TEM (c) of bare gold nanoparticles and hydrogel-coated gold nanoparticles.

The FE-SEM and TEM images of the gold nanoparticle cores and of the hydrogel-coated nanoparticles are shown in Figure 2. The images show that while the gold nanoparticle cores are highly spherical, the hydrogel-coated nanoparticles are substantially more irregular in appearance. We have found that the use ofsurfactants (e.g., sodium dodecyl sulfate) in the polymerization process affords smoother surfaces but thinner coatings. Furthermore, while the growth of thin hydrogel coatings reproducibly leads to complete coverage of the gold cores, the growth of thick hydrogel coatings often leads to non-uniform coverage.

Both the TEM images (Figure 2c) and the DLS data collected at 25 °C (not shown) indicate that the bare gold nanoparticles are ~60 nm in diameter. However, analysis of the hydrogel-coated nanoparticles by TEM suggests composite diameter sizes that are slightly smaller that that indicated by DLS in aqueous solution.[11] It seems plausible that the electron beam and/or the high vacuum environment of the TEM instrument can give rise to partial shrinkage of the hydrogel coatings.

CONCLUSIONS

This research has demonstrated that surfactant-free emulsion polymerization is an efficient method for preparing NIPAM-AAc hydrogel-coated gold nanoparticles in which the thickness of the hydrogel coating varies from 20 to 90 nm. Characterization of the optical properties and structural morphologies of the composite particles by UV-vis spectroscopy, FE-SEM, TEM, and DLS support the formation of discrete hydrogel-coated gold nanoparticle species. Future studies will examine the temperature lability of these unique nanoparticles, including the use of light to effect structural modulations.

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