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Gold nanospheres/nanorods as highly promising candidates for the hydrophilic/hydrophobic balance of poly(N-vinylcaprolactam): A thoughtful design of nanocomposites

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Instrumentation

Fluorescence experiments

Fluorescence intensity measurements of the sample solutions are ascertained by using a Cary Eclipse fluorescence spectrofluorometer (Varian optical spectroscopy instruments, Mulgrave, Victoria, Australia) containing an intense xenon flash lamp as the light source. The emission spectra is recorded with a PMT voltage of 720 V and slit width of 10/10 nm. By mixing a fixed concentration of polymer (5 mg/mL) and increasing concentration of AuNSs and AuNRs from 0.002 to 0.010 nM at a constant temperature of 25 ^{o}C, the ongoing interactions between AuNSs, AuNRs and PVCL are studied. Thermal fluorescence experiments were performed by varying the temperature of solution between 25-60 ^{o}C. The excitation wavelength is set at 360 nm and emission wavelength is collected at different wavelengths.

Dynamic light scattering (DLS) measurements

To assess the hydrodynamic diameter (d_H) of PVCL in the presence of different concentrations of AuNSs and AuNRs, the Zetasizer Nano ZS90 dynamic light scattering (DLS) instrument (Malvern Instruments Ltd., UK) is used. The instrument is equipped with a fixed wavelength of 633 nm and 4 Mw He-Ne laser. A quartz sample cell containing 1.0 ml of a filtered sample is sealed with a Teflon- coated screw cap to protect from air and dust. The Brownian motions of particles are detected by DLS and correlated to the particle size. The data collected was analyzed using the Malvern Zetasizer software version 7.01

zeta potential experiments

Zeta potential measurements were also performed on Zetasizer Nano ZS90 instrument using DTS1070 disposable cuvettes. The data collected was analyzed using the Malvern Zetasizer software version 7.01

scanning electron microscopy (SEM)

Scanning electron microscope reveals the detailed surface characteristics and three dimensional structure of the sample under consideration. Freeze dried samples were used to explore the morphology of polymer and the complex formed by polymer and AuNPs on the instruement JEOL Japan Mode: JSM 6610LV with an EHT voltage of 10.00 kV and tungsten as the electron source.

transmission electron microscope (TEM)

Morphological characterization of PVCL and AuNSs, AuNRs is carried out using TECNAI 200 kV (Fei, electron optics) equipped with digital imaging and 35 mm photography system. For a better understanding of ongoing interactions among AuNSs, AuNRs and PVCL, images were taken at different magnifications.

Fourier transform infrared spectroscopy (FTIR) measurements

All the Fourier transform spectrum are acquired by an Is 50 FT-IR (Thermo- Fischer scientific) spectrometer. The two ZnSe windows and bubble free samples are placed into an IR cell. Inside the sample chamber, a chromel alumel K-type thermocouple was provided for monitoring of temperature. Each IR spectrum reported here is an average of 240 scans using a spectral resolution of 4 cm^{-1}. Before the sample spectra, a background spectrum is collected. Furthermore, for each sample containing PVCL, the deuterium oxide (D_2O) spectrum was used as background. The FTIR spectrum of PVCL in presence and absence of AuNSs and AuNRs is represented in Fig. 1S.

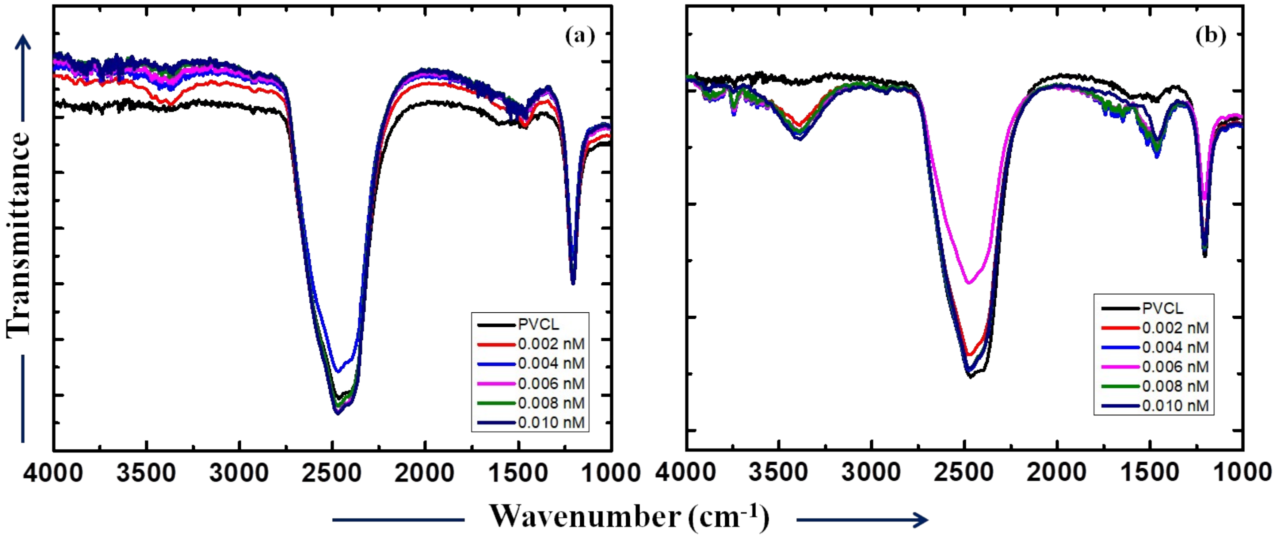


Fig. 1S. FTIR spectrum of (a) PVCL in AuNSs and (b) PVCL in AuNRs.

Thermogravimetric analysis (TGA)

The weight loss with varying temperature is determined and represented by TGA curves in Fig. 2S which are correlating with the reported literature.[1] PVCL-AuNSs is exhibited to show the weight loss in two different regions such as (190-230 °C) and (380-450 °C). On the other hand, PVCL-AuNRs attributed a weight loss in the region (350-450 °C).

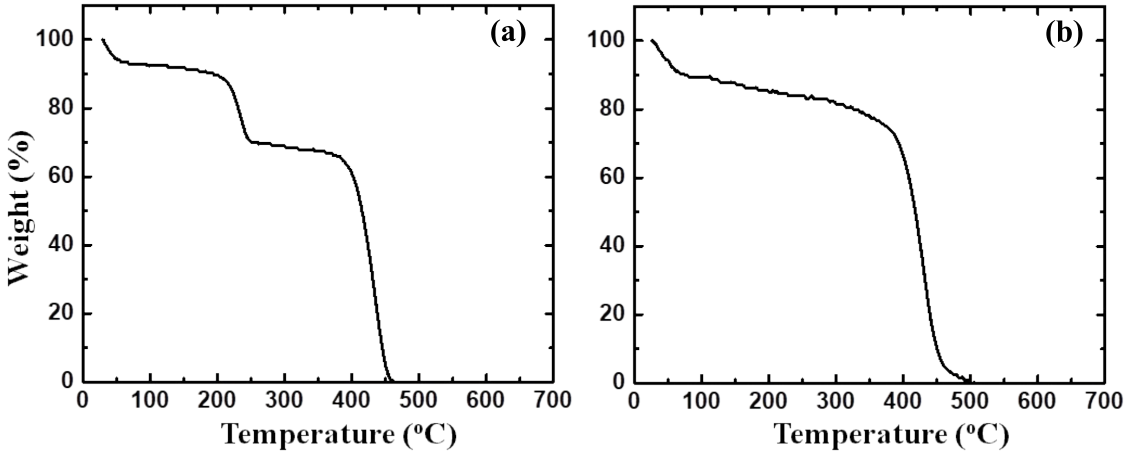
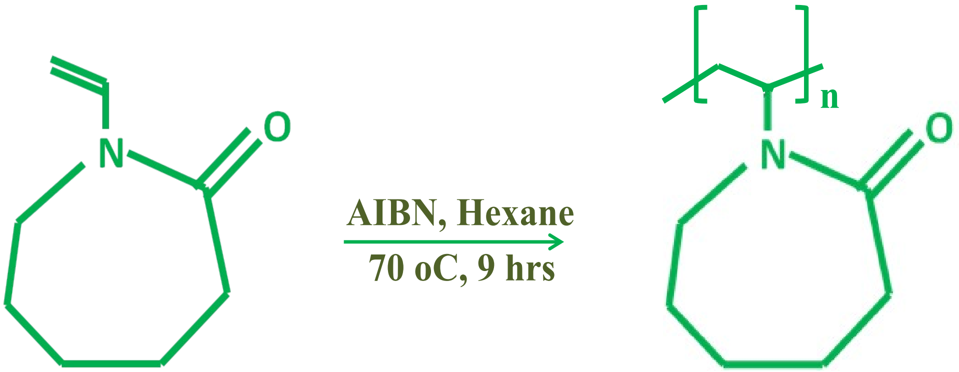


Fig. 2S. TGA curves for the nanohybrids of (a) PVCL-AuNSs (b) PVCL-AuNRs.

Synthetic procedure of PVCL

The solution polymerization of vinylcaprolactam (VCL) was carried out by using the initiator (AIBN) for the synthesis of PVCL.[2] 50 mL of C_6H_{14}, 0.01 g of AIBN and 10 g of NVCL were subsequently added to prepare the stock solution. Afterwards, 4 mL of this solution was placed in glass tubes which were further immersed in an oil bath maintaining the temperature at 70 ^oC. The reaction ultimately leads to the polymerization of VCL and the polymer was precipitated with diethyl ether, filtered and dried under vacuum at 40 ^oC. Scheme 1 depicts the polymerization reaction of VCL.



Scheme 1. Synthetic route of PVCL through solution polymerization from VCL in the presence of AIBN as an initiator.

^{1}H NMR characterization of PVCL:

^{1}H NMR characterization of PVCL is briefly discussed in previously reported literature.[2] Different peaks of the protons named as (H_a, H_b, H_c, H_d) were observed in the ^{1}H NMR spectrum of PVCL. There is a small peak in the spectrum of the PVCL at 7.29 ppm. This peak corresponds to the solvent, deuterated chloroform. The ^{1}H NMR spectrum of PVCL exhibited peaks at 4.36 ppm (1H, −NCH− of the α position), 3.1 ppm (2H, $-NCH_2-$), 2.4 ppm (2H, $-COCH_2-$) and 1.65 ppm (6H, $-CH_2-$ of the caprolactam ring, and 2H, $-CH_2-$ of the backbone).

The molecular weight determined from GPC is already reported by our research group in the literature.[3]

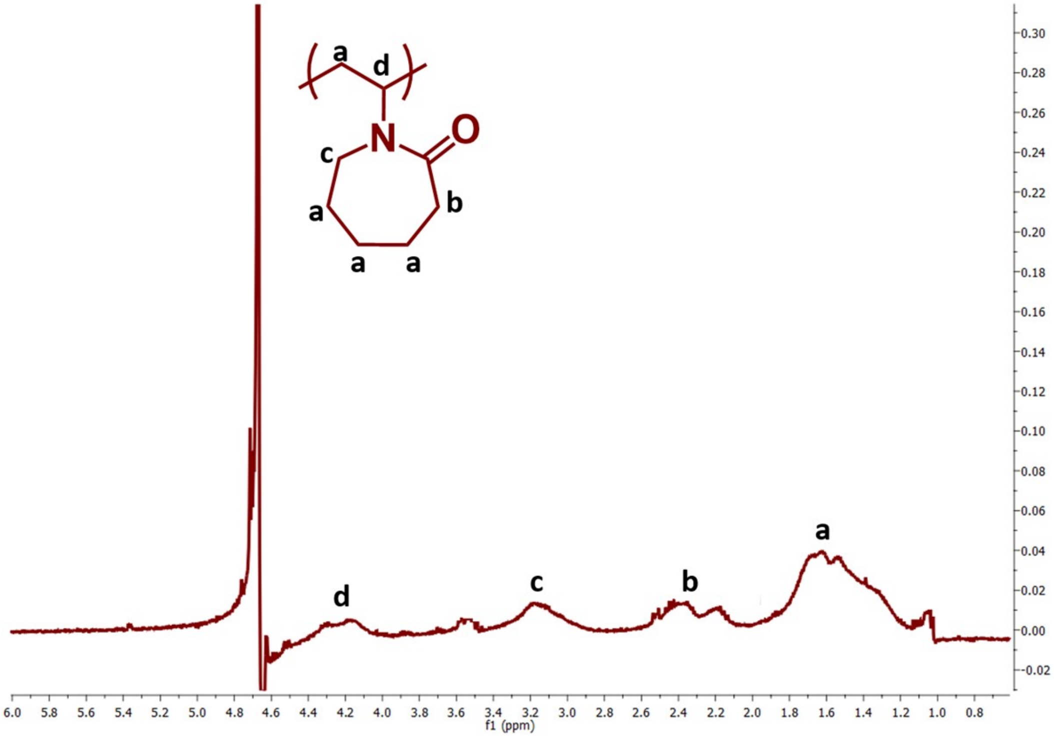


Fig. 2S. ^{1}H NMR spectrum of PVCL.

Synthesis of AuNRs/AuNSs

AuNSs are prepared using sodium borohydride ($NaBH_4$) for the reduction of $HAuCl_43H_2O$ and CTAB for stabilizing the Au nanoparticles (AuNPs). 0.01 mmoles of $HAuCl_43H_2O$ was taken in 5 ml double distilled water, followed by addition of 4 mL of 0.1 M CTAB for stability of AuNPs. Finally, 50 µL of 0.1 M $NaBH_4$ (freshly icely prepared) is added in the above solution.[4,5] Solution was kept on strong stirring for about 30 sec. and followed by a mild stirring for 2 hrs. Appearance of wine red colour gives the indication of spherical AuNPs formation. The final solution has been centrifuged at 8000 rpm for 10 min to wash out the unattached CTAB from the solution, thereafter the spherical AuNPs have been dispersed again in equivalent amount of aqueous solution.

AuNRs are prepared by performing a simple modification to the method reported by Sau and Murphy.[4] Herein, the seed solution for the rods was prepared by the addition $HAuCl_43H_2O$ (250 µL of 0.01 M) into CTAB (7.5 mL of 0.1 M) using a 15 mL glass test tube followed by slow mixing. Afterthat, a fresh ice water prepared $NaBH_4$ solution (600 µL of 10 mM) was being added fastly into the abovesaid reaction mixture which was further followed by rapid inversion for ~ 2 mins. This seed solution was kept for 2 hrs at room temperature conditions before further use.

For preparing growth solution for AuNRs, (250 µL of 0.01 M) $HAuCl_43H_2O$ was added to (7.5 mL of 0.1 M) CTAB followed by (30 µL of 0.01 M) $AgNO_3$. Using H_2SO_4 solution, pH of solution was maintained at ~2. Finally ascorbic acid (32 µL of 0.1 M) was added followed by 10 µL recently prepared seed solution into the growth solution. The solution was being mixed very gently for approximately 20 sec then left undisturbed for 3 hrs for the formation of Au nanorods. Similarly as spherical AuNPs, the nanorods are being centrifuged at 10000 rpm to remove excess CTAB from the solution, thereafter the nanorods have been dispersed again in equivalent amount of aqueous solution.

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