Supplementary Material (ESI) for *Soft Matter*

Supporting Information

Recovery of Gold Nanoparticles Using pH-sensitive Microgels

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1. Microgel synthesis

Both the anionic poly(N-isopropylacrylamide) (PNIPAM referred to as MG$^-$) and cationic poly(NIPAM-co-2-vinylpyridine) (abbreviated MG$^+$) were synthesized using methods introduced by Snowden *et.al.*[1]. MG$^-$ was synthesized using the following reagents and quantities. In a reaction flask, 800 ml of mili-Q water (PureLab, Elga) was added to 0.51g of potassium persulfate initiator. Separately, 5.0g of NIPAM and 0.51g of cross-linking agent N,N-methylenebisacrylamide (BA) were dissolved in 200 ml of mili-Q water. The dissolved reagents were added to the reaction flask and the polymerization reaction was set at 70 °C under an inert atmosphere.[1,2].

MG$^+$ was prepared in a similar manner, briefly, 800 ml of mili-Q water was purged with nitrogen for 30 min in a 1L, five-neck round bottom flask fitted with a mechanical stirrer operating at 150 rpm. 0.50g cationic initiator 2,2'-azobis(2-methylpropionamidine)dihydrochloride (V50, *Waco*) was then added to the reaction flask and stirred. 200 ml of mili-Q water standard (PureLab, Elga), 3.75g of NIPAM and 0.55g of BA, together with 1.25 g of 2-vinylpyridine (2VP) were added in a beaker and stirred for 15 min, this solution was added to the reaction vessel with the temperature raised to 70 °C. The polymerization reaction was left to proceed for 6 h with continuous stirring (~150 rpm). The resulting dispersion was filtered through glass wool, followed by extensive dialysis against mili-Q water for one week, with two changes of water per day. Table S1 lists chemicals and components used in this research.

Table S1: The chemicals, names and shorthand nomenclature used in this paper

Chemicals	Names	Shorthand nomenclature
Au with MES stabilizer	Colloidal gold	AuMES
PNIPAM	Anionic microgel	MG^-
P2VP-PNIPAM	Cationic microgel	MG^+
AuMES-(P2VP)-PNIPAM	Combination of colloidal gold and cationic microgel	AuMES-MG^+
AuMES-(P2VP)-PNIPAM	Combination of AuMES, and mixed cationic and anionic microgels	AuMES-MM

2. Mixed microgel (MM) stability

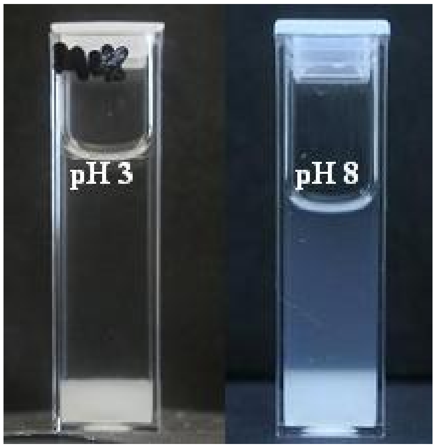

Figure S1: The stability of mixed microgel (MM) systems (MG^+ plus MG^-) at pH 3 and 8.

Figure S1 shows the mixed microgel systems (MG^- plus MG^+). Preliminary dispersion stability characterization was done by adjusting the system from pH 8 to pH 3.

3. AuMES characterizations

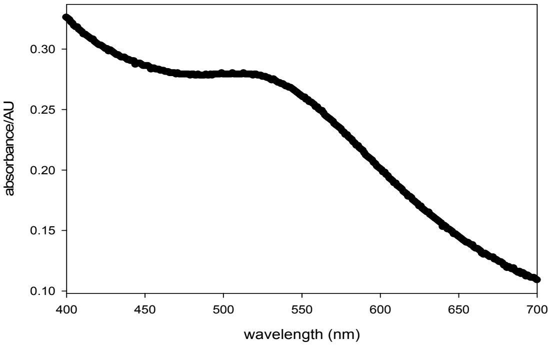

Figure S2: UV-visible spectrum of AuMES gold sol

Figure S2 shows the UV spectrum for a MES-stabilized gold sol (AuMES). It is typical of those seen for the absorbance of small particles through Mie Scattering [2]. The result obtained is similar to that reported by Davies and Vincent [2] where there is the absence of significant Plasmon band which is usually found at 520 nm. This suggests that small particles are produced (i.e d<5nm) and also the possibilities that S coordinates to Au, suppressing the plasmon absorption[2].

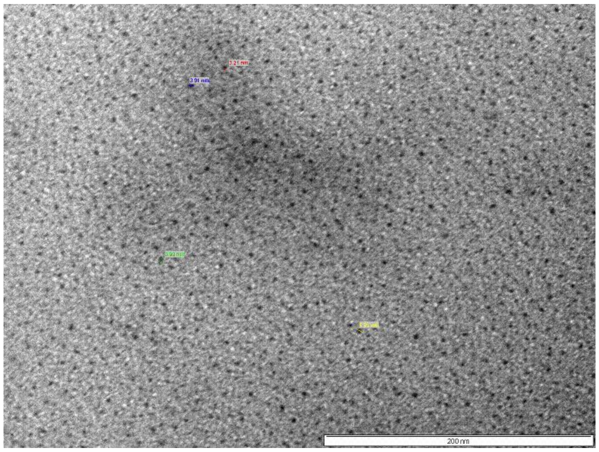

Figure S3: TEM image of AuMES nanoparticles

The TEM image of AuMES nanoparticles shown in Figure S3 confirms the existence of small, relatively polydisperse and spherical gold nanoparticles, of average diameter 3.5 ± 1.3 nm.

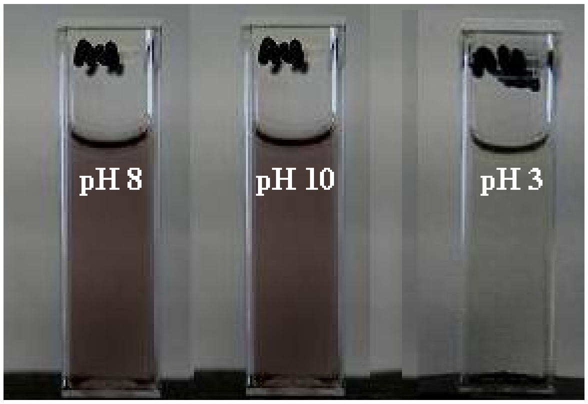

Figure S4: AuMES stability at different pH 8; pH 10 and pH 10

The observation of AuMES stability was made at pH 3 and 10 (Figure S4). Results show that the gold sol is stable in the pH range 3-10, which agrees with the requirement for the negatively charged AuMES to interact with $MG^{+1,2}$ over this pH range.

4. Selection of optimum AuMES-MM mixture and pH conditions

Heteroaggregation behavior for each sample is clearly influenced by the different concentration of oppositely charged microgels, as described in detail by Snowden *et. al.*[1]. Based on that approach[1] over 200 AuMES-MM samples were prepared with varying concentrations, dispersion compositions, and mixed microgel ratios. Hence a large matrix of samples was screened, varying all composition parameters over certain appropriate ranges. In this section the four most significant samples from that array are discussed (Table S2). All samples were examined based on their aggregation as a function of pH at a constant AuMES concentration. The physical state of all samples was determined visually at room temperature.

Table S2: Composition of samples prepared

Sample	MG^- (wt%)	MG^+ (wt%)	water (wt%)
A	35	15	50
B	25	25	50
C	40	10	50
D	10	40	50

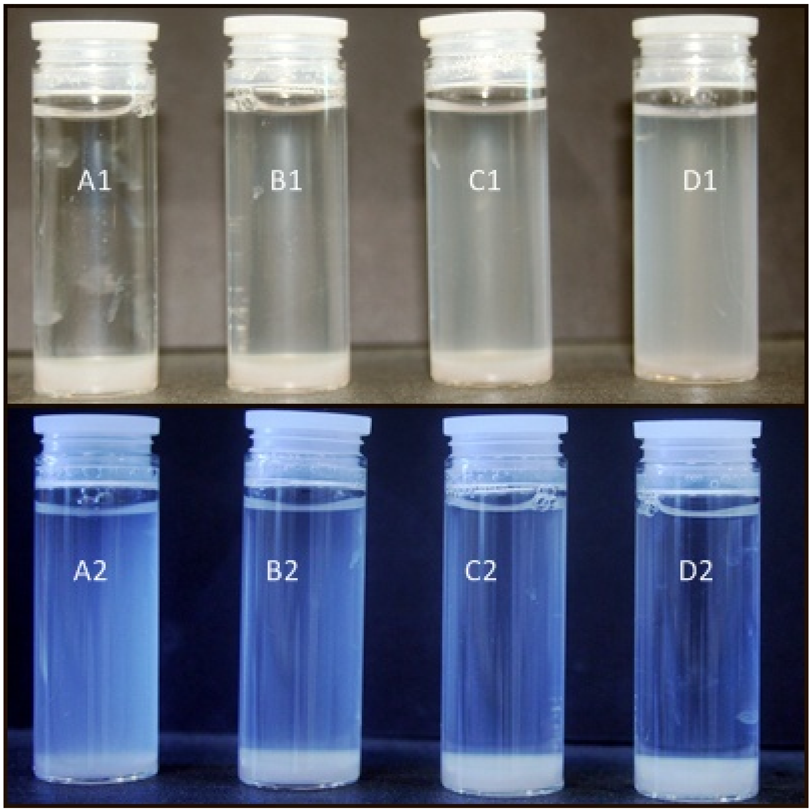

Figure S5: AuMES-MM dispersion behavior with different relative ratios of microgel at pH 3 (1) and pH 10 (2)

Figure S5 shows the AuMES-MM dispersions at pH 3 and pH 10 for the sample described in Table S2. At pH3 samples A, B and C separated into two distinct phases with a lower turbid phase separating from a clear upper majority portion. It took up to 7 days to achieve final separation. Sample D remained as a stable dispersion at pH3; a similar observation was reported by Snowden *et. al.*[1]. Upon increasing pH to 10 the only sample that showed flocculation was A, which was therefore chosen as the optimum composition for recovery purposes.

5. References

(1) Hall, R. J.; Pinkrah, V. T.; Chowdhry, B. Z.; Snowden, M. J. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2004**, *233*, 25-38.

(2) Davies, P. T.; Vincent, B. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2009**, *In Press, Corrected Proof*.