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Monothiols derived from glycols as agents for stabilizing gold colloids in water: synthesis, self-assembly and use as crystallization templates

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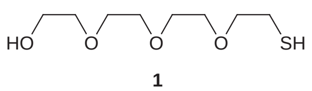
Tetraethylene glycol ($HO-(C_2H_4O)_4-H$) can be monofunctionalized by replacing one of the terminal hydroxy groups with the thiol SH group. The resulting molecule can be self-assembled on gold (111) surfaces. More importantly, this molecule allows the simple one-step preparation of protected, water-soluble gold colloids within a single aqueous phase. Attempts are made to use such protected water-soluble colloids as nucleating 'seeds' around which calcium carbonate can be crystallized.

Interest in preparation, characterization, properties and use of self assembled monolayers (SAMs) has grown tremendously in the last few years.[1–3] Amongst the different applications of thiol self-assembly to form monolayers on gold surfaces is the possibility of preparing stable gold colloids which display *quasi*-molecular behaviour.[4] Gold colloids have been prepared and studied at least since the time of Faraday but the colloids in question always required stabilization through dispersion in a liquid medium.[5] There was usually no possibility of precipitating the gold colloids and then redispersing them—precipitation usually resulted in the formation of bulk gold particles. This also happened when one attempted to prepare sols of gold colloids in high concentrations. Only in recent times, through the use of protecting groups including long chain thiols, has it become possible to prepare colloidal materials in high sol concentrations, and more importantly, obtain them as solids that can be redissolved.

The availability of these molecular nanocrystals has opened a range of possibilities for novel chemical architectures. In our group we have used different ω-terminated thiols assembled on flat gold-coated glass slides for the templated crystallization of calcium and strontium carbonates[6] and of iron oxide-hydroxides.[7] We have recently been able to carry over such crystallization into homogeneous media by using thiol-stabilized gold colloids instead of gold-coated glass slides for templating the crystallization.[8] By carrying over SAM chemistry to colloids, we have the advantage of being able to perform many chemical manipulations within the homogeneous medium and to follow the individual steps using conventional analytical techniques.[9] This has for example permitted us to immobilize homogeneous catalysts on gold colloids to obtain systems that combine the advantages of heterogeneous and homogeneous catalysts.[10] While protected gold colloids possess nearly molecular behaviour, they retain the (111) surface of bulk gold.[5] They therefore form a class of materials that bridge the world of discrete molecules and the world of extended solids.[11]

In this study, we present the synthesis and use of a monothiol **1** derived from tetraethylene glycol for preparing protected gold colloids in water. The thiol is water soluble without being polar. This has been an important motivation for the present study—our previous attempts[8] to make stable water-soluble colloids involved the use of phenolic thiols with the problem that they only dissolved at a rather high pH, or involved the use of sulfonate salts with the associated problem of polarity of the colloids so formed.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The self-assembly of the thiol on flat gold surfaces has been followed using surface plasmon spectroscopy. Gold salts can be reduced in the presence of the thiol to yield stabilized colloidal gold particles in solution. The colloids so formed retain the water-solubility of the thiol. Dispersing the colloids through spin-casting on a mica surface has permitted their characterization by tapping-mode atomic force microscopy. We have attempted to use the protected gold colloids as seeds for the nucleation of calcium carbonate from solution. The products of such crystallization have been examined by powder X-ray diffraction and scanning electron microscopy.

Experimental

Preparation of the thiol

The thioglycol was obtained by a modified reaction described by Tsymbal *et al.*[12] from the tetraethylene glycol by reaction with tosyl chloride. The mono- and bifunctionalized glycols were separated by column chromatography on silica gel and the mono-functionalized product was treated with LiBr to give the monobromoglycol. This was converted to the monothiol **1** with $Na_2S_2O_3$ and HCl by using the Bunte salt method.[13–15]

12-(*p*-Tolylsulfonyl)-3,6,9,12-tetraoxadodecan-1-ol (a). 10 g of tetraethylene glycol (0.05 mol) and 5.06 g of triethylamine (0.05 mol) were dissolved in acetonitrile (150 ml). 9.5 g of toluene-*p*-sulfonyl chloride (0.05 mol) were added dropwise over 1 h. The reaction mixture was stirred for 14 h at 25 °C. The white precipitate of triethylamine hydrochloride was filtered off and washed with acetonitrile. The solution was evaporated and the residue was chromatographed from silica gel with the eluant chloroform–acetone 10 : 3. The second fraction was the monosulfonate. Yield: 8.7 g (50%). (^{1}H) NMR: 7.79–7.73 (m, 4H arom.), 4.14–3.51 (m, 16 H, OCH_2), 2.42 (s, 3H, CH_3), 2.14 (s, 1H, $-CH_2OH$).

12-Bromo-3,6,9,12-tetraoxadodecan-1-ol (b). 17 g LiBr (0.2 mol) were dissolved in p.a. acetone (200 ml). 8 g of (**a**) (0.023 mol) were added and the mixture was stirred for 4–5 h at 80 °C. The mixture was then cooled to room temperature and stirred overnight. The solvent was evaporated and 100 ml chloroform was added to the residue. A white precipitate was filtered and the solution was washed two times with water. The organic layer was dried with Na_2SO_4 and the solvent was evaporated. Yield: 3.9 g (65%). (^1H) NMR: 3.72 (t, 2 H, CH_2OH), 3.63–3.49 (m, 12 H, OCH_2), 3.36 (t, 2 H, CH_2Br). EI-MS *m/z*: 256.41 (54.4%), 258.39 (21.2%).

12-Mercapto-3,6,9,12-tetraoxadodecan-1-ol (c). 20 g of (**b**) (7.8×10^{-2} mol) were dissolved in ethanol (200 ml) and stirred under reflux. A solution of 2.5 g of $Na_2S_2O_3$ (0.11 mol) in water (200 ml) was added dropwise. The mixture was stirred at 20 °C for 48 h. The solvent was evaporated and 1 M HCl (60 ml) was added to the residue. The mixture was heated under reflux for 2 h. The solvent was evaporated and the residue was dissolved in dichloromethane (50 ml) and dried with Na_2SO_4. The solvent was evaporated and the residue was dissolved in acetone (5 ml). A yellow precipitate was filtered off. The solution was evaporated and the product obtained as a yellow oil. Yield: 6.7 g (40%). (^1H) NMR: 3.72 (t, 2H, CH_2OH), 3.57 (m, 12H, OCH_2), 2.8 (m, 2 H, CH_2S). IR 3410 (-OH), 2925–2850 ($-CH_2$), 1454 (CH_2), 1300–1020 cm^{-1} (C-O-C).

Study of the self-assembly of 1 on Au surfaces

After resistive evaporation (using a Balzers Baltec instrument at a pressure of 10^{-5} hPa) of a 2 nm adhesion layer of Cr on clean glass substrates, a further 50 nm of Au was deposited. The rate of deposition was monitored using a quartz crystal microbalance. The freshly prepared Au–glass substrates were placed in solutions of the thiol **1** in ethanol (1 mM) overnight for studies by surface plasmon spectroscopy.

Gold colloids protected by 1

A 5 ml solution of $HAuCl_4$ (2 g per 100 ml water) was diluted with water to 40 ml. 50 µl of the thiol **1** were added then. A solution of $NaBH_4$ (0.01 g) in water (10 ml) was added slowly with vigorous shaking until the mixture exhibited a dark red colour. In the absence of the thiol, there is immediate precipitation of fine, black gold particles under these conditions. It was also verified that the simple tetraethylene glycol (without the thiol functionality) provides no protection to the gold colloids. Excess thiol and salts left over from the reduction could be removed by containing the solutions of the thiol-protected colloids in cellophane dialysis bags and washing with copious quantities of water.

Crystallization of $CaCO_3$ in the presence of gold colloids protected by the thiol 1

A 10 mM solution of $CaCl_2$ was prepared in water (250 ml) and a freshly prepared solution of the colloid (50 ml, 0.2 g per 100 ml) was added. Glass slides were placed at the bottom of the vessel containing the solution. The vessel was placed in a closed desiccator with solid $(NH_4)_2CO_3$ at the bottom for 2 days at 22 °C. In the CO_2-rich atmosphere, crystallites precipitate from solution. The precipitated material was collected on the glass slides and dried at 50 °C in air before being examined by scanning electron microscopy and powder X-ray diffraction.

Instrumental techniques

X-Ray diffraction patterns were obtained using a Siemens D5000 powder diffractometer equipped with a Ge(111) monochromatized CuKα_1 radiation ($\lambda = 1.54056$ Å) in $\theta/2\theta$ transmission geometry. The crystals were collected by scratching the surfaces of the glass slides and were mounted on Scotch-Tape. Measurements were taken from $20° \leqslant 2\theta \leqslant 40°$ with a step size of 0.02° and a step time of 60 s. SPS measurements were performed in the Kretschmann configuration.[16] Optical coupling was achieved with a LASFN9 prism ($n = 1.85$ at $\lambda = 632.8$ nm) and index matching fluid ($n = 1.70$) between the prism and the BK270 glass slide. The surface plasmon was excited with *p*-polarized electromagnetic light using a He–Ne laser (632.8 nm, 5 mW). Kinetic experiments of the assembly of the thiol on gold-coated glass slides were monitored by following the plasmon reflectivity corresponding to an initial reflectivity of 40%. The initial time was taken to correspond to the injection of the solution into the cuvette. Tapping-mode atomic force microscopy (AFM) images using silicon cantilevers were acquired on colloidal samples that were spin-cast onto mica substrates from aqueous solution. A Nanoscope IIIa was used for this purpose. FTIR spectra were recorded in transmission mode (KBr pellets) using a Mattson Instrument Galaxy 2030 IR-spectrometer. FTIR spectra in reflection mode were obtained by using a Nicolet (5DXC) GI-FTIR spectrometer equipped with a Spectra-Tech specular reflectance cell and an MCTA-detector with an angle of incidence of 85°.

Results and discussion

Self-assembly of the thiol on gold-coated glass substrates

Fig. 1 shows angle dispersive surface plasmon spectra of a clean gold surface in water, and the plasmon spectra of a gold surface exposed to the thiol **1**. The shift of the plasmon curve is corresponding to an angular change of 0.4° and could be fitted using the Fresnel formula. Assuming the refractive index of the thiol **1** to be no different from that of bulk tetraethylene glycol ($n = 1.4598$) a thickness of 18 Å for the SAM of **1** on gold was determined. Modeling the structure of the thiol using molecular mechanics at the MM2 level (as implemented in Chem3D® version 3.5) of the thiol **1** suggests that chain expansions of as much as 15 Å are reasonable from the point of view of energetics. Considering additional gold–sulfur binding for the adsorbed thiol, we obtain the result that nearly complete monolayer coverage of the gold surface by the thiol has been achieved.

The kinetics of the thiol binding could be followed from changes in the surface plasmon. Fig. 2 displays the adsorption of the thiol on flat gold surfaces followed from changes in the plasmon reflectivity at a fixed scattering angle. The initial time for this experiment was taken as the time of exposure of the gold surface to the thiol (1 mM in water). It is seen that near-saturation in the reflectivity takes as long as 100 min. After 150 min no further changes in the reflectivity are seen and the complete spectrum recorded after this time is consistent with a monolayer of the thiol being present. In comparison, long chain alkylthiols adsorb much more rapidly from ethanolic

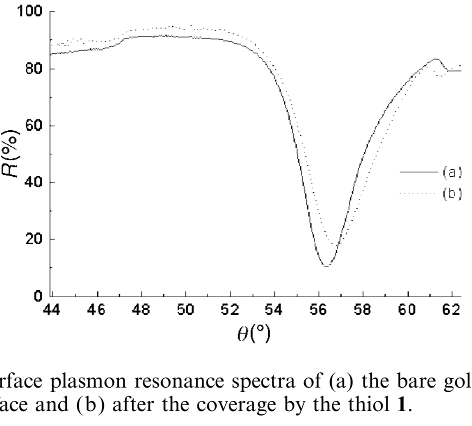

Fig. 1 Surface plasmon resonance spectra of (a) the bare gold-coated glass surface and (b) after the coverage by the thiol **1**.

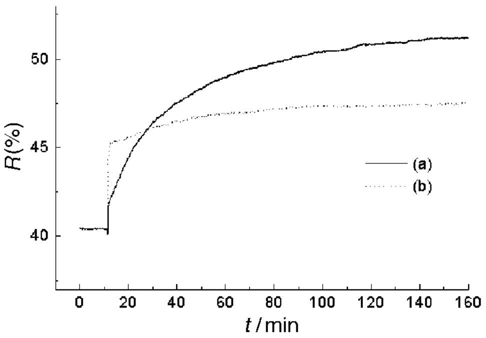

Fig. 2 Kinetics of monolayer formation followed from the surface plasmon reflectivity: (a) is the thiol **1** adsorbed from water and (b) for comparison is ω-mercaptohexadecanoic acid adsorbed from ethanol.

solution. A second trace corresponding to the kinetics of ω-mercaptohexadecanoic acid adsorption (from ethanol, 1 mM concentration) is also shown in this figure. It seems that the adsorption kinetics for the glycolic thiol **1** are much slower than those for the alkylthiol perhaps as a result of much stronger solvent–thiol interactions in the case of the glycolic thiol. After 2 h in both cases the monolayers seem to be complete.

Water contact angle measurements on the flat gold-coated glass slides after thiol adsorption yielded an advancing contact angle of 65.1° and a receding angle of 59.5°. The hysteresis is surprisingly small and the contact angles themselves are much higher than what would normally be expected for such a hydrophilic surface. OH terminated surfaces have contact angles usually smaller than 10°.[17] At the present time, we are able to explain neither the small hysteresis (which normally indicates very well-ordered surfaces) nor the large contact angles.

Gold colloids protected by the thiol 1

The reduction of chloroauric acid in the presence of the thiol **1** yields protected gold colloids in solution. These can be dried by evaporating the solvent water and then redissolving in water. This behaviour is usually considered to be indicative of complete protection of the gold colloid by the thiol monolayer. The recorded IR-spectra of these functionalized and dried gold colloids are presented in Fig. 3. The spectra are consistent with those of the free thiol, and of the thiol SAM on flat gold-coated glass substrates (taken in specular reflectance mode). These are also displayed in Fig. 3.

The panels of Fig. 4 display atomic force micrographs of the glycol-thiol protected gold colloids that were spin-cast on mica surfaces. Panel (a) shows an AFM top view and panel (b) the surface plot. Both images display the heights of the objects. We observe two kinds of spherical objects on the surface, the first are clusters of the colloids forming spherical aggregates around 10 nm in diameter [from the heights surface plot in panel (b)]. These large aggregates are seen not to have smooth profiles but show up the individual colloidal particles which they comprise. The second feature is the individual colloidal particles with diameters around 2–3 nm [from the heights surface plot in panel (b)]. Elsewhere,[18] we have examined the utility of tapping-mode AFM to examine gold colloids spin-cast on mica-surfaces through comparison with TEM images. We find consistent sizes and morphologies through the two techniques. Tip-sample convolution in determining the sizes of these colloidal particles does not seem to be a problem.

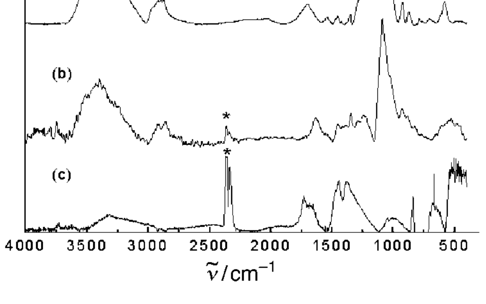

Fig. 3 FT-IR spectra of (a) the thiol **1** in transmission, (b) gold colloids protected by the thiol **1** in transmission and (c) the thiol **1** adsorbed on gold-coated glass substrates taken in specular reflectance. The asterisk indicates the absorption of sorbed CO_2.

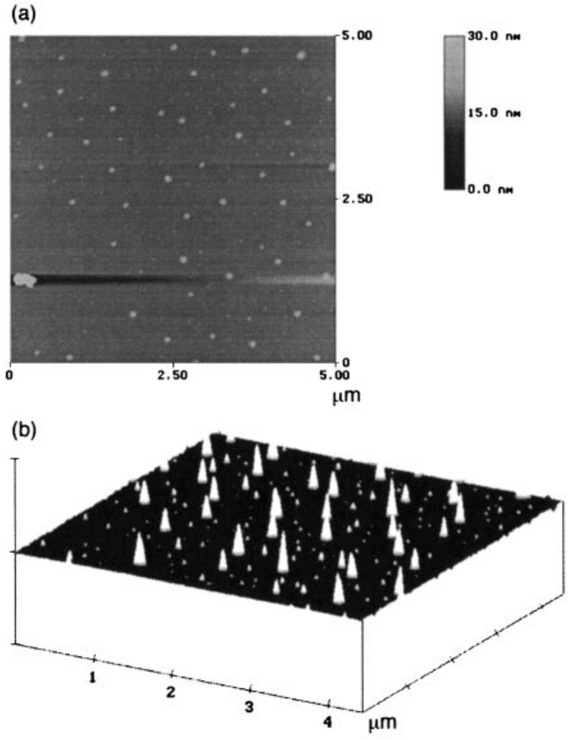

Fig. 4 Tapping mode AFM images of the thiol-protected gold colloids deposited on a mica substrate: (a) is a top view and (b) the surface plot.

Calcium carbonate crystallization in the presence of the colloids

At a pH of 8.5 calcium carbonate crystallizes in its three modifications aragonite, vaterite and calcite. Typical scanning electron micrographs of materials collected after the crystallizations are displayed in Fig. 5. Panel (a) shows rhombohedral calcite crystals with the typical (104) habit grown in the absence of the protected gold colloids. Panel (b) displays a micrograph of a typical aggregate obtained after calcium carbonate crystallization in the presence of the protected gold colloid seed (100 mg l^{-1} in terms of the Au). Analysis of the phase composition of the material collected from such a crystallization was followed through Rietveld refinements of the X-ray powder diffraction profiles as previously reported.[6] The analysis suggested that the ratio of calcite : vaterite : aragonite was 73 : 7 : 20 compatible with the ability of aragonite to form at this pH. However we focus on the calcite crystals in the micrograph displayed in this panel. While in our previous work, we have been able to infer unambiguously that (at a pH around 12) calcite crystals form spheroidal aggregates around the colloidal nuclei, from the micrograph in Fig. 5(b), we are unable to arrive at such a conclusion. Indeed, it would seem that the thiol-protected colloids, rather than acting as nuclei, act in this case as growth and habit modifiers. The precise plane on which the colloid acts is difficult to determine from this image. To confirm that the colloids indeed act as

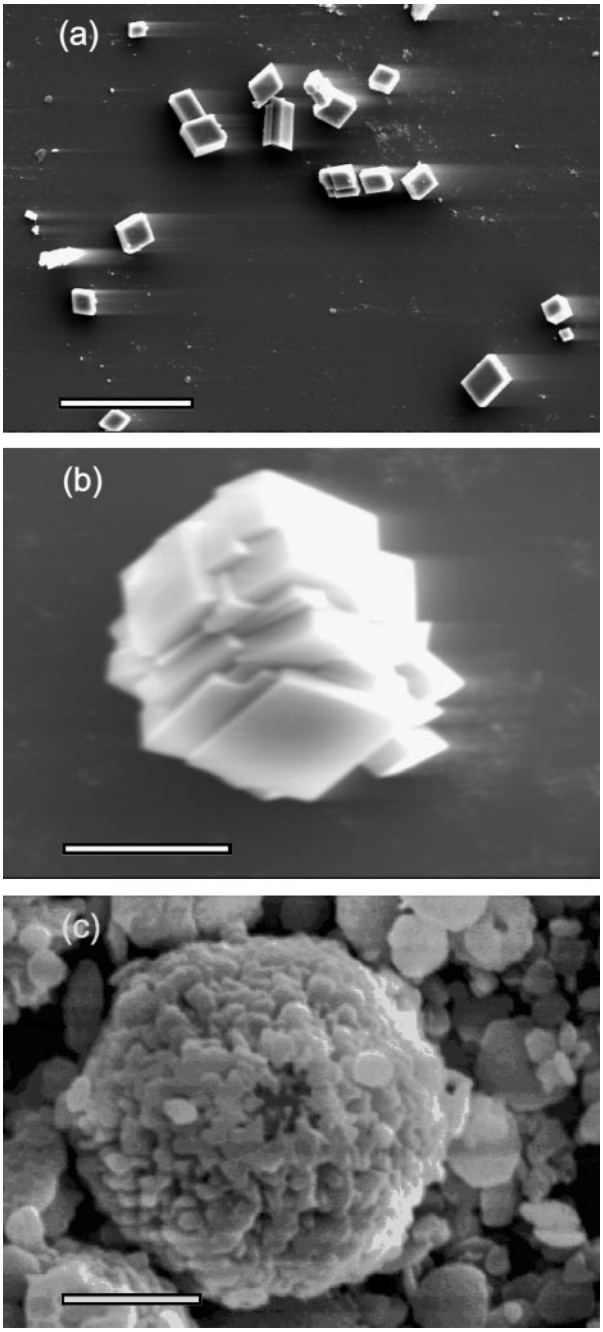

Fig. 5 Scanning electron micrographs of the crystallizations performed at a pH of 8.5: (a) shows the crystals formed in the absence of the colloid, (b) in the presence of the thiol-protected colloids and (c) in the presence of tetraethylene glycol. The scale bars are (a) 50 μm, (b) 5 μm and (c) 5 μm.

modifiers, we have performed the $CaCO_3$ crystallization in the presence of tetraethylene glycol (6 μM). In Fig. 5(c), we show a typical crystal aggregate after such crystallization. There is significant inhibition causing the normally faceted calcite crystals to develop with edges that are rounded, making the calcite crystals form quasi-spheroidal morphologies.

When the pH is raised to 12, the only phase formed is calcite as verified from the X-ray powder diffraction profiles. Fig. 6(a) shows calcite crystals precipitated from solutions in the absence of thiol-protected gold colloid seeds. The crystal aggregates formed in the presence of the colloids are shown in Fig. 6(b). The nature of the rhombohedral crystals arranged in spheroidal aggregates suggests that the crystallization has indeed taken place around the colloidal nuclei. In this, the results correspond more to the kind of assemblies we have previously observed in our crystallizations around *p*-mercaptophenol coated gold colloids.[8] The same problem, that aragonite is suppressed under a high pH, is retained. The present work provides additional impetus to the use of gold colloids as controlled seeds for the crystallization of inorganic materials from solution. Glycol seems to inhibit $CaCO_3$ crystallization, and a future direction to the present work would be to functionalize the exposed glycol group in order to obtain organic interfaces that are more compatible with the growth of the inorganic crystals.

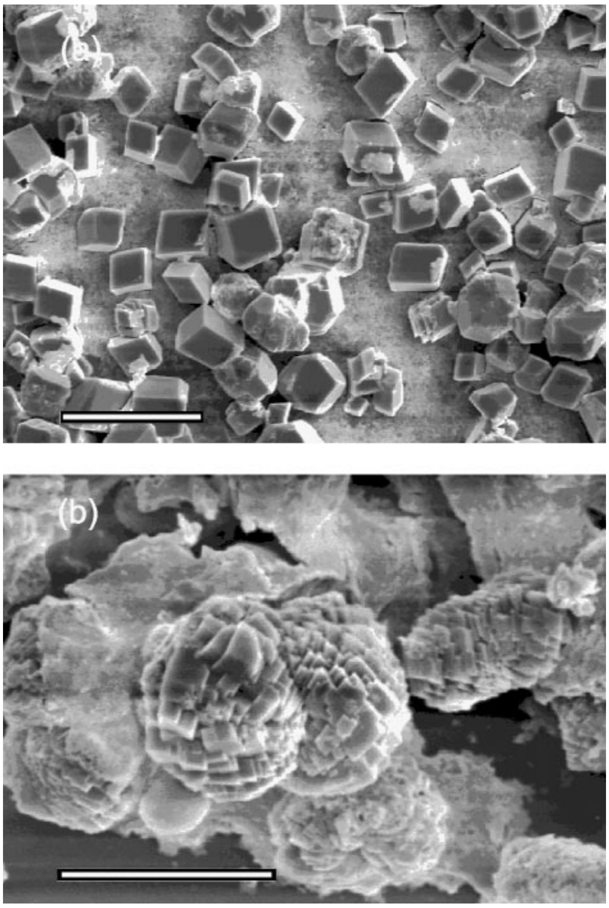

Fig. 6 Scanning electron micrographs of crystallizations performed at a pH of 12: (a) is in the absence of colloids and (b) in the presence of the thiol-protected colloids. The scale bars are (a) 50 μm and (b) 20 μm.

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