Colloid-roughened surfaces as templates for the heterogeneous nucleation of lepidocrocite γ-FeO(OH) nanoparticles

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Lepidocrocite γ-FeO(OH) crystals can be specifically nucleated by sulfonate-terminated SAM/gold surfaces from solutions at room temperature; previously 'roughening' the gold surface through the tethering of gold colloids increases yields.

Extensive studies by Rieke and coworkers[1] have established the propensity of sulfonate modified surfaces (of polymers and of self-assembled monolayers (SAMs) of alkylsilyl compounds on silicon) to heterogeneously nucleate the formation of FeO(OH) crystallites from $\mathrm{Fe^{III}}$ solutions. We have been interested in extending this chemistry to the use of SAMs of ω-substituted alkylthiols on gold as substrates for such heterogeneous nucleation. This would simultaneously permit greater freedom for manipulation of the surface chemistry of the nucleating substrate, facilitate atomic force microscopic (AFM) investigations and most importantly, permit the use of surface plasmon spectroscopy (SPS) to monitor *in situ*, the accretion of material on the substrate. In the course of these investigations, we have been able to unambiguously confirm that only on sulfonate-terminated substrates is there significant nucleation of FeO(OH) (in the γ modification) at room temperature from $\mathrm{Fe^{III}}$ solutions that are otherwise stable to hydrolysis.

Primarily the influence of the sulfonate head-group on the nucleation of FeO(OH) is acidity; nucleation usually being carried out from acidic solutions at pH < 3. Under these conditions, of the typical ω substituents used by us (carboxylates, phosphonates, *etc*.) only the sulfonate group is ionised, permitting its binding to $\mathrm{Fe^{III}}$ ions. Size is not a consideration since the O–O distances in SO_3 groups are about 20% smaller than O–O distances in the FeO_6 octahedra that are the principal structural motifs in the different FeO(OH). These points have been discussed extensively by Reeves and Mann who have examined binding between different tetrahedral anions and the iron oxides.[2] Epitaxis between substrate and crystallite is thus not an issue. A strategem to increase the number of nucleation sites on the substrate would then be to chemically tether (using alkyl dithiols) nanometre-sized gold colloids to the substrates in order to microscopically roughen their surfaces. This has previously proved useful in stabilising aragonite.[3]

Gold-coated glass substrates were placed overnight in 1 mM solutions of 1,12-dodecanedithiol (DDDT) in ethanol. After this, they were dipped in toluene sols of gold colloids† for 2 min. Placing these substrates in solutions of iron(III) nitrate resulted in nearly no deposition of material. FeO(OH) does in fact nucleate heterogeneously on bare gold substrates (because the high conductivity and surface energy of gold permits ions that attach initially to be discharged) so we could conclude that the lack of a deposit on the untreated colloid-tethered surface arises from the continued presence of amphiphiles (left over from the colloid preparation). Further treatment of the colloid-covered gold surfaces through exposure to 1 mM ethanolic solutions of the sodium salt of 3-mercaptopropane sulfonic acid (MPS) results in their being able to nucleate the deposition of thin films of orange–brown powders from the $\mathrm{Fe^{III}}$ solutions.‡ The use of MPS/colloid/DDDT/gold architectures resulted in significantly greater amounts of the orange–brown powders being deposited than when only MPS/gold substrates are used.

As at least eighteen different crystalline compounds are formed in the Fe–O–H system,[4] it is important to unambiguously establish the nature of the orange brown powders. This could be achieved using grazing-incidence X-ray diffraction, combined with Rietveld profile fitting. Fig. 1 displays experimental and fitted X-ray diffraction profiles,§ acquired with a fixed grazing angle of $\Omega = 0.5°$. The lepidocrocite structure[5] was used in the fit, refining scale, profile and preferred orientation parameters. The various parameters of gold (peaks indicated using asterisks) as a second phase were also refined. Below the fitted profile is a simulation of crystalline lepidocrocite with the *hkl* indices marked.

Fig. 2(a) displays tapping mode AFM images¶ of the gold substrate to which colloids were tethered with DDT. The image is displayed at a magnification wherein it is difficult to distinguish the individual colloid particles, but is necessary for comparison with the other images. The crystals were nucleated under identical conditions on two different substrates, (b) MPS/gold and (c) MPS/colloid/DDDT/gold. The crystals are lath-like. On the MPS/gold substrate, they have typical dimensions of 100 nm × 20 nm in the plane of the substrate. On the colloid modified surface (c) the density of crystals is larger presumably as a result of a greater nucleation,‖ and the crystals are simultaneously bigger, extending to about 200 nm. The

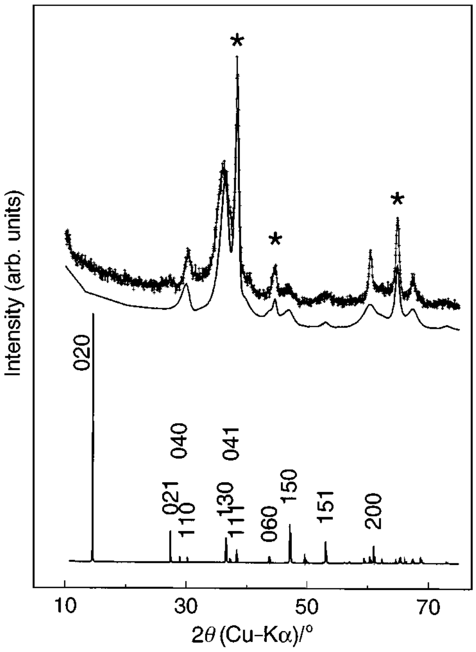

Fig. 1 Experimental and fitted grazing incidence xrd pattern of the FeO(OH) crystals on the MPS/colloid/DDDT/gold assembly. The two profiles have been slightly offset for clarity. The asterisks mark the peaks due to the gold substrate. At the bottom is a simulation of isotropic crystalline lepidocrocite with the *hkl* indices marked.

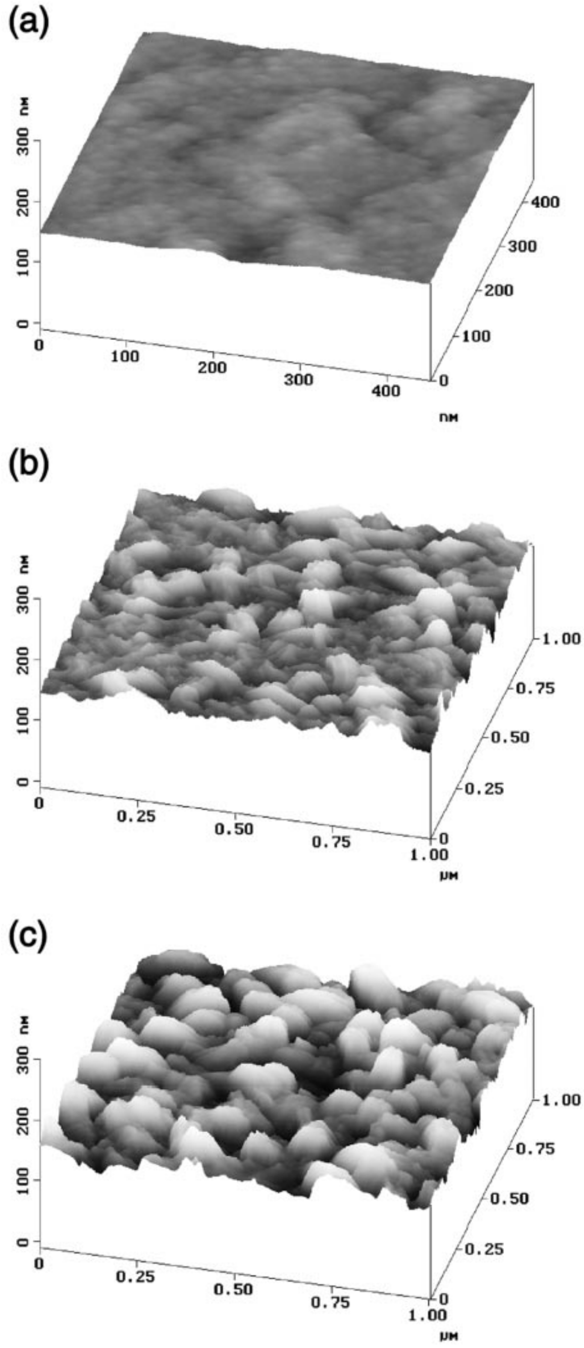

Fig. 2 AFM images of (a) the colloid/DDDT/gold substrate, (b) lepidocrocite crystals grown on MPS/gold and (c) on MPS/colloid/DDDT/gold. The shading is indicative of the height with black referring to the bottom of the scanned image, through gray to white referring to a relative height of 150 nm.

morphology is slightly altered, being a little more rounded. Lepidocrocite is layered,[4] and possesses sheets of FeO_6 double octahedra. An analysis of the structure does not reveal any mode of epitaxy between the O atoms in the structure and a model sulfonate terminated thiol SAM. The layering however suggests that the expected growth direction of the crystals with reference to the substrate would be the direction normal to the sheets namely [010]. The 0*k*0 lines are supressed in the XRD pattern, rather than being enhanced, as one would expect in this case. This arises from two causes. The first is that employing the small grazing Ω angles used in the measurements, one would expect that the incident X-ray will not sample very many 0*k*0 layers. The other is that the pattern clearly displays crystalline correlation lengths that are *hkl* dependent; the peaks with a finite *h* index are more narrow while along those with finite *k*, the peaks are broad, reflecting the poor crystallinity along this direction.

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Notes and References

† Gold colloids were prepared in two-phase toluene/water systems following the procedure of Brust *et al.*[6] Details on the formation and nature of colloid-tethered gold surfaces can be found in ref. 3.

‡ FeO(OH) crystallisations were performed by placing the substrates in polypropylene flasks containing 2 mM solutions (freshly prepared) of iron(III) nitrate for a period of 48 h at room temperature.

§ X-Ray diffraction data were acquired on a STOE θ–2θ diffractometer and were treated using the XND Rietveld program (version 1.16, J.-F. Bérar, ESRF, Grenoble, France, 1997).

¶ Tapping mode AFM images were acquired using a Nanoscope IIIa, employing Si cantilevers.

‖ From the present data, we infer that higher initial nucleation results in greater deposition on the colloid-roughened surfaces. That the FeO(OH) crystals are simultaneously larger suggests that the small crystals formed initially could anneal into larger ones. Initial X-ray measurements indeed suggest that crystallinity increases (linewidths narrow) with time even on keeping deposited Fe oxides and oxide–hydroxides at room temperature.

1 B. J. Tarasevitch, P. C. Rieke and J. Liu, *Chem. Mater.*, 1996, **8**, 292; P. C. Rieke, B. D. Marsh, L. L. Wood, B. J. Tarasevitch, J. Liu, L. Song and G. E. Fryxell, *Langmuir*, 1995, **11**, 31; P. C. Rieke, B. Tarasevitch, L. Wood, M. Engelhard, D. Baer, G. E. Fryxell, C. John, D. Laeken and M. Jaehning, *Langmuir*, 1994, **10**, 619.
2 N. J. Reeves and S. Mann, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3875.
3 J. Küther, R. Seshadri, G. Nelles, H.-J. Butt, W. Knoll and W. Tremel, *Adv. Mater.*, 1998, **10**, 401.
4 R. M. Cornell and U. Schwertmann, *The iron oxides*, VCH, Weinheim, 1996.
5 H. Christensen and A. N. Christensen, *Acta Chem. Scand.*, 1978, **32**, 87.
6 M. Brust, M. Walker, D. Bethell, D. J. Schiffrin and R. Whyman, *J. Chem. Soc., Chem. Commun.*, 1994, 801.

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