

Supplementary Information

Nano-patterned monolayer and multilayer structures of FePtAu nanoparticles on aluminum oxide prepared by nanoimprint lithography and nanomolding in capillaries

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Synthesis of FePtAu NPs

The NPs were prepared using a modification of the reported procedure by Jia et al.¹ The synthesis was performed by heating the precursors' solution at 350° for 3 h. At first, a solution of platinum acetylacetonate (0.5 mmol), gold acetate (0.35 mmol), and 1,2-hexadecanediol (1.5 mmol) in 20 mL octyl ether and 20 mL hexadecylamine was heated up to 100° C in a three-necked, round-bottom flask under a nitrogen atmosphere. To this solution was added, via syringe, oleic acid (0.5 mmol), oleylamine (0.5 mmol), and iron pentacarbonyl (1 mmol). The mixture was heated to reflux and allowed to reflux for 3 h resulting in a black dispersion. Then the heat source was removed and the dispersion was allowed to cool to the room temperature. The inert gas protected solution could then be opened to ambient environment. Adding 40 mL of ethanol led to precipitation of the black product. The mixture was centrifuged to isolate the particles from the brown supernatant. The particles were redispersed in hexane, precipitated with ethanol, and isolated by centrifuging. The particles were dried at room temperature in a vacuum oven to give 100–200 mg of particles. The dispersion and precipitation removed impurities. During synthesis, the relative amounts of platinum acetylacetonate and iron pentacarbonyl and gold acetate were fixed in order to produce NPs with similar compositions (FePt)₈₅Au₁₅.

Synthesis of PO₃ terminated FePtAu NPs

The NPs were prepared using a modification of the procedure reported by Bagaria et al.²⁻³ Cyclohexanone was chosen as the solvent for the ligand exchange because it dissolves FePt NPs and mercaptoundecylphosphonic acid (MUP). A solution of MUP was prepared by mixing 2.7 mg MUP with 5 ml cyclohexanone. 50 mg of FePtAu nanoparticles dispersed in 0.5 ml hexane was added to this solution. The mixture stirred overnight, then centrifuged and the supernatant was discarded. Cyclohexanone (10 ml) was added to the precipitate to remove FePtAu with oleic acid and oleylamine ligands and any excess MUP. The solution was centrifuged and the supernatant was discarded. As a final cleaning, the precipitate was mixed with 10 ml acetone. The solution was again centrifuged and the supernatant was discarded. The particles were then dispersed in 3ml of ethanol:Et₃N (10:1).

Preparation and Characterization of MUP SAMs on Al₂O₃

To observe the orientation of MUP molecules, angle-dependent-XPS was done and the result is shown in figure S1. The electron take off angles varied between 5-90° (angle values are relative to the surface plane). Elemental peak intensities show a clear dependence of the on the detection angle. As the detection angle increases, the amount of S2p from the terminal group decreases and the contribution of P2p from the headgroup increases. This indicates that P is located in the inner part of the SAM which is closer to the substrate surface when compared to S.⁴ The result is in line with the literature, since alkylphosphates and alkylphosphonates were reported to bind metal oxides through the phosph(on)ate headgroup.⁴⁻⁶

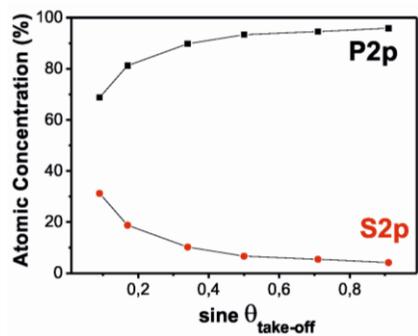


Fig. S1. Angle-dependent XPS of MUP-modified Al_2O_3 substrate. Atomic concentration values are normalized to S+P.

References

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