

Facile synthesis, assembly, and immobilization of ordered arrays of monodisperse magnetic nanoparticles on silicon substrates†

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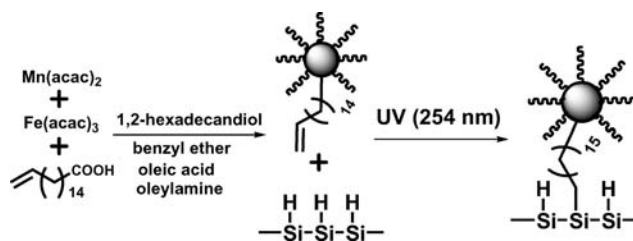
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This paper outlines the preparation of monodisperse MnFe_2O_4 nanoparticles modified with ω -alkenyl moieties in a one-pot reaction, requiring no ligand-exchange step, followed by deposition of the resulting surfactant-coated nanoparticles onto a hydrogen-terminated silicon (111) wafer and covalent anchoring to the surface *via* UV-initiated bonding, creating a stable two-dimensional array of monodisperse magnetic nanoparticles.

The need to develop efficient methods for the assembly of monodisperse magnetic nanoparticles on selected substrates has been driven by interest in applications ranging from nanoscale magnetic sensing to ultrahigh density data storage.¹ In general, the properties needed for the successful application of such magnetic nanoparticles are a highly regular size and a reliably uniform shape.² Moreover, the immobilization and assembly of the nanoparticles on technologically useful substrates requires a dependable assembly process to afford reproducible arrays for activation/addressing on the nanoscale.

MnFe_2O_4 nanoparticles—one of the most widely used magnetic nanostructures³—have been prepared using a variety of synthetic routes, including a widely used “hot” procedure that involves nucleation and growth from organometallic precursors at elevated temperatures in the presence of a mixture of long-chain surfactants.^{2,4} Using a similar approach, Cattaruzza *et al.* and Altavilla *et al.* prepared oleic acid/oleylamine-stabilized magnetite nanoparticles, where the initial stabilizing ligands were replaced in a subsequent step by ligands having terminal unsaturation.^{5,6} These nanoparticles were then attached to the surface of hydrogen-terminated silicon *via* thermal hydrosilylation. In this procedure, a silicon wafer was immersed in a nanoparticle solution and heated to 180 °C for several hours. It is known, however, that the milder conditions used in photochemical hydrosilylation typically lead to monolayer films having enhanced order when compared to those prepared using thermal hydrosilylation.⁷

Given this background, we report here a new strategy for the preparation, assembly, and photo-anchoring of monodisperse ω -alkene-terminated MnFe_2O_4 nanoparticle arrays, starting with a one-pot reaction that requires no separate



Scheme 1 Preparation of ω -alkene-terminated MnFe_2O_4 nanoparticles and their immobilization onto a hydrogen-terminated silicon (111) surface.

ligand-incorporation step or any additional surface modification (see Scheme 1). Drawn from a reported synthesis,^{2,4} our modified procedure involves the thermal decomposition of selected metal precursors in the presence of a specifically tailored mixture of surfactants. A combination of $\text{Fe}(\text{acac})_3$ (0.71 g, 2.0 mmol) and $\text{Mn}(\text{acac})_2$ (0.25 g, 1.0 mmol), 1,2-hexadecandiol (2.6 g, 10 mmol), 16-heptadecenoic acid (0.13 g, 0.50 mmol), oleic acid (1.6 g, 5.5 mmol), oleylamine (1.6 g, 6.0 mmol), and benzyl ether (25 mL) was stirred under argon in a 100 mL three-necked flask. The mixture was heated to 110 °C for 1 h, and the temperature was then carefully raised to 210 °C at a rate of 10 °C min^{-1} . This temperature was maintained for 1 h and followed by reflux at 290 °C for 1 h. After cooling, the crude solution of vinyl-terminated magnetic nanoparticles was mixed with absolute ethanol (30 mL). A black precipitate was isolated by centrifugation. Several post-preparative steps were applied to remove excess stabilizer. The resulting precipitated nanoparticles were stored in a non-polar solution (*e.g.*, toluene).

X-Ray diffraction (XRD) studies confirm that the diffraction peaks of the ω -alkene-terminated MnFe_2O_4 nanoparticles closely match the reported diffraction pattern of MnFe_2O_4 (JCPDS card number 10-0319; see Fig. S1 in the ESI†). The width of the diffraction peaks was used to determine an estimated particle size, leading to a calculated average size for the nanoparticles of 7.4 nm through application of Scherrer's formula. This value is consistent with that obtained from a statistical analysis of the TEM images (*vide infra*).

In the Fourier transform infrared (FTIR) spectrum of the MnFe_2O_4 nanoparticles, broad bands appear for the antisymmetric and symmetric stretching vibrations of the carboxylate anions, $\nu_{\text{as}}(\text{COO}^-)$ and $\nu_{\text{s}}(\text{COO}^-)$, appearing at 1559 and 1427 cm^{-1} , respectively, (see Fig. S2†). The bands of the C=C terminal group appear at 3074, 1637, and 910 cm^{-1}

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due to the antisymmetric $=\text{CH}_2$ stretching mode, the $\text{C}=\text{C}$ stretching mode, and the $\text{C}-\text{H}$ out-of-plane deformation of the $=\text{CH}_2$ moiety, respectively.^{8,9} The broad band at $\sim 3400\text{ cm}^{-1}$ has been attributed to the presence of hydroxyl moieties in related systems.⁸ Typically, two bands consistent with the amino group are found in this region for nanoparticles coated with oleylamine.¹⁰ This fact and the observation that the characteristic band for oleates and oleylamine found at $\sim 3006\text{ cm}^{-1}$ (associated with the $\text{C}-\text{H}$ stretching vibration for the carbon adjacent to the double bond) is absent from the spectrum suggests a reduced presence for these two adsorbates when compared to their ratio in the reaction solution.^{11,12} On the basis of FTIR data in a related system, Petridis and co-workers proposed that the COO^- group binds to $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles primarily as a bidentate ligand.¹¹ Such binding would leave the olefinic tail group free to react with the surface of the substrate.⁸ Based on this prior work and the analysis of our own FTIR data, we similarly conclude that the carboxylate anions from 16-heptadecenoic acid successfully bind to the surface as the dominant adsorbate of the MnFe_2O_4 nanoparticles through the COO^- group, and the pendant ω -alkene group is then available for covalent attachment to the surface of hydrogen-terminated silicon.

Further characterization of the MnFe_2O_4 nanoparticles by TEM demonstrates their monodisperse size distribution ($8.6 \pm 1.4\text{ nm}$); moreover, deposition onto the carbon-coated copper grid led to the formation of a hexagonally ordered array, with little or no nanoparticle aggregation (see Fig. 1). Apparently, the unique and diverse set of organic ligands used

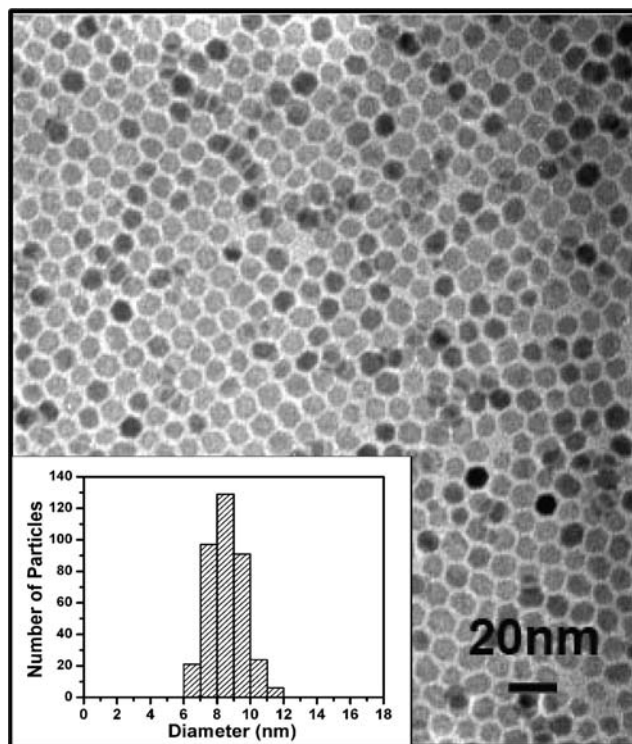


Fig. 1 TEM image of MnFe_2O_4 nanoparticles with a size of $8.6 \pm 1.4\text{ nm}$ deposited from toluene on a carbon-coated copper grid, followed by drying at room temperature. The inset shows the particle size histogram of the MnFe_2O_4 nanoparticles.

in our one-pot synthesis procedure inhibits particle aggregation during the deposition process.¹³

The vinyl-terminated magnetic nanoparticles were separately deposited onto hydrogen-terminated silicon and anchored by UV photolysis at 254 nm .^{5,6,14} In this process, the vinyl groups react directly with the hydrogen-terminated silicon surface as depicted in the second step in Scheme 1.⁷ To our knowledge, there has been only one report of the UV-promoted immobilization of nanospheres and nanorods on hydrogen-terminated silicon.⁸ Our work, however, represents the first example in which the covalently bound nanoparticles, both magnetic in nature and monodisperse in size, are assembled into densely packed ordered arrays without requiring any post-synthesis processing. This combination of features is paramount for the development of functioning nanoscale magnetic devices (*e.g.*, nanomagnetic sensors and ultrahigh density data storage), where uniform and highly ordered arrays for addressing and detection are required.

The specific details of the anchoring procedure are straightforward. To eliminate possible side reactions, the process was conducted entirely under oxygen-free conditions. Hydrogen-terminated silicon wafers were positioned horizontally (face up) on a glass filter frit and flooded with a dilute solution of the vinyl-terminated MnFe_2O_4 nanoparticles, which was immediately vacuum-filtered through the frit. The wafers were then irradiated under a UV lamp for 2 h. The resulting array was then washed at room temperature with toluene, acetonitrile, and ethanol under sonication for 10 min each in an effort to remove any unbound nanoparticles.^{5,6,8} As a final step, the wafers were dried under a stream of argon before characterization.

The ω -alkene-terminated MnFe_2O_4 nanoparticle arrays formed *via* the aforementioned anchoring process were characterized by scanning electron microscopy (SEM). Fig. 2 shows that either a submonolayer or a well-ordered, tightly packed array of spherical nanoparticles was deposited on the silicon surface, depending on whether the sample was subjected to UV radiation. The rightmost image in Fig. 2 demonstrates that the union of our nanoparticle synthesis method with the UV treatment process leads to the generation

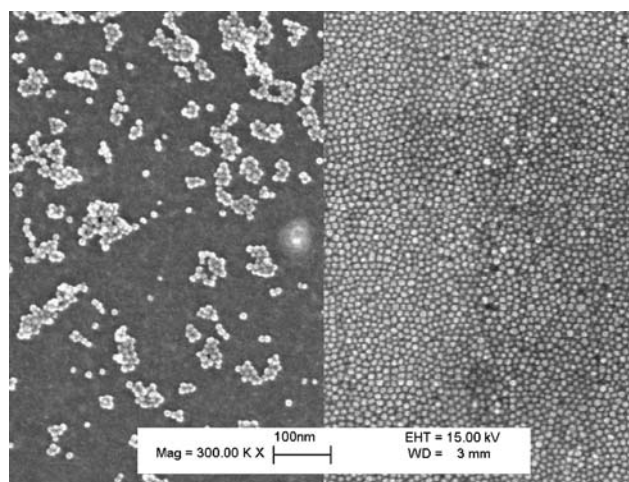


Fig. 2 SEM images at 300 K magnification of ω -alkene-terminated MnFe_2O_4 nanoparticles on Si wafers (left) with no UV treatment and (right) with UV treatment.

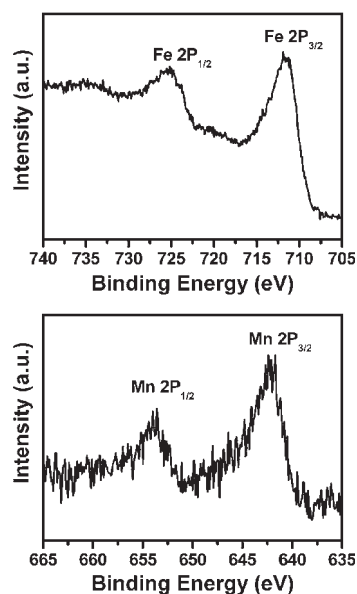


Fig. 3 XPS spectra of covalently attached nanoparticles on silicon(111) wafers under UV irradiation after washing with non-polar and polar solvents under sonication.

of a nanoparticle surface where both the density of packing and the degree of organization are unprecedented for covalently bound magnetic nanoparticles.^{5,8,14}

The presence of the MnFe_2O_4 nanoparticles on the silicon surface was further confirmed by XPS analysis of the surface chemical composition. The Fe 2P and Mn 2P spectra in Fig. 3 show clearly defined peaks associated with the MnFe_2O_4 nanoparticles that are bound to the substrate, even after the silicon wafer had been rigorously washed as described in the anchoring procedure. The Fe ($2\text{P}_{3/2}$) and Fe ($2\text{P}_{1/2}$) binding energies appear at 711.9 eV and 725.1 eV in the XPS spectra, respectively. Furthermore, the Mn ($2\text{P}_{3/2}$) and Mn ($2\text{P}_{1/2}$) binding energies appear at 641.7 eV and 654.0 eV, respectively. These results are consistent with those in a previous study,¹⁵ and support the MnFe_2O_4 formulation. Furthermore, the presence of both Mn and Fe in the nanoparticles is bolstered by the results from energy dispersive X-ray (EDX) analysis (see Fig. S3†).

As a final note, independent research has demonstrated the ability to generate patterned submicron DNA oligonucleotide arrays on silicon substrates using hydrosilylation initiated by laser photolysis at 248 nm under a photomask.¹⁶ Future studies in our laboratories will explore the similar attachment of our nanoparticles in an effort to prepare magnetic

nanoparticle arrays having well defined patterned domains on the submicron scale.

In conclusion, monodisperse MnFe_2O_4 nanoparticles modified with ω -alkene-terminated ligands were successfully prepared in a one-pot reaction and covalently bound by UV irradiation to the surface of hydrogen-terminated silicon, creating stable, ordered monolayer arrays of magnetic nanoparticles. These arrays were resistant to removal by a variety of solvents, even when subjected to sonication for more than 10 min. Furthermore, the simplicity of our assembly procedure renders it attractive for integration with existing photomask-based patterning technologies to generate custom nano-patterned surfaces for magnetic nanodevice applications.

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