

Preparation and Characterisation of Metallorganic Precursors Derived Iron Oxides on Porous Silicon Layers

Sivakumar Balakrishnan,^{1, 2, a} Yurii K Gun'ko,^{1, b} Gerhard F Swiegers^{3, c} and Tatiana S Perova^{4, d}

¹*School of Chemistry, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland*

²*Department of Applied Sciences, PNG University of Technology (Unitech), Papua New Guinea*

³*Intelligent Polymer Research Institute, University of Wollongong, NSW 2522, Australia*

⁴*School of Engineering, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland*

^asivakumar.balakrishnan@pnguot.ac.pg, ^bigounko@tcd.ie, ^cswiegers@uow.edu.au, ^dperovat@tcd.ie

Keywords: Porous silicon, magnetic nanoparticles, FTIR, Raman spectroscopy

Abstract. Porous silicon has generated interest in scientific community after its photoluminescence discovery and thereafter, research was focused on to the chemical functionalization of silicon and subsequent anchoring of nanoparticles onto silicon. In the present work, the porous silicon has been effectively modified with magnetic nanoparticles which were prepared through metallorganic approach. The as-fabricated magnetic-porous silicon composites were characterised using FTIR and Raman spectroscopies, Scanning Electron Microscopy (SEM) as well as magnetic measurements.

Introduction

The ability of porous silicon to incorporate various types of nanoparticles such as magnetic and semiconducting (quantum dots) nanoparticles is an interesting aspect in porous silicon chemistry. This is feasible because of its large surface area, which can be easily functionalised using chemical methods. Magnetic nanoparticles are known for its applications in various fields [1] and the material has been studied extensively over the past few decades. The unique properties of the nanoparticles combined with those of the silicon or porous silicon might results in new composite materials with various applications [2]. The surface of porous silicon modified using amorphous iron oxide nanoparticles has proved to possess very interesting properties [3]. The incorporation of Fe₂O₃ nanoparticles onto flat silicon wafer and further heat treatment leading to multiple functionality (magnetic, metallic, semiconducting, insulating and optical) has been reported in literature, in which the authors describe about a “plug and play” approach where externally synthesized nanoparticles of desired size and functions are incorporated onto the semiconductor surface [4].

There are various methods by which nanoparticles can be deposited onto porous silicon and among them are electroless metal deposition, metal salt dissolution etc [5]. Researchers have used functionalised magnetic materials as a method to anchor magnetic nanoparticles on to silicon. For example, Altavilla *et al.*, reported on the immobilisation of trimethoxy-7-octen-1-yl silane functionalised magnetite nanoparticles onto a hydrogen-terminated silicon surface [6]. However, in this paper, we report on the metallorganic approach, where the magnetic nanoparticles are anchored onto the porous silicon substrate after suitably functionalising the porous silicon matrix. To the best

of our knowledge, this is a novel approach for the preparation of magnetic nanoparticle-porous silicon composite materials. The as-prepared materials were characterised using various characterisation methods such as FTIR, Raman and magnetic measurements.

Experimental

Samples preparation. All preparation and handling of starting materials and subsequent products were carried out under vacuum or argon by using Schlenk techniques. Solvents were dried over sodium-potassium alloy and distilled under argon prior to use and then condensed into a reaction flask under vacuum shortly before use. The starting materials Sodium t-Butoxide (NaOBu^t) and FeBr_2 (ferrous bromide) were purchased from Aldrich. Ferric chloride and ferrous chloride which were used in the second part of the experiment were obtained from BDH (British Drug House) chemicals and Merck respectively.

P-type macro-porous silicon samples were prepared by using a standard procedure of anodic etching of p-type Si(100) 3 inch wafer (with resistivity of $10\ \Omega\cdot\text{cm}$) with 4% HF in DMF (dimethyl formamide) in a Teflon cell. Silicon wafers ($1\text{cm} \times 1\text{cm}$) were first etched by a 2 % HF for 10 minutes followed by rinsing with de-ionised water (Millipore, $18.2\ \text{M}\Omega\cdot\text{cm}$) taking less than one minute. These etching conditions produce a hydrogen terminated silicon surface [7]. The samples were then dried under argon gas.

Preparation of iron oxide from metallorganic precursors. In the present study, we have used a metallorganic precursor and a sol-gel approach to prepare iron oxide-porous silicon composite materials. The iron oxides were prepared using new metallorganic iron(II) alkoxide precursor, $[\text{Fe}(\text{O}^t\text{Bu})_2(\text{THF})]_2$, which has been previously reported in [8], as single source precursor for the preparation of magnetite and maghemite nanoparticles. In brief, solution of NaOBu^t (0.68 g, 7.08 mmol) was added to FeBr_2 (0.76 g, 3.54 mmol) in dry degassed THF (100 ml) at ca. 0°C under argon. The mixture was stirred for 24 h at ambient temperature, filtered and the filtrate then was used for further reactions. The porous silicon samples were hydroxyl functionalized, prior to the reactions, as reported earlier [9] with slight modifications. Briefly, for the hydroxyl functionalization the porous silicon samples were cleaned for 1 hour in a $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ (7:3 v/v) mixture at $\sim 80^\circ\text{C}$ and then cooled to room temperature. The cleaned substrates were rinsed with de-ionised water and then treated further with a $\text{H}_2\text{O}/\text{H}_2\text{O}_2/\text{NH}_3$ (5:1:1 v/v/v) mixture and dried under vacuum. The hydroxylated porous silicon samples were treated with $[\text{Fe}(\text{O}^t\text{Bu})_2(\text{THF})]_2$ precursor solution in dry THF and subjected to sonication. After the ultrasonic treatment, the PS samples were washed with dry diethyl ether, twice with wet diethyl ether followed by drying under vacuum. Then porous silicon samples were heated up to 100°C under vacuum for 12 hours. SEM image of porous Si sample before and after deposition of iron oxide is shown in Figs. 1a,b.

FTIR spectroscopy. Fourier transform infrared (FTIR) measurements were performed in transmission mode using a Digilab FTS-6000 spectrometer. The sample was placed either in the main chamber of spectrometer, using a Perkin-Elmer micro-sampling attachment, or on the positional stage of a UMA 500 IR microscope. For measurements in the main chamber a wide band MCT detector in the wavenumber range of $450\text{--}6000\ \text{cm}^{-1}$ with a resolution of $2\ \text{cm}^{-1}$ and $8\ \text{cm}^{-1}$ was used. A narrow band MCT detector with a spectral range of $4500\text{--}750\ \text{cm}^{-1}$ was used in a UMA 500 IR microscope. A total of 128 scans were summed to increase the signal-to-noise ratio in both cases.

Raman spectroscopy. Room temperature Raman spectra were measured with a Renishaw 1000 micro-Raman system. The excitation wavelength was 514.5 nm from an Ar^+ ion laser (Laser Physics Reliant 150 Select Multi-Line) with a typical laser power of $\sim 10\ \text{mW}$. The 50x

magnifying objective of the Leica microscope focused the laser beam into a spot of about 1 μm in diameter.

Magnetic measurements. Magnetic measurements were carried out both at 5 K and 300 K using a MPMS super-conducting quantum interference device (SQUID) magnetometer.

Results and Discussions

The preparation of iron oxides from metallorganic precursor route gives two types of magnetic materials – magnetite (Fe_3O_4) and maghemite ($\gamma\text{-Fe}_2\text{O}_3$). The preparation of iron oxide layers on porous silicon samples were performed according to the scheme depicted in Fig. 2. Briefly, the hydroxylated porous silicon samples were treated with $[\text{Fe}(\text{O}i\text{Bu})_2(\text{THF})]_2$ precursor solution in dry THF and subjected to sonication. After the ultrasonic treatment, the PS samples (composite samples) were washed with diethyl ether and heated up to 100°C under vacuum for 12 hours. The mechanism of formation of iron oxide involves an oxidation of Fe(II) into Fe(III) by ultrasonically generated radical and peroxide species from THF. A similar type of process has been reported in [10]. The formation of Fe_2O_3 nanoparticles proceeds via precursor materials containing $-\text{Fe}-(\text{OH})-\text{Fe}-$ [8] interacts with the $-\text{OH}$ groups of porous silicon. Further, the nanoparticles get anchored on the surface of the silicon material. The thermal treatment at 100°C allows the completion of conversion from the precursor into iron oxide coating.

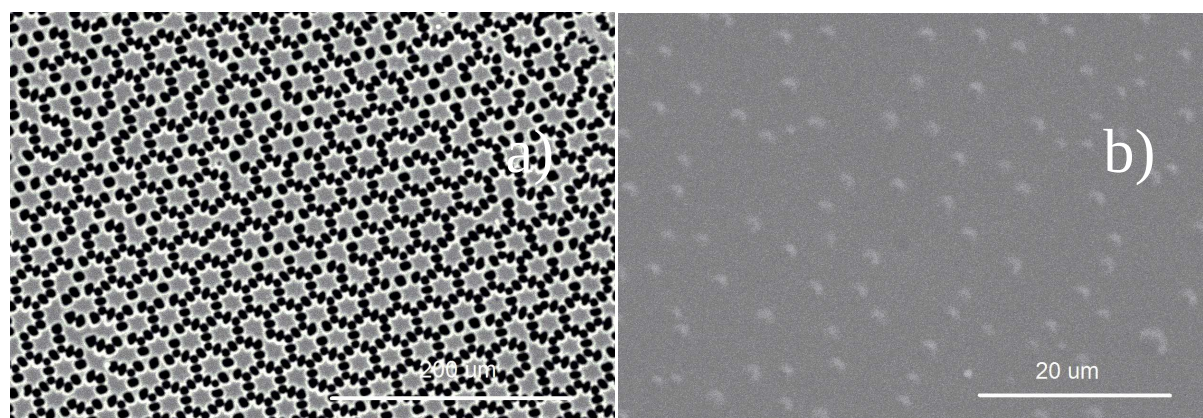


Figure 1. SEM images of p-type porous Si sample before (a) and after (b) deposition of iron oxide layer.

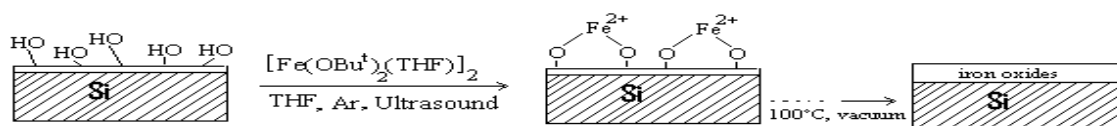


Figure 2. A schematic representation of the preparation of iron oxide layers on porous silicon surface.

The SEM image of the p-type porous silicon alone shows the pores in the range 5 to 10 μm range and the figure 1 (b) shows the uniform deposition (thin layer) of iron oxide layer on the silicon surface. The as-prepared layers have been studied by FTIR and micro-Raman spectroscopy. Figure 3a shows the infrared (IR) spectrum of iron oxide layers on porous silicon and it provide information about the various stretching and bending modes of iron oxides on porous silicon. A band at 1625 cm^{-1} is characteristic for bending mode of Fe–OH groups, which are present at the surface of iron oxides. The IR spectrum shows a shoulder at 1027 cm^{-1} which was assigned to Fe–O–Si stretching vibrations [11]. The broad bands at 1097 cm^{-1} and 825 cm^{-1} were attributed to Si–O and Fe–O bonds respectively [7, 12]. The presence of Fe–O–Si bands confirm the bond formation between the substrate (porous silicon) and the magnetic nanoparticles formed from the metal alkoxide reaction route.

Raman spectrum of the sample (Fig. 3b) clearly shows peaks belonging to a mixture of magnetite and maghemite [13]. The peaks at 193 and around 680 cm^{-1} are attributed to magnetite, whereas the peaks at 161, 617 and 710 cm^{-1} are attributed to maghemite [13]. The strong peak around 520 cm^{-1} is attributed to silicon substrate [14].

The magnetic measurement studies (magnetic moment) on the iron oxide–porous silicon composite sample (figure 4) showed a weak magnetic response of the iron oxide layer on porous silicon. This can be attributed to the presence of very thin layer of magnetic iron oxide. The magnetisation (which is measured in emu/g or Am^2/kg) of the sample is limited in this study due to the formation of thin layer sample as such the amount of material (magnetic nanoparticles) on the surface could not be calculated. Therefore, the magnetic moments of the material could be determined and it gives information that the material formed, through this novel metallorganic approach, is magnetic in nature.

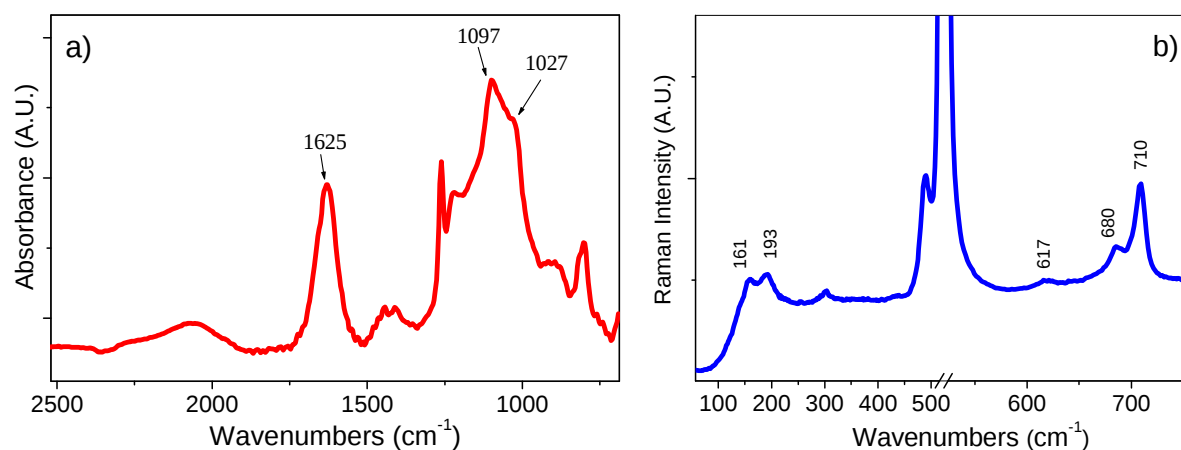


Figure 3. (a) FTIR spectrum of iron oxide layers on porous silicon. (b) Raman spectrum demonstrating the presence of magnetite and maghemite iron oxides on porous Si.

Conclusions

In conclusion, we have shown that porous silicon can be effectively functionalized with iron oxides materials which are prepared through the metallorganic route. Although the results presented in this

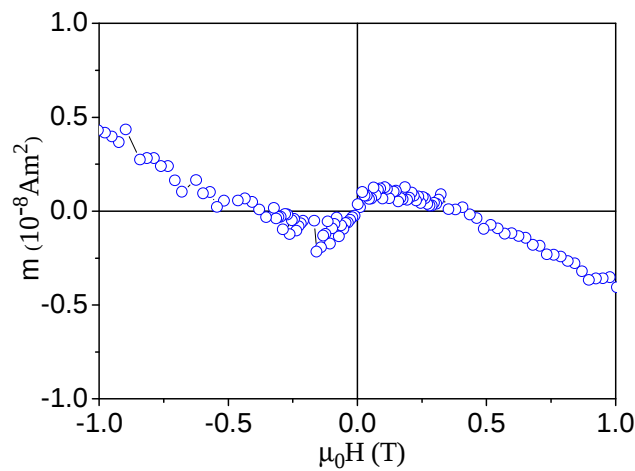


Figure 4. Magnetic measurements of the iron oxide-porous silicon composite.

paper are still preliminary, it shows that porous silicon could be functionalized with magnetic nanoparticles that have been prepared through a metallorganic approach. The as-functionalized porous silicon surfaces are conveniently characterized by FTIR, Raman, SEM and magnetic measurements.

Acknowledgements

We gratefully acknowledge Enterprise Ireland (Basic Research Grant Scheme) and HEA PRLTI programme for financial support and staff members of the Electron Microscopy Unit of TCD for their kind support during this work. The authors thank Dr Venkatesan for useful discussions and carrying out the magnetic measurements.

References

- [1]. (a) A. G. Audram, and A. P. Huguenard, U.S. Patent 4,302,523 (1981). (b) R. F. Ziolo, U.S. Patent 4,474,866 (1984). (c) N. M. Pope, R. C. Alsop, Y.-A. Chang and A. K. Sonith: J. Biomed. Mater. Res., Vol. 28 (1994) p.449. (d) S. P. Bhatnagar and R. E. Rosensweig: J. Magn. Magn. Mater., Vol. 149 (1995) p.198.
- [2]. (a) K. S. Nustad, T. E. Funderud, A. Berge and J. Ugelstad, in *Scientific Methods for the Study of Polymer Colloids and their Applications*, ed. F. Candau and R. H. Ottewill, 1990, Kluwer Academic, Dordrecht, 517. (b) J. Ugelstad, P. Stenstad, L. Kilaas, W. S. Prestvik, P. Herje, A. Berge and E. Hornes: Blood Purification, Vol. 11 (1993) p.349.

- [3]. K. Prabhakaran, Y. Watanabe, K. G. Nath, Y. Homma, T. Ogino, K. V. P. M. Shafi and A. Ulman: *Surf. Sci.*, Vol. 545 (2003) p.191.
- [4]. K. Prabhakaran, K. V. P. Mohammed Shafi, A. Ulman, and T. Ogino, *Adv. Mater.*, Vol.13 (2001) p.1859.
- [5]. C. Xu, X. Zhang, K. N. Tu and Y. Xie, *J. Electrochem. Soc.*, 154 (2007) p.D170.
- [6]. C. Altavilla, E. Ciliberto, D. Gatteschi and C. Sangregorio, *Adv. Mater.* Vol. 17, no. 8, (2005), p.1084.
- [7]. J. E. Bateman, R. D. Eagling, B. R. Horrocks, A. Houlton and D. R. Worrall: *Chem. Commun.*, Vol. 23 (1997) p.2275.
- [8]. G. B. Biddlecombe, Y. K. Gun'ko, J. M. Kelly, S. C. Pillai, J. M. D. Coey, M. Venkatesan and A. P. Douvalis: *J. Mater. Chem.*, Vol.11 (2001) p.2937.
- [9]. R. Cohen, N. Zenou, D. Cahen, and S. Yitzchaik: *Chem. Phys. Lett.*, Vol.279 (1997) p.270
- [10]. (a) X. Cao, Yu. Kolytyn, G. Katabi, R. Prozorov, I. Felner and A. Gedanken: *J. Mater. Chem.*, Vol.7 (1997) p.1007; (b) R. Vijayakumar, Yu. Kolytyn, I. Felner and A. Gedanken: *Mater. Sci. and Eng. A.*, Vol.286 (2000) p.101; (c) R. V. Kumar, Yu. Kolytyn, Y. S. Cohen, Y. Cohen, D. Aurbach, O. Palchik, I. Felner and A. Gedanken: *J. Mater. Chem.*, Vol.10 (2000) p.1125.
- [11]. A. W. Jung: *Magnetic Resonance Imaging*, Vol.13 (1995) p.675.
- [12]. E. Pinakoulaki, S. Gemeinhardt, M. Saraste, and C. Varotsis: *J. Biol. Chem.*, Vol.277 (2002) p.23407.
- [13]. (a) D. Bersani, P. P. Lottici and A. Montenero: *J. Raman Spectrosc.*, Vol.30 (1999) 355. (b) O. N. Shebanova and P. Lazor: *J. Solid-State Chem.*, Vol.174 (2003) p.424.
- [14]. V. Craciun, C. B. Leborgne, E. J. Nicholls and I. W. Boyd: *Appl. Phys. Lett.*, 69 (1996) 1506.

Authors' background

Your Name	Title*	Research Field	Personal website
Sivakumar Balakrishnan	Lecturer	Inorganic chemistry, Intelligent polymer systems	https://www.researchgate.net/profile/Sivakumar_Balakrishnan3
Yurii Gounko	Full Professor	Organometallic chemistry, Science of materials and nano-technology	www.tcd.ie/chemistry/staff/people/yg/index.html
Gerhard Swiegers	Professor	Intelligent Polymer systems, "Mechanical" (machine-like) catalysis	http://ipri.uow.edu.au/people/UOW068498.html
Tatiana Perova	Fellow Emeritus	Materials Science, Optical characterisations, Si Photonic Crystals	https://www.tcd.ie/eleceng/staff/perovat/