

Preparation and characterization of magnetic Chitosan/Fe₃O₄ Nanocomposite particles

黃新義、

E-mail: 321808@mail.dyu.edu.tw

ABSTRACT

There were two studies in this research. The first one included the preparation of magnetic chitosan/iron (II, III) oxide composite nanoparticles by a spray-drying method. Field emission scanning electron microscopy (FESEM) micrographs indicate that nanoparticles so prepared have a good sphericity and a rough surface morphology. The average diameters of samples are in range of 200 to 400 nm. Superconducting quantum interference device (SQUID) results indicate that all samples manifest zero coercivity and zero remanence, which infers that each of the samples has a superparamagnetic property. The highest saturation magnetization of samples is about 27.91 emu/g. Dynamic light scattering (DLS) data shows that the zeta potential of samples is higher than 40 mV, indicating that the samples can steadily distribute in water. The second part included the preparation and separation of magnetic chitosan/iron (II, III) oxide micro/nano- particles. In this study, a two-fluid atomizer and spray-drying method was used to prepare magnetic chitosan/iron (II, III) oxide micro/nano- particles. Samples were collected by cyclone collector, multi-stage electromagnet collector, and electrostatic precipitator (ESP), separately. In the multi-stage electromagnet collector, the higher the number of turns (500, 1000, and 1500 turns) in a coil on an electromagnet collector, the higher the strength of electromagnet (200, 250, and 300 G) was found, which was used to collect different size of magnetic micro/nano- particles. Scanning electron microscopy (SEM) micrographs indicate that particles collected by cyclone collector have average diameters in range of 1200 to 5000 nm. Particles collected by multi-stage electromagnet collector have average diameters in range of 300 to 2200 nm. The particles size decreased with increasing the strength of electromagnet. The smallest particles which have diameters in range of 200 to 600 nm were collected by ESP.

Keywords : Chitosan、 Spray drying、 Iron oxide

Table of Contents

封面內頁	簽名頁	ii	授權書	iii	中文摘要	iv	英文摘要	v	誌謝	vii	目錄	viii	圖目錄	x	表目錄	xii	附錄	xiii	1. 緒言	1	2. 文獻回顧	2	2.1 磁性材料	2	2.1.1 物質之磁性歸納	3	2.2 幾丁質與幾丁聚醣	5	2.2.1 幾丁聚醣的基本特性	6	2.2.2 幾丁聚醣的應用	7	2.3 奈米科技	14	2.3.1 奈米材料維度	14	2.3.2 奈米藥物的定義	15	3. 以噴霧乾燥法製備磁性幾丁聚醣/四氧化三鐵奈米複合顆粒	16	3.1 文獻回顧	16	3.1.1 磁性幾丁聚醣顆粒之製備	16	3.1.2 功能性複合粒子	18	3.2 研究目的	20	3.3 實驗流程	21	3.4 材料與儀器設備	22	3.4.1 藥品及耗材	22	3.4.2 儀器設備	22	3.5 研究方法	25	3.5.1 幾丁聚醣/氧化鐵(II,III)懸浮液之製備	25	3.5.2 噴霧乾燥法製備磁性奈米複合顆粒	25	3.5.3 產物分析	26	3.6 結果與討論	30	3.6.1 磁性幾丁聚醣/氧化鐵(II,III)奈米複合懸浮液之製備	30	3.6.2 磁性幾丁聚醣/氧化鐵(II,III)奈米複合顆粒之組成及結構	30	3.6.3 富立葉紅外線光譜儀試驗(FTIR)	32	3.6.4 X光繞射分析試驗(XRD)	38	3.6.5 場發射電子顯微鏡觀察(FESEM)	40	3.6.6 磁的性質分析	53	3.6.7 磁的性質及表面電荷的分析	55	3.7 結論	58	4. 磁性幾丁聚醣/四氧化三鐵微奈米粉末之製備及分離	59	4.1 文獻回顧	59	4.1.1 電磁學由來及發展過程	59	4.1.2 磁性分離技術	60	4.2 研究目的	61	4.3 材料與儀器設備	62	4.3.1 儀器設備	63	4.4 研究方法	64	4.4.1 磁性流體之製備	64	4.4.2 收集設備製造及安裝	65	4.4.3 噴霧乾燥法	65	4.5 結果與討論	69	4.5.1 磁性幾丁聚醣/四氧化三鐵複合懸浮液	69	4.5.2 五段收集器分離微奈米顆粒	69	4.5.3 多段式電磁鐵收集器於磁性微奈米顆粒之分離效果	69	4.5.4 掃描電子顯微鏡粒徑及型態觀察	70	4.5.5 原子吸收光譜儀試驗	78	4.5.6 富立葉紅外線光譜儀試驗	78	4.5.7 熱重分析儀試驗	81	4.6 結論	84	5. 總結	85	附錄	94
------	-----	----	-----	-----	------	----	------	---	----	-----	----	------	-----	---	-----	-----	----	------	-------	---	---------	---	----------	---	---------------	---	--------------	---	-----------------	---	---------------	---	----------	----	--------------	----	---------------	----	-------------------------------	----	----------	----	-------------------	----	---------------	----	----------	----	----------	----	-------------	----	-------------	----	------------	----	----------	----	------------------------------	----	-----------------------	----	------------	----	-----------	----	------------------------------------	----	--------------------------------------	----	-------------------------	----	---------------------	----	-------------------------	----	--------------	----	--------------------	----	--------	----	----------------------------	----	----------	----	------------------	----	--------------	----	----------	----	-------------	----	------------	----	----------	----	---------------	----	-----------------	----	-------------	----	-----------	----	-------------------------	----	--------------------	----	------------------------------	----	----------------------	----	-----------------	----	-------------------	----	---------------	----	--------	----	-------	----	----	----

REFERENCES

1. 王三郎。2000。生物技術。台灣。
2. 李玉寶。2006。奈米生醫材料。台灣。
3. 林錫杰。2001。幾丁質/幾丁聚醣專輯。
4. 林芳新、董瑞安。2006。奈米核殼複合粒子的製備及生醫應用。科儀新知28(1):7-16。
5. 袁國芳、林新榜、賴進此、陳慶元。2001。幾丁質/幾丁聚醣專輯。
6. 秦靜如。2005。磁性分離技術。化工資訊與商情。20:74-78。
7. 涂世雄、王雄正、蔡耀州。2004。電磁學的故事。科學發展378:62-67。
8. 莊淑惠。2001。幾丁質/幾丁聚醣專輯。
9. 陳美惠、莊淑惠、吳志律。2001。幾丁質/幾丁聚醣專輯。
10. 陳文章、徐俊旭、呂博文、李坤易、林志鴻。2005。功能性奈米材料及其應用。真空科技19(1):4-16。
11. 陳東煌。2005。複合奈米粒子有趣的人造原子。科學發展408:40-45。
12. 陳煜斌。2006。磁性。物理:321-339。
13. 張揚狀、陳東煌。2005。披覆幾丁聚醣之多功能磁性奈米載體的製備及應用。化工52(5):53-62。
14. 張國揚。2001。奈米複材。化工資訊5(12):10-18。
15. 傅昭銘、王昱峰。2003。奈米磁顆粒之放射性標化及應用簡介。物理雙月刊25(3):1-4。
16. 劉伊郎、陳恭。2000。氧化鐵(Fe₃O₄)薄膜與超晶格。物理雙月刊22(6):592-605。

- 17.葉晨聖。2004。磁性奈米粒子的製備與其在生醫領域之應用。奈米專輯:1 (7) :64-72。 18.楊謝樂。2006。磁性奈米粒子於生物醫學上之應用。物理雙月刊28 (4) :692-697。 19.鄭文桐、黃山峰。2004。超微粒子分散技術與應用概況。化工技術8 (4) :174-190。 20.謝慰親。2010。雷射光散射儀。德芮克國際股份有限公司。 <http://hvic.hk.edu.tw/cpsub/data/NanoZS.pdf> 21.簡紋濱、陳怡然。2006。奈米顆粒的磁性。物理雙月刊28 (5) :831-835。 22.Amidi, M., Romeijn, S. G., Borchard, G., Junginger, H. E., Hennink, W. E. and Jiskoot, W. 2006. Preparation and characterization of protein-loaded N-trimethyl chitosan nanoparticles nasal delivery system. *Journal of Controlled Release*. 111:107-116. 23.Baoqiang, Li., Dechang, Jia., Yu, Zhou., Qiaoling Hu. and Wei, Cai. 2006. In situ hybridization to chitosan/magnetite nanocomposite induced by the magnetic field. *Journal of Magnetism and Magnetic Materials*. 306 : 223-227. 24.Berry, C. C. and Curtis, A. S. G. 2003. Functionalisation of magnetic nanoparticles for application in biomedicine. *Journal of Physics D:Applied Physic*. 36:198-206. 25.Bose, A., Ghebremeskel, A. N. 2003. A continuous hybrid field-gradient device for magnetic colloid-based separations. *Journal of Magnetism and Magnetic Materials*. 261 : 66-72. 26.Chatterjee, J., Haik, Y. and Chen, C. J. 2003. Size dependent magnetic properties of iron oxide nanoparticles. *Journal of Magnetism and Magnetic Materials*. 257 : 113-118. 27.Choi, J. W., Ahn, C. H., Bhansali, S., Henderson, T. 2000. A new magnetic bead-based filterless bio-separator with planar electromagnet surfaces for integrated bio-detection systems. *Sensors and Actuators B* 68:34-39. 28.Coey, J. M. D. 2002. Permanent magnet applications. *Journal of Magnetism and Magnetic Materials*. 248 : 441-456. 29.Denkbas, E. B., Kilicay, E., Birlikseven, C. and ?瑣t? 貞k,E.2002.Magnetic chitosan microspheres:preparation and characterization. *Reactive & Functional Polymers*. 50 : 225-232. 30.Desai, K. G. H., and Park, H. J. 2005.Preparation and characterization of drug-loaded chitosan-tripolyphosphate microspheres by spray drying. *Drug Development Research* 64:114-128. 31.Donadel, K., Felisberto, M. D.V., Favere, V. T., Rigoni, M., Batistela, N. J. and Laranjeira, M, C. M. 2008. Synthesis and characterization of the iron oxid magnetic particle coated with chitosan biopolymer. *Material Science and Engineering C*. 28 : 509-514. 32.Furlani, E. F. and Fulani, P. 2007. A model for predicting magnetic targeting of multifunctional particles in the microvasculature. *Journal of Magnetism and Magnetic Materials*. 312 : 187-193. 33.Grenha, A., Seijo, B. and Remu??鴨-L? 檣ez. 2005. Microencapsulated chitosan nanoparticles for lung protein delivery. *European Journal of Pharmaceutical Sciences* 25:427-437. 34.Guo, Y. H., Li, F. R., Bao, S. Y., Han, T., Cao, J. J. and Zhou, H. X. 2007. Preparation and characteristic of carboplatin-Fe@C-loaded chitosan nanoparticle with dual physical drug – loaded mechanisms. *Current Applied Physics*. 7S1 : e97-e102. 35.Gupta, K. A. and Gupta, M. 2005. Synthesis and surface engineering of iron oxide nanoparticle for biomedical application. *Biomaterials*. 26 : 3995-4021. 36.Gupta, A. K., Curtis, A. S. G. 2004. Lactoferrin and ceruloplasmin derivatized superparamagnetic iron oxide nanoparticles for targeting cell surface receptors. *Biomaterial*, 25 :3029-3040. 37.Hong, J., Gong, P., Xu, D., Dong, L. and Yao, S. 2007. Stabilization of -chymotrypsin by covalent immobilization on amine-functionalizes superparamagnetic nanogel. *Journal of Biotechnology*. 128:597-605. 38.Hong, R. Y., Pan, T. T., Han, Y. P., Li, H., Ding, Z. J., and Han, S. 2007. Magnetic field synthesis of Fe₃O₄ nanoparticles used as a precursor of ferrofluid. *Journal of Magnetism and Magnetic Materials*. 310 : 37-47. 39.Huber, D. L. 2005. Synthesis properties and applications of iron nanoparticle. *Small*. 5:482-501. 40.Hu, Q., Chen, F., Li, B. Shen, J. 2006. Preparation of three-dimensional nano-magnetite/chitosan rod. *Material Letters*. 60:368-370. 41.Ito, A., Shinkai M., Honda, H. and Kobayashi, T. 2005. Medical Application of functionalized magnetic nanoparticles. *Journal of Bioscience and Bioengineering*. 1:1-11. 42.Jang, M. K., Kong, B. G., Jeong, Y. I., Lee, C. H. and Nah, J. W. 2004. Physicochemical characterization of -chitin -chitin and -chitin separated from natural resource. *Journal of Polymer Science : Part A : Polymer Chemistry*. 42 : 3423-3432. 43.Jayakumar, R., Nwe, N., Tokura, S. and Tamura, H. 2007. Sulfate chitin and chitosan as novel biomaterials. *International Journal of Biological Macromolecules*. 40 : 175-181. 44.Jeong, J. R., Chul, S., Lee, S. J., and Kim, J. D. 2005. Magnetic properties of superparamagnetic - Fe₂O₃ nanoparticles prepared by coprecipitation technique. *Journal of Magnetism and Magnetic Materials*. 286 : 5-9. 45.Jia, Z., Yujun, W., Yangcheng, L., Jingyu, Ma. and Guangsheng, L. 2006. In situ preparation of magnetic chitosan/Fe₃O₄ composite nanoparticles in tiny pools of water-in-oil microemulsion. *Reactive & Functional Polymer*. 66:1552-1558. 46.Jotania, R. B., Khomane, R. B., Chauhan, C.C., Menon, S.K. and Kulkarni, B. D. 2008. Synthesis and magnetic properties of barium-calcium hexaferrite particle prepared by sol-gel and microemulsion techniques. *Journal of Magnetism and Magnetic Materials*. 320 : 1095-1101. 47.Kawaguchi, H. 2000. Functional polymer microspheres. *Progress in Polymer Science*. 25:1171-1210. 48.Kim, D. K., Zhang, Y., Voit, W., Rao, K. V. and Muhammed, M. 2001. Synthesis and characterization of surfactant-coated superparamagnetic monodispersed iron oxide nanoparticles. *Journal of Magnetism and Magnetic Materials*. 225 : 30-36. 49.Kim, E. H., Ahn, Y. and Lee, H. S. 2007. Biomedical applications of superparamagnetic iron oxide nanoparticles encapsulated within chitosan. *Journal of Alloys and Compounds*. 434:633-636. 50.Lai, M. F., Lee, C. P., Wei, Z. H. 2010 Magnetic particle separation using controllable magnetic force switches. *Journal of Magnetism and Magnetic Materials*. 322 : 19-24. 51.Li, B., Jia, D., Zhou, Y., Hu, Q. and Cai, W. 2006. In situ hybridization to chitosan/magnetite nanocomposite induced by the magnetic field. *Journal of Magnetism and Magnetic Materials*. 306 : 223-227. 52.Li, G. Y., Jiang, Y. R., Huang, K. L., Ding, P. and Chen, J. 2008. Prerparation and properties of magnetic Fe₃O₄-chitosan nanoparticles. *Journal of Alloys and Compounds*. 466:451-456. 53.Meyers, M. A., Chen, P. Y., Lin, A. Y. M., Seki, Y. 2008. Biological materials:Structure and mechanical properties. *Progress in Materials Science*. 53:1-206. 54.Neuberger, T., Sch? 兕f, B., Hofmann, H. and Hofmann, M. 2005. Supereparamagnetic nanoparticle for biomedical application Possibilities and limitations of a new drug delivery system. *Journal of Magnetism and Magnetic Materials* . 293 : 483-496. 55.Park, J. H., Im, K. H., Lee, S.H., Kim, D. H., Lee, D. Y., Lee, Y. K., Kim, K. M. 2005. Preparation and characterization of magnetic chitosan particles for hyperthermia application. *Journal of Magnetism and Magnetic Materials* . 293 : 328-333. 56.Pillai, C. K. S., Paul, W., Sharma, C. P. 2009. Chitin and chitosan polymers:Chemistry solubility and fiber formation. *Progress in Polymer Science*. 34:641-678. 57.Racka, K., Gich, M., ?lawska-Waniewska, A., Roig A. and Molins, E. 2005. Magnetic properties of Fe nanoparticle system. *Journal of Magnetism and Magnetic*

Materials . 290 : 127-130. 58.Ravi Kumar, M. N. V. 2000. A review of chitin and chitosan applications, *Reactive & Functional Polymer*. 46:1-27.

59.Rellinghaus, B., Stappert, S., Acet, M. and Wassermann, E. F. 2003. Magnetic properties of FePt nanoparticles. *Journal of Magnetism and Magnetic Materials* . 266 : 142-154. 60.Rana, S., Gallo, A., Srivastava, R. S., Misra, R. D. K. 2007. On the suitability of nanocrystalline ferrites as a magnetic carrier for drug delivery: functionalization conjugation and drug release kinetics. *Acta Biomaterialia*. 3:233-242. 61.Rinaudo, M. 2006. Chitin and chitosan: Properties and applications, *Progress in Polymer Science*. 31:603-632. 62.Shahidi, F., Arachchi, J, K, D. and Jeon, Y, J. 1999. Food applications of chitin and chitosans. *Trend in Food Science & Technology*. 10 : 37-51. 63.Sun, Y. K., Ma, M., Zhang, Y. and Gu, N. 2004. Synthesis of nanometer-size maghemite particle from magnetite. *Colloids and Surfaces A: Physicochemical. Engnreringe. Aspects* 245:15-19.

64.Tsouris, C., Noonan, J., Ying, T. Y., Yiacomou, S. 2006. Surfactant effects on the mechanism of particle capture in high-gradient magnetic filtration. *Separation and Purification Technology*. 51:201-209. 65.Wang, J., Zhang, K., Peng, Z. and Cheng, Q. 2004. Magnetic properties improvement in Fe₃O₄ nanoparticles grow under magnetic fields. *Journal of Crystal Grow*. 266 : 500-504. 66.Wei, Z. H., Lee, C. H., and Lai, M. F. 2010 Magnetic particle separation using controllable magnetic force seitches. *Journal of Magnetism and Magnetic Materials* . 322 : 19-24.

67.Wu, Y., Guo, Wang, C. and Fu, S. 2006. Preparation and characterzation of chitosan-poly(acrylic acid) polymer magnetic microspheres. *Polymer*. 47 : 5287-5294. 68.Xu, C. and Sun, S. 2007. Monodisperse magnetic nanoparticle for biomedical application. *Polymer International*. 56 : 821-826. 69.Yan, G. P., Robinson, L. and Hogg, P. 2006. Magnetic resonance imaging contrast agents: Overview and perspectives. *Radiography*. 13:5-19. 70.Zhu, A., Yuan, L. and Liao T. 2008. Suspension of Fe₃O₄ nanoparticles stabilized by chitosan and o-carboxymethyl-chitosan. *International Journal of Pharmaceutics*. 350:361-368. 71.Zhang, W., Shen, H., Xie, M. Q., Zhuang, L., Deng, Y. Y., Hu, S. L. and Lin, Y. Y. 2008. Synthesis of carboxymethyl-chitosan-bound magnetic nanoparticles by the spraying co-precipitation method. *Scripta Material*. 59 : 211-214.