

# Core-shell magnetic nanogel synthesis in aqueous solution *via* surfactant free photochemical reaction

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**ABSTRACT** Core-shell poly (acrylamide) modified magnetic nanogels with narrow particle size distribution were synthesized in aqueous solution with surfactant free *via* photochemical method. The size of the nanogels can be controlled by varying the reaction time, or the concentrations of monomer and cross-linker. After Hoffmann degradation of amido groups, the magnetic nanogels with amino groups were also obtained. The magnetic nanogels were characterized by Fourier transform infrared spectroscopy (FTIR), photo correlation spectroscopy (PCS), atomic force microscopy (AFM) and transmission electron microscopy (TEM), respectively.

**KEYWORDS** Magnetic nanogels, Photochemical method, Core-shell structure, Controllable synthesis

**CLC** O635, O611.62, O644.1

Magnetic nanogels are composites with a magnetic core and a polymeric shell, which consists of polymer hydrogels that are much better than the surface of traditional magnetic nanoparticles in hydrophilicity and biocompatibility with organism. These superparamagnetic nanogels are capable of forming stable aqueous suspensions and can be easily redispersed after agglomeration in the presence of a magnetic field. In recent years, magnetic nanogels have attracted increased attention due to their potential applications in many areas, including enzyme and protein immobilization<sup>[1]</sup>, RNA and DNA purifications<sup>[2]</sup>, magnetic resonance imaging (MRI) techniques for cancer diagnosis, cancer therapy with magnetically controlled drug carriers and hyperthermia<sup>[3,4]</sup>, and removal of toxic elements from industrial wastes<sup>[5,6]</sup>. Several methods have been developed to prepared magnetic nanogels<sup>[7]</sup>. In this letter, we introduce a novel method to synthesize magnetic nanogels in controllable sizes *via* surfactant-free photochemical reaction. Poly (acrylamide) magnetic nanogels with narrow particle size distributions were prepared in aqueous solution. Magnetic nanogels with amino groups were obtained *via* Hoffmann degradation of amido groups.

Typical procedures to prepare the magnetic nanogels are given as follows. A mixture aqueous solution of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, acrylamide, and N, N'-methylene-bis-(acrylamide), without any surfactant, was irradiated by UV light on-line, and stirred under nitrogen atmosphere at room temperature for several hours. Poly(acrylamide) magnetic nanogels were separated from the reaction products with a magnetic field, and were washed thoroughly with double distilled water. After Hoffmann degradation of amido groups by using aqueous solution of NaClO and NaOH, the magnetic nanogels with amino groups, or poly(acrylamide-vinyl amine) magnetic nanogels, were obtained. The magnetic nanogels were characterized by Fourier transform infrared spectroscopy (FTIR), photo correlation spectroscopy (PCS), transmission electron microscopy (TEM) and atomic force microscopy (AFM), respectively.

Table 1 shows typical size of the nanogels, with the polydispersity index and zeta potential being measured by AFM and PCS. The narrow size distribution of the nanogels were confirmed by their low polydispersity index. The core-shell structure and regular morphology of magnetic nanogels were identified by AFM (Fig.1) and TEM (Fig.2), respectively. By adjusting

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reaction time, or concentrations of the monomer and crosslinker, we were able to control size of the synthesized nanogels from 25 nm to 180 nm.

**Tabel 1 Particle size, polydispersity index and zeta potential of the magnetic nanogels measured by PCS and AFM**

| Samples                     | PCS characterization  |                      |                            | AFM characterization / nm |
|-----------------------------|-----------------------|----------------------|----------------------------|---------------------------|
|                             | Mean particle size/nm | Polydispersity index | Zeta potential / mV (pH=7) |                           |
| Before Hoffmann degradation | 78                    | 0.217                | 3                          | 72                        |
| After Hoffmann degradation  | 72                    | 0.241                | 30                         | —                         |

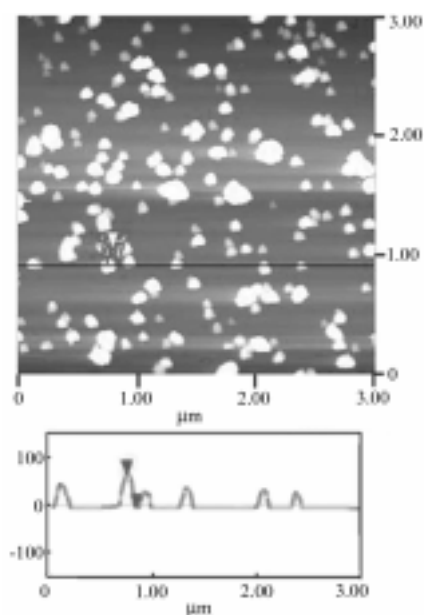


**Fig.1** AFM image of the magnetic nanogels with amino groups. Z scale, 72 nm. Scannig area, 3μm×3μm

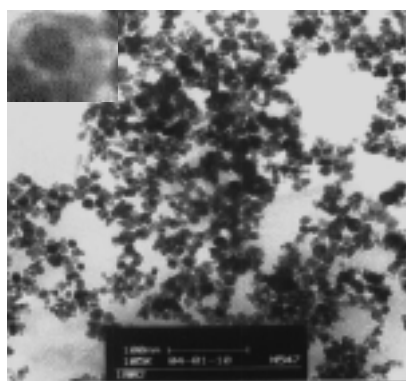


**Fig.2** TEM image of the magnetic nanogels after Hoffmann degradation. Insert: TEM image of a magnetic nanogel magnified by 10 times

In conclusion, magnetic nanogels with amino groups with narrow particle size distributions and high zeta potential were synthesized by photochemical reaction for the first time, and the new approach will be of help to production of functional magnetic nanogels. Papers will be published about studies with the nanogels as magnetically targeted drug carriers.

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#### References

- 1 Koneracká M, Kopčanský P, Antalík M, *et al.* J Magn Magn Mater, 1999, **201** (1-3): 427-430
- 2 Jürgen Oster, Jeffrey Parker, Lothar à Brassard, *et al.* J Magn Magn Mater, 2001, **225**(1-2): 145-150
- 3 Gries H, Utzel W M, Zurth C, *et al.* Magnetic particles for diagnostic purposes, US Pat. 5746999, 1998
- 4 Lacava L M, Lacava Z G M, Azevedo R B, *et al.* J Magn Magn Mater, 2002, **252**(1-3): 367-369
- 5 Yamaura M, Camilo R L, Felinto M C F C. J Alloys Compd, 2002, **344** (1-2): 152-156
- 6 Ambashta R D, Wattal P K, Singh S, *et al.* J Mag Magn Mater, 2003, **267**(3): 335-340
- 7 Deng Y, Wang L, Yang W, *et al.* J Magn Magn Mater, 2003, **257**(1): 69-78

# 水溶液体系中光化学可控合成核壳结构磁性纳米凝胶

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**摘要** 通过光化学方法合成并经进一步的 Hoffmann 降解获得了壳层带有伯胺基核壳结构磁性纳米凝胶, 该磁性纳米凝胶粒径分布窄且粒径可控。由于磁性纳米凝胶的壳层水凝胶具有很好的亲水性和生物相容性, 且反应过程中不加入任何表面活性剂, 为该磁性纳米凝胶的生物应用奠定了良好的基础。通过光化学方法合成窄粒径分布且粒径可控的磁性纳米凝胶就我们认识而言尚未见到文献报道, 有望为磁性纳米凝胶的合成提供一种新的方法。我们对合成的磁性纳米凝胶分别用傅立叶变换红外光谱 (FTIR)、光子相关光谱 (PCS)、原子力显微镜 (AFM) 和透射电子显微镜 (TEM) 进行了表征。

**关键词** 磁性纳米凝胶, 光化学方法, 核壳结构, 控制合成

**中图分类号** O635, O611.62, O644.1