Synthesis of Large Pore Sized Mesoporous Silica Nanoparticles Embedded with Magnetic Nanoparticles for Loading of Large Sized Molecules

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Statement of Purpose: Mesoporous silica nanoparticles (MSNs) have been applied to delivery carrier for various cargo molecules due to their large surface area, high pore volume, and easy surface modification.^[1] However, previously reported MSNs have pore size with about 3nm, which is a limitation to load large sized molecules for various bioapplication. Although there have been reports on the preparation of large pore-sized MSNs, it is still challenging to control pore structure of MSNs with large pores and to combine with functional nanoparticles. For multi-functional diagnostic properties, superparamagnetic nanoparticles can be embedded in MSNs. Superparamagnetic nanoparticles have been studied for multimodal imaging and simultaneous diagnosis and therapy.^[2] In this study, we demonstrate the synthesis of magnetic nanoparticle-embedded MSNs with large pore size.

Methods: The large pore-sized MSNs embedded with magnetic nanoparticles were prepared by using waterdispersed magnetic nanoparticles^[3] in the presence of cosolvent. The surface of the resulting MSNs was modified with amine group by silane chemistry for the adsorption study. The model proteins and DNA were loaded on large-pore sized MSNs by adsorption and compared with small pore sized MSNs.

Results: Figure 1 showed TEM images of the resulting MSNs, revealing that large pores and conventional small pores were simultaneously formed in the MSNs. The size of the MSNs could be controlled in the range of $100 \sim 200$ nm.



Figure 1. TEM images of large pore sized MSNs. Size of MSNs a) 100nm, b) 150nm, c) 200nm, d) large-magnification TEM image of b).

The nitrogen sorption analysis showed that the large pore sized MSNs had larger surface area and higher pore volume than small pore sized MSNs (Figure 2a). The pore size distribution indicated that the resulting MSNs were bimodal structure composed of both small sized pore (3.2nm) and large sized pore (10~30nm) (Figure 2b).



Figure 2. a) Nitrogen adsorption and desorption isotherms and b) the corresponding pore size distribution obtained from the adsorption branch.

The surface of the large pore sized MSNs were modified to amine groups for the protein loading (Figure 3a). The protein adsorption data showed that, compared to the small pore sized MSNs, the amine modified large pore sized MSN had much larger amount of protein adsorbed (Figure 3b). In similar to the adsorption of model protein, the amine modified large pore sized MSN showed the largest model DNA adsorption (Figure 3c). These represents that the large pores and positively charged surface are critical to the high loading of large sized molecules.



Figure 3. a) FT-IR of large pore sized MSNs before and after amine modification. Adsorption of b) model protein and c) model DNA.

Conclusions: We prepared large pore-sized MSNs embedded with magnetic nanoparticles by using cosolvent in sol-gel method. The large pore sized MSNs had large surface area, pore volume and bimodal pore structure. The surface of large pore sized MSNs were modified with amine group by silane chemistry for efficient loading of model protein and DNA, resulting in significantly enhanced adsorption than small pore sized MSNs. The large pore sized MSNs might have a potential for large molecules delivery vehicles for antigens, growth factors, and enzymes.

References:

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