Water-soluble Fluorescent Nanospheres as Fluorosensor for Detection of Cu^{2+}

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A novel water-soluble fluorescent nanosphere as fluorosensor was prepared by emulsifier-free emulsion copolymerization of styrene with naphthalimide derivative (A). The fluorosensor was high sensitive for detection of Cu^{2+}. Comparied with other fluorosensors based on organic fluorophore, it has two advantages. First, there is no pollution to environment in the use of it. Second, it can be used repeatedly.

Recently, the development of new polymer structures and architectures has become an intensely studied field of nanotechnology. This is clearly evident by the burgeoning number of publications on this subject. In addition to inherent intellectual curiosity, interest in this topic is driven by the potential that unique nanometer-sized structures have shown toward performance in a broad range of medical, mechanical, and electronic applications.[1–6] The properties of macromolecules and macromolecular assemblies are affected by their sizes and shapes; thus a great deal of effort has been directed toward controlling the geometries of individual polymers and larger aggregates. Chemical functionality, physical means, and self-assembly are techniques that have been used to generate an array of designed structures. For example, templating,[5,7] micromolding,[3] and capillary action[2] are techniques that have been used to provide structural control in the nanofabrication of large and complex patterns of materials through physical manipulation. Similarly, self-organization, driven by attractive and/or repulsive forces, has provided a powerful and simple method for the creation of unique structural assemblies.[8–10]

Polymeric nanospheres are usually refered to polymeric microspheres with diameters of less than an micrometer. Polymeric nanospheres are being actively investigated for a number of potential applications that would take advantage of their large surface-to-volume ratio; for example, they are showing promise as carriers for catalyst[11,12] and biomolecule.[13] So, there is currently much interest in the preparation of polymer nanospheres. Until now, many techniques have been developed for the preparation of polymer nanospheres. For example, microemulsion polymerization[14] is a technique that has been used to prepare polymer nanospheres. Precipitation[15] and self-assembly of amphipathic block copolymers[16] have also been used to prepare polymer nanospheres.

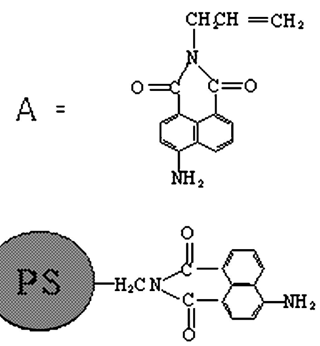
With the rising awareness of the public vulnerability to chemical and biological terrorism, there is a heightened need for high sensitive detection techniques. Fluorphore-based fluorosensors have emerged as powerful tools. For examples, Ranachandram et al.[17,18] prepared naphthalimide-based fluorosensors for the transition metal ions. Adams et al.[19] prepared a perylene-based single-molecule fluorosensor. However, these fluorosensors were only soluble in organic solvents. There is pollution to environment by the use of these fluorosensors. Moreover, these fluorosensors do not recovered and reused.

The preparation of water-soluble fluorescent nanosphere as fluorosensor with the structure illustrated in Scheme 1 has never been reported. The nanospheres were prepared by emulsifier-free emulsion copolymerization of styrene with compound A. The sensing behavior of the fluorescent nanosphere towards some ions was studied.

Emulsifier-free emulsion polymerization has been widely used to prepare monodisperse microspheres. By adding A afterward, it is feasible to synthesize core-shell microspheres whose cores and shells are mainly made up of polystyrene and polyA. In synthetic experiment, the molar ratio of styrene and A was 60:1.

Figure 1 shows a typical SEM photograph of the polymeric microspheres. It can be seen that the microspheres with a diameter of 70 nm are spherical in shape and monodisperse in size. N1s XPS (Figure 2) of polymeric microspheres suggests that A is contained in them.

It is well known that H^+, Ag^+, Cu^{2+} can react with amine groups, so HCl, $AgNO_3$, and $CuCl_2$ were chosen to investigate the sensing behavior of the fluorescent nanosphere. In our experiment, the excitation light wavelength was 370 nm, the excitation light intensity and the concentration of A of fluorescent nanosphere were both kept unchanged.



Scheme 1. A molecular structure and chemical structure of the fluorescent nanosphere.

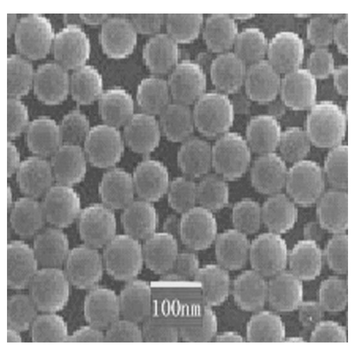


Figure 1. SEM photograph of the fluorescent nanospheres.

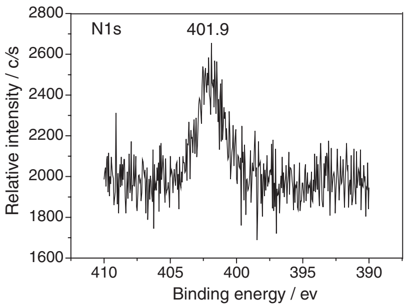


Figure 2. XPS spectra of the fluorescent nanospheres: N_{1S} spectrum.

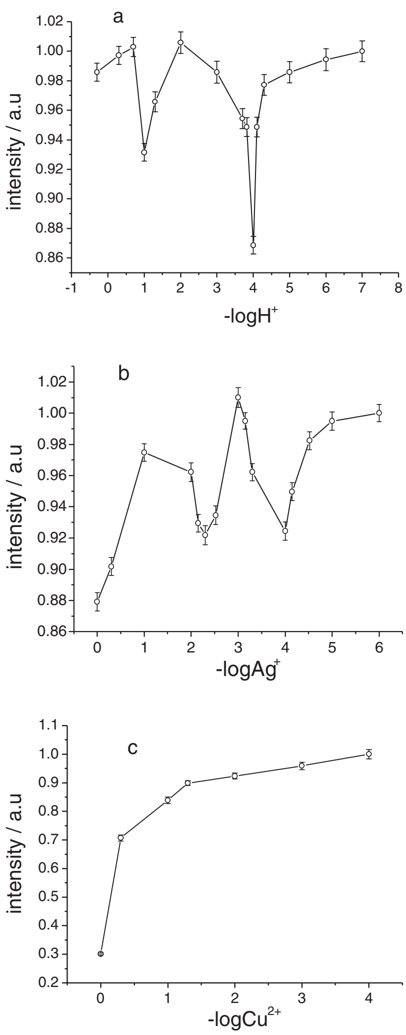


Figure 3. Effect of ions of different concentration on fluorescence intensity. (a) H^+; (b) Ag^+; (c) Cu^{2+}. Volume of ions solution: 3 mL; Volume of the fluorescent nanosphere: 50 μL, concentration of A of the nanospheres: 4.15×10^{-3} $molL^{-1}$.

Figure 3a illustrates the effect of H^+ on the fluorescence intensity of the fluorescent nanosphere. The change of the fluorescence intensity is complicated. This is probably due to the combined action of protonation[20] and surface effect of nanoparticle.

Figure 3b illustrates the effect of Ag^+ on the fluorescence intensity of the fluorescent nanosphere. The combined action of the quenching interaction between Ag^+ and 4-amino-1,8-naphthalimide[17] and surface effect of nanoparticle is suggested to make the change of the fluorescence intensity.

The effect of Cu^{2+} on the fluorescence intensity of the fluorescent nanosphere is shown in Figure 3c. This is mainly due to the quenching interaction between Cu^{2+} and 4-amino-1,8-naphthalimide.[17]

In addition to H^+, Ag^+, and Cu^{2+}, effect of Na^+ was also investigated NaCl and NaF were examined and there was no change in the light performance of the nanospheres. This result shows that Na^+, Cl^- and F^- do not affect optical performance of the nanospheres.

Moreover, after dialysis for a week, the fluorescence of the nanospheres did be recovered. So, it can be used repeatedly. Furthermore, because the nanospheres were soluble in water, they were taintless.

In conclusion, these nanospheres act as desinged preparation of fluorosensors. Comparing with previous fluorosensors, the nanosphere has two advantages. First, it is taintless. Second, it can be used repeatedly. It is expected that interplay between nanochemisty and organic fluorphores may open a new route for preparation of fluorosensors. Future work will be directed toward studing in detail the surface effect of the nanosphere on the fluorescent perfomance of the nanosphere and attempting to design biosensor for special biological assay.

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