

A Novel Method for the Synthesis of Organic Nanoparticles in Aqueous Solution

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We have newly developed a simple method for the synthesis of organic nanoparticles ranging from tens to hundreds of nanometers in aqueous solution. We used pseudoisocyanine (PIC) dye and sodium tetraphenylborate (NaTPB) to prepare the dye nanoparticles. Ion association between PIC cations and TPB anions, $(\text{PIC}^+ \cdot \text{TPB}^-)_m$, leads to water-insoluble nanoparticle formation. The obtained particles were spherical and had amorphous nature revealed by transmission electron microscopy (TEM) and selected area electron diffraction (SAED) measurements. We also found that the particle size could be controlled by changing the molar ratio (R) of the loaded NaTPB to PIC. The mean particle size decreased with increasing R , implying that the adsorption of TPB anions on particles surface might suppress the growth of nanoparticles.

Key words: organic nanoparticles, ion association technique, hydrophobic, dynamic light scattering, optical property

1. INTRODUCTION

Nano-structured materials with dimensions in the range of about tens to a few hundreds of nanometers greatly contribute to our life in the many forms [1]. In a thorough study of the scientific literatures in the topic of colloidal systems, nanoparticles composed of metals, semiconductors and other inorganic materials have been numerous reported [1-3]. However, the preparation of nanoparticles from general organic molecules has been paid little attention. Because of the diversity and physiological activity of organic molecules, there is a tendency to extend the research on nanoparticles from metals and semiconductors into the organic field. In the case of organic particles whose electronic and optical properties are fundamentally different from those of inorganic materials, promising characteristics for the fabrication of light-emitting diodes, nonlinear optical devices, and electrically conductive films are expected. To understand how these properties develop as a function of size is of fundamental and technological interest [4-5].

For preparing organic nanoparticles, most of the constituent molecules are poorly soluble in water, or even insoluble. Therefore, the formation strategy of organic nanoparticle lies mostly on the conversion of the products or educts dissolved in suitable organic solvents into nanodispersed systems by precipitation or condensation [4,6]. Further additives such as surfactants and polymers are involved for the role of surface-active colloidal stabilizers. In our laboratory, on the other hand, we have revealed that self-assembling of organic dye

molecules formed mesoscopic supramolecular structures such as strings, sheets, or tubular rods in solution [7-9]. These mesoscopic assemblies are composed of ionic species, which are greatly influenced by counterions of the dyes [10-11]. Hence, we have considered that the organic dye nanostructures involving their shape and size should be controlled by optimizing the interionic interaction. In the present work, we report a newly developed method for the synthesis of organic nanoparticles composed of small dye molecules in aqueous solution based on the "ion association technique".

2. EXPERIMENTAL

2.1 Synthesis of Pseudoisocyanine (PIC) Organic Dye Nanoparticles

Cationic pseudoisocyanine (PIC) dye and sodium tetraphenylborate (NaTPB) were used to prepare the dye nanoparticles. Briefly, 0.5-1.0 mL of aqueous PIC bromide solution (0.1mM) was added rapidly into the 2.0-3.0 mL of NaTPB solution (0.1mM). 10 min of ultrasonic agitation was further employed. The obtained solutions (or dispersions) showed a slight turbidity due to the light scattering of the nanoparticles. In the reaction, TPB^- acts as a hydrophobic anion. Therefore, ion association between PIC cations and TPB anions, $(\text{PIC}^+ \cdot \text{TPB}^-)_m$, leads to water-insoluble nanoparticle formation. The particle size could be controlled by changing the molar ratio (R) of the loaded NaTPB to PIC-Br.

2.2 Apparatus

Absorption spectra were measured with a Hitachi U-4100 spectrophotometer. Fluorescence spectra were obtained with a Hitachi F-4500 spectrofluorometer. Particle size was measured by a dynamic light scattering (DLS) method using an Ohtsuka Electronics ELS-800 electrophoretic photometer. Transmission electron microscopy (TEM) was conducted with a Hitachi-8100 electron microscope operated at 200 kV. Before measurements, the sample solutions were filtered by a 200-nm pore size membrane filter (Sartorius, RC-15). Samples for the TEM observation were prepared by placing the solution on a carbon grid and dried at room temperature. Selected area electron diffraction (SAED) pattern was obtained at a camera length of 1m. During the SAED measurements, no damage could be seen for the dye nanoparticles.

3. RESULTS AND DISCUSSION

The UV-vis absorption spectra of PIC nanoparticles in aqueous solution prepared at different R ($R=2, 4$ or 6) are shown in Fig.1. Note that nanoparticles prepared at $R=1$ were quite unstable and formed agglomerate easily. However, at $R>1$, the particles were observed to be stable with no precipitates. For comparison, we added the spectrum of PIC-Br solution (0.1mM) in Fig.1. The spectral shapes of nanoparticles are quite similar to that of PIC monomer, indicating that the PIC chromophore unit did not aggregate themselves within nanoparticles, different from H and/or J aggregates frequently observed for the dye/anionic-site adsorption systems [12-14]. Compared to the absorption peak (0-0 band originated from π - π transition) of PIC monomer in water, a large red-shift is found for PIC nanoparticles. Such a large red-shift of the 0-0 transition substantially comes from the "solvent effect" that is related to the matrix polarizability [15]. Within the nanoparticles, it is conceivable that PIC is distributed in a TPB matrix with high polarizability due to the phenyl substituents, and thus, the red-shift of the 0-0 band is expected.

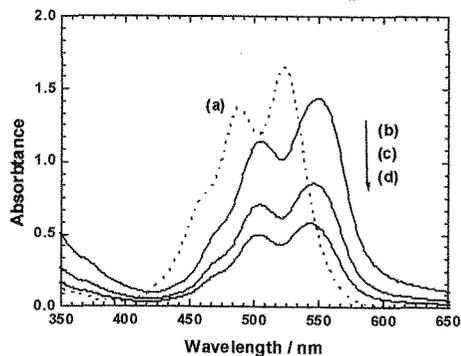


Fig.1 (a): Absorption spectrum of PIC solution (0.1mM). (b)-(d): Absorption spectra of PIC nanoparticles in aqueous solution prepared at different R ; (b) $R=2$, (c) $R=4$, and (d) $R=6$.

It is well known that PIC monomers are practically non-fluorescent in water at room temperature [16]. However, we could obtain fluorescence spectra for PIC nanoparticles (Fig.2). The fluorescence spectra exhibit only weak vibronic structure, which is quite similar to that of PIC in a solid matrix of polyvinyl alcohol [16]. This result supports strongly that the PIC is distributed in a hydrophobic TPB matrix within nanoparticles.

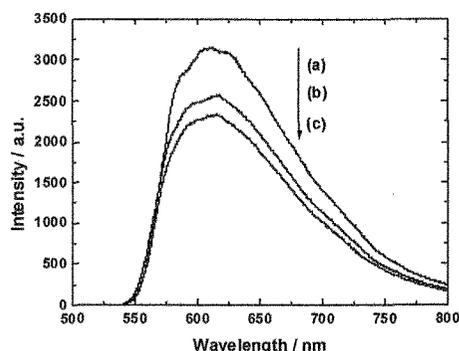


Fig.2 Fluorescence spectra of PIC nanoparticle dispersions at different R : (a) $R=2$, (b) $R=4$, and (c) $R=6$.

DLS was used for the size characterization of the PIC nanoparticles. Figs. 3a-3c, show the nanoparticle size distributions determined by DLS, in which the average nanoparticle diameters are 125 nm, 84nm, 64nm, respectively. From Fig.3, we can know that the average nanoparticle size decreased with increasing R .

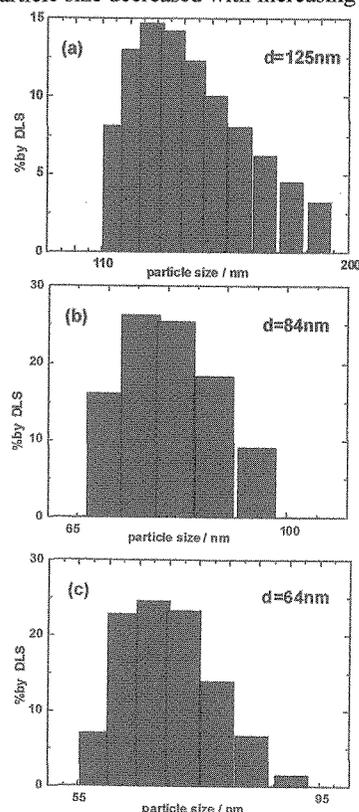


Fig.3 Particles size distributions of PIC nanoparticles characterized by DLS: (a) $R=2$, (b) $R=4$, and (c) $R=6$.

Figs. 4a-4c show the TEM images of the respective nanoparticles representing a spherical shape. The particle size was in the range of 130-240, 80-130, or 60-90 nm for the sample prepared at $R=2$, 4, or 6, respectively. These values agreed roughly with those determined by DLS in spite of the polydispersity of nanoparticles. Therefore, we conclude that a series of PIC nanoparticles from several tens to hundreds of nanometers could be prepared. Our method provides a novel and a simple approach for the synthesis of organic nanoparticles in aqueous solution.

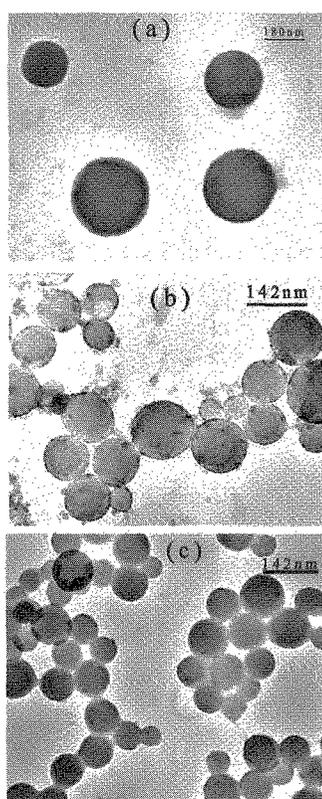


Fig.4 Representative TEM images of the corresponding nanoparticles at different R : (a) $R=2$, (b) $R=4$, and (c) $R=6$. (d) Typical electron diffraction pattern of PIC nanoparticles.

To clarify whether the spherical nanoparticle comes from PIC or redundant NaTPB, SAED measurements were conducted under the TEM observation. Note that we confirmed a crystalline nature of NaTPB solid. Whereas, the selected area electron diffraction taken from on the spherical nanoparticles indicates that PIC nanoparticles are amorphous. The similar TEM and SAED results have been observed for naphthylprolinol nanoparticles [17].

As described previously, PIC nanoparticles prepared at $R=1$ are unstable to form precipitate. At $R>1$, namely, excess NaTPB is present in solution, stable nanoparticle formation was observed. The results indicate that the

PIC nanoparticles are electrostatically stabilized by the adsorption of TPB anions. Electrophoretic measurement showed that the particles are negatively charged. Furthermore, we found that the mean particle size decreased with increasing R . When the sample was prepared at $R=2$, 4, 6, the average nanoparticle diameters are 125 nm, 84nm, 64nm, respectively. It implies that the adsorption of TPB anions on particle surface might suppress the growth of nanoparticles. Similar phenomena showing that surface adsorption of ions suppresses the size growth of metal oxide nanoparticles have been observed [18].

In summary, we have newly developed the “ion association method” for the preparation of organic dye nanoparticles in aqueous solution. We believe this technique is simple and general for the synthesis of organic nanoparticles consisting of binary ionic components.

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