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Synthesis of Water-Soluble 2,2'-Diphenyl-1-Picrylhydrazyl Nanoparticles: A New Standard for Electron Paramagnetic Resonance Spectroscopy

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The discovery of size-dependent properties in inorganic colloidal nanoparticles (NPs) has stimulated efforts to develop synthetic methods for making NPs of small organics.¹ Small-molecule organic NPs are formed through noncovalent intermolecular interactions such as van der Waals forces, H bonds, and $\pi-\pi$ and solvophobic interactions.¹ To date, a variety of organic NPs have been synthesized using small molecules possessing a rigid π system.¹ These NPs exhibit interesting size-dependent optical properties and are emerging as a new class of functional materials with potential applications as key components in optoelectronics.^{1,2} Here we report the synthesis and characterization of paramagnetic NPs made of 2,2'-diphenyl-1-picrylhydrazyl (DPPH).

DPPH has historically played an important role in the development of electron paramagnetic resonance (EPR) and has been just the second organic free radical detected by EPR.³ Because of its single narrow resonance line and its stability, DPPH is used as a standard field marker for *g*-factor determination and magnetic scan calibration in both low- and high-field EPR measurements^{4a} and as a primary spin-concentration standard in quantitative EPR spectrometry for the determination of free-radical concentrations in various samples.^{4b} However, the low solubility of DPPH in water limits its application in aqueous solutions. To overcome this limitation and allow the use of DPPH as a spin probe for aqueous solutions, Tamano et al. recently developed an approach in which DPPH is stabilized by encapsulation into aggregates of amphiphilic block copolymers in water.⁵ The DPPH-containing polymer aggregates exhibit single-line EPR spectra with linewidths of 5.0–15 G,⁵ which is much broader than the typical line width of microcrystalline DPPH (~1.5 G) observed in the X-band.^{3,4} Here we report a colloidal synthesis of stable, water-soluble DPPH NPs and show that the resulting particles exhibit single-line EPR spectra with linewidths of ~1.5–1.8 G, which are nearly identical to those commonly observed for microcrystalline DPPH.

The synthesis of water-soluble DPPH NPs is based on a modified reprecipitation method. In a reprecipitation-based synthesis, the nucleation of organic NPs is initiated by a sudden introduction of solvophobic interactions between the molecular building blocks (i.e., small-molecule precursors) and their surrounding solvent molecules; this is achieved by the addition of a poor solvent (e.g., water) for the molecular building blocks.^{1,6} The subsequent NP growth, however, cannot simply be terminated by a temperature-quenching process, as in advanced high-temperature syntheses of inorganic nanocrystals, because this reprecipitation-based synthesis is normally carried out near room temperature. This difficulty has limited the number of approaches available for size control of organic NPs. In this work, we have found that gelatin, a common surfactant for organic NPs, can rapidly terminate the growth of DPPH NPs in water. Accordingly, we have demonstrated that size control of DPPH NPs can be achieved simply by the injection of a gelatin solution at a chosen particle-growth time. In contrast to previously reported methods for making small-molecule NPs, in which control of the final particle size is achieved by varying the concentrations of precursors and surfactant molecules,^{1a,b} the present method uses only particle-growth time to control the final size of the NPs.

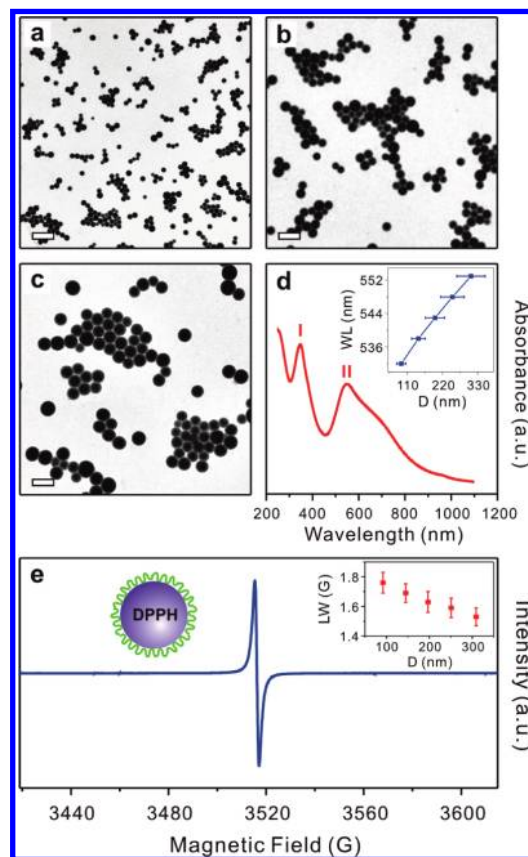


Figure 1. TEM images of DPPH NPs with diameters of (a) 90, (b) 200, and (c) 310 nm. Scale bars are 500 nm. (d) Absorption spectrum of 250 nm DPPH NPs. Inset: peak position of the NP visible absorption band (II) vs diameter (*D*). (e) EPR spectrum of 250 nm DPPH NPs (9.5 GHz, 298 K). Inset: NP EPR line width (LW) vs diameter.

In a typical experiment, DPPH (0.01 mmol) was dissolved in THF (1 mL) under Ar to form a deep-purple-colored stock solution, of which 100 μ L was injected into a flask with 5 mL of water (Nanopure, 18.2 M Ω) at room temperature with vigorous stirring. After a predetermined growth time (0–2 h), aqueous gelatin solution (1.8 mL, 2 wt %) was injected into the growth solution, which was kept under stirring for 5 more minutes; the DPPH NPs were then isolated from the growth solution through centrifugation. The resulting NPs were highly dispersible in water. Transmission electron microscopy (TEM) showed that NPs with different growth times (0–2 h) have diameters of 90–310 nm with a relative standard deviation of ~14% (Figure 1a–c). Also, these DPPH NPs exhibit high stability in water, and no size-ripening was observed for over 6 months.

Electron diffraction showed that the as-prepared DPPH NPs possess an amorphous structure (Figure S1 in the Supporting Information).⁷ The DPPH NPs have absorption bands in the UV and visible regions [I and II, respectively] (Figure 1d). These two bands originate from $\pi-\pi^*$

transitions of DPPH radicals, and the delocalized radical electron makes a major contribution to II.⁸ Both of the NP absorption bands exhibit a size-dependent red shift relative to free DPPH molecules in THF: the bigger the NPs, the larger the red shift, and vice versa (Figure 1d inset and Figures S2 and S3). The red shift of these π – π^* absorption bands is due to J-type aggregation of DPPH molecules inside an NP.^{1,9} We attribute the size-dependent red shift of these bands to stronger average intermolecular interactions between DPPH molecules with increasing NP size, as proposed by Yao and co-workers.^{1,9}

A typical EPR spectrum of DPPH NPs consists of a characteristic single narrow Lorentzian line (Figure 1e). The EPR line width is weakly dependent on NP size. As the NP diameter decreases from 310 to 90 nm, the EPR line width increases from 1.5 to 1.8 G. The single Lorentzian EPR line and narrow line width of these NPs are due to the spin exchange-narrowing effect in the limit of fast exchange.¹⁰ In this limit, the EPR lines of individual DPPH radicals, which would otherwise be broadened by dipolar electron–electron and electron–nuclear interactions, merge into a single Lorentzian line whose width linearly decreases with increasing spin-exchange interaction.^{4a,10} Thus, the slightly broader line width observed for 90 nm DPPH NPs is likely caused by a slower average spin-exchange rate than in the bigger NPs. This slower exchange rate may be associated with weaker average intermolecular interactions between DPPH molecules in 90 nm NPs, as indicated by the peak position of their absorption bands (Figure 1d inset and Figures S2 and S3).

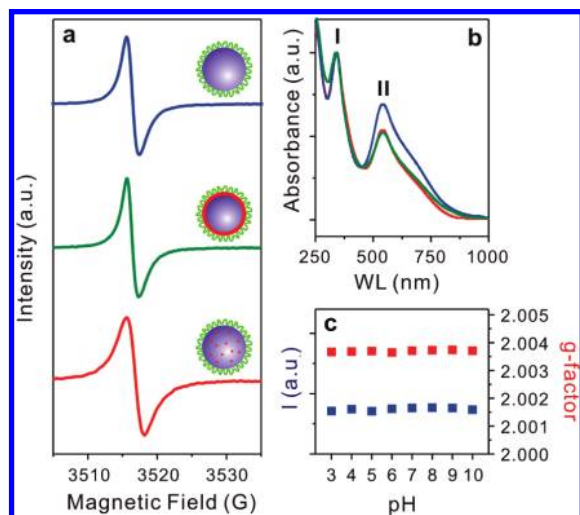


Figure 2. (a) EPR spectra of DPPH NPs (blue), DPPH/DPPH-H core/shell NPs (green), and DPPH-H-doped DPPH NPs (red). (b) Corresponding absorption spectra of these NPs. (c) Integrated intensity of EPR absorption (I) and g factor of DPPH NPs (310 nm diameter) as functions of pH. The uncertainty in the g -factor determination was ± 0.0001 , and the relative uncertainty in the EPR intensity determination was $\sim 2.0\%$.

To further understand the spin-exchange interaction and J-type aggregation of DPPH molecules inside the NPs, we designed and synthesized three types of NPs: (1) DPPH, (2) core/shell particles with a DPPH core coated with a shell of 2,2'-diphenyl-1-picrylhydrazine (DPPH-H), and (3) DPPH particles doped with DPPH-H (Figure 2a).⁷ All of these NPs had a nearly identical size of 180 nm (Figure S4); the core/shell and doped NPs had a similar DPPH-H concentration of $\sim 20\%$. DPPH-H is a closed-shell, reduced form of DPPH.¹¹ Without the radical electron, DPPH-H loses the visible band (II) of DPPH but maintains its UV band (I) at the same wavelength and similar extinction.¹¹ Indeed, because of the similar concentration of DPPH-H components, the core/shell and doped NPs exhibit nearly identical reduction in the intensity of their visible bands (II) relative to that of their UV bands (I) (Figure 2b). The maxima of the two bands in these two types of particles exhibit no shift from those in

their DPPH counterparts (Figure 2b), indicating that the presence of DPPH-H does not substantially perturb the packing of DPPH molecules inside the NPs.^{1,9} However, the location of DPPH-H significantly affects the EPR line width of the NPs (Figure 2a). With DPPH-H in the shell, the core/shell particles have an EPR line width of 1.7 G, identical to that of pure DPPH particles of the same size. In contrast, the DPPH-H-doped NPs show an EPR line width of 2.2 G, which corresponds to a reduction of $\sim 30\%$ in the spin-exchange interaction relative to that in the pure DPPH NPs (Figure 2a).¹⁰ This result is likely due to the fact that the insertion of DPPH-H molecules into the DPPH aggregates blocks the effective exchange interaction between the DPPH radicals.¹⁰ In addition, the results for the core/shell-type NPs further suggest that surface effects do not play a major role in controlling the optical and paramagnetic properties of DPPH NPs (Figure 2a,b).

To verify their suitability as EPR standards, we studied the stability of DPPH NPs as a function of pH. The UV–vis absorption spectrum (including the position and extinction of the two absorption bands), g factor, EPR line width, and integrated EPR absorption intensity of the DPPH NPs showed no measurable variation over a pH range of 3.0–10.0 (Figure 2c and Figure S5). These results show that these NPs are stable under these conditions and therefore that these NPs are practically useful as both a standard field marker and a primary spin-concentration standard for aqueous samples over a wide pH range.⁴

In conclusion, we have reported a size-controlled synthesis of water-soluble DPPH NPs, which exhibit size-dependent absorption spectra, fast exchange-narrowed single-line EPR spectra with linewidths of ~ 1.5 – 1.8 G, and stability over a wide pH range. These properties make DPPH NPs suitable for use as a new type of water-soluble EPR standard, which is important for many applications in fields such as the food industry and the life sciences.^{3,4} Furthermore, the DPPH NPs can potentially be used as a spin probe in biomedical studies.^{3,5}

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Supporting Information Available: Detailed synthetic procedures and supporting figures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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