

IDENTIFICATION OF METALLOPORPHYRIN-CONTAINING COORDINATION POLYMER PARTICLES BY SURFACE-ENHANCED RAMAN SCATTERING THROUGH SURFACE METALLIZATION

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Abstract

In this work, metalloporphyrin-containing coordination polymer particles (Z-CPPs) with 1D nanorod structures were synthesized by a surfactant-assisted self-assembly process. Furthermore, the identification of Z-CPPs in aqueous solution was achieved by surface-enhanced Raman scattering (SERS) through surface metallization. Our approach illustrates a novel method to detect coordination polymer particles in solution.

Keywords: Surface-enhanced Raman Scattering, Coordination Polymers, Surface Metallization, Metalloporphyrin

1. INTRODUCTION

Metal-organic interactions have been the focus of intense multidisciplinary research such as catalytic chemistry, materials science and molecular electronics.¹ Surface-enhanced Raman scattering (SERS) has been widely recognized as a powerful spectroscopic tool for studying molecular adsorbates on a metal surface due to its high surface sensitivity and accessibility to low wavenumber region, which gives direct information on metal-molecule interactions, even in IR-opaque media such as aqueous solutions.²

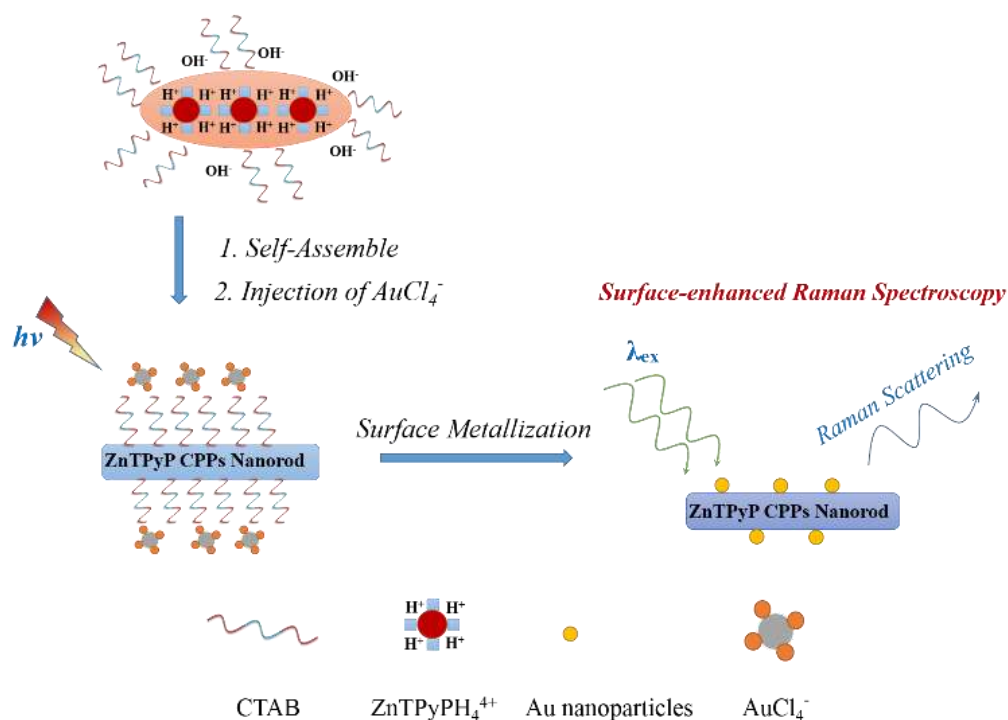


Fig. 1 Illustration of ZnTPyP-CPPs by surface-enhanced Raman scattering through surface metallization.

The intensive research of metal-organic interactions by SERS detection has been focused on two different types: (1) molecular modification on substrates, including physical and chemical adsorption³, and (2) molecular aggregation through self-assembly on substrates.⁴

On the other hand, metalloporphyrins are compounds formed by a combination of porphyrin and metal ions, playing an important role in catalysis, fluorescence, sensing, optical imaging, electronics, photochemistry and biological applications.⁵

Recently, many worldwide research groups reported that diverse metalloporphyrin-containing nano/micro-scale particles can be synthesized through a bottom-up self-assembly process assisted by surfactants, such as Pluronic F-127, SDS and CTAB.⁶ However, less work has been dedicated to the identification of metalloporphyrin-containing CPPs in aqueous solution. In the present work, we chose a metalloporphyrin, zinc 5-, 10-, 15- and 20-tetra(4-pyridyl)-21H, 23H-porphyrin (abbreviated to ZnTPyP), to investigate the identification of metalloporphyrin-containing CPPs in aqueous solution by SERS methods (Fig. 1).

2. EXPERIMENTAL

2.1. MATERIALS

Zinc 5-, 10-, 15- and 20-tetra(4-pyridyl)-21H, 23H-porphine (ZnTPyP), Cetyltrimethylammonium bromide (CTAB), sodium tetrachloroaurate (III) dihydrate, ascorbic acid from Aldrich Chemical Co., Sodium hydroxide, hydrochloric acid from Wako Chemical were used without a further purification. All solvents were prepared by using Milli-Q water.

2.2. PREPARATION OF STOCK SOLUTIONS

As ZnTPyP does not readily dissolve in water, its homogeneous stock solution (0.01 M) was prepared by dissolving an appropriate amount of ZnTPyP in a HCl solution (0.2 M) to acidify the pyridyl groups, forming soluble tetrapyridium cations. The basic stock solution of surfactants was prepared by dissolving 0.01 M CTAB and 0.02 M sodium hydroxide in aqueous solution.

2.3. SYNTHESIS OF Z-CPPS AND Au-DECORATED Z-CPPS

An amount of 250 μ L of a ZnTPyP stock solution (0.01 M) was injected into 5 mL of basic stock solution with mild stirring for 12 h. Subsequently, 0.5 mL NaAuCl₄ (10 mM) and 1 mL ascorbic acid solution (0.1 M) were added into a as-prepared Z-CPPs solution. After continuous stirring for 30 min under visible light illumination, the mixed solution turned into dark red color, suggesting the formation of metal-decorated Z-CPPs.

2.4. CHARACTERIZATION

Powder X-ray diffraction data were collected by a Rigaku (D/MAX-2500/PC) diffractometer using Cu-K α radiation ($\lambda = 1.54056$ Å) at room temperature. To prepare samples for the field-emission scanning electron microscopy (FE-SEM, TESCAN, MIRA3), the as-prepared ZnTPyP particles were first re-dispersed in pure water, then dropped onto silicon wafer substrate and finally dried at 50°C in the oven.

The procedures for TEM measurements were the same as that of the SEM measurement, except for dropping on Cu-grid. UV-vis absorption spectroscopy data (using Lambda 750 UV/VIS spectrometer, PerkinElmer) were also measured by re-dispersing particles in pure water. Raman measurements were performed using a Renishaw 2000 Raman microscope system (Renishaw, UK).

A Melles Griot He-Ne laser operating at $\lambda = 785$ nm was used as excitation source, with a laser power of approximately 15 mW. The Rayleigh line was removed from the collected Raman scattering using a holographic notch filter located in the collection path. The Raman scattering was collected using a charge-coupled device (CCD) camera at a spectral resolution of 4 cm⁻¹.

All spectra were calibrated to the 520 cm⁻¹ silicon line. An additional CCD camera was fitted to an optical microscope to obtain optical images. A 20× objective lens was used to focus a laser spot on the glass tube.

3. RESULTS AND DISCUSSION

The external morphology of the synthesized Z-CPPs was characterized by scanning electron microscopy (SEM). As shown in Figure 1(A), Z-CPPs nanorod structures with an average length of ~230 nm and width of ~60 nm were synthesized. The internal structures of the as-prepared Z-CPPs nanorods were investigated by X-ray diffraction (XRD) measurements (Figure 1(B)), which are found to match well the simulated pattern based on the crystal structure of ZnTPyP compounds obtained by Goldberg and co-workers (CCDC ref. code YOVTOS).⁷ This indicates that the crystal structure of the 1D nanorod structures have the *R*3 space group.

In these structures, the zinc atom at the center of ZnTPyP should be six-coordinated to four pyrrole nitrogens of the porphyrin core and to two pyridyl N-atoms of the other porphyrin molecules, which approach from both sides of the molecular frameworks.⁸ As reported in our previous work⁹, the electronic absorption properties of metalloporphyrins can be determined by UV-vis spectra due to their characteristic color derived from the highly conjugated π -electron systems.

As a reference, the electronic absorption spectrum of the ZnTPyP monomer was determined, showing a single Soret band at 426 nm and two weak Q-bands at 565 nm and 593 nm, respectively. The Soret band clearly splits into two bands with a relatively weak intensity appearing at 417 (blue-shifted) and one with a stronger intensity appearing at 447 nm (red-shifted). The former and latter Soret-band splits were ascribed to the transition moments parallel and perpendicular to the aggregate axis, respectively. We confirmed the aggregation type of ZnTPyP-CPPs synthesized in the presence of CATB is J-type aggregation.^{9,10}

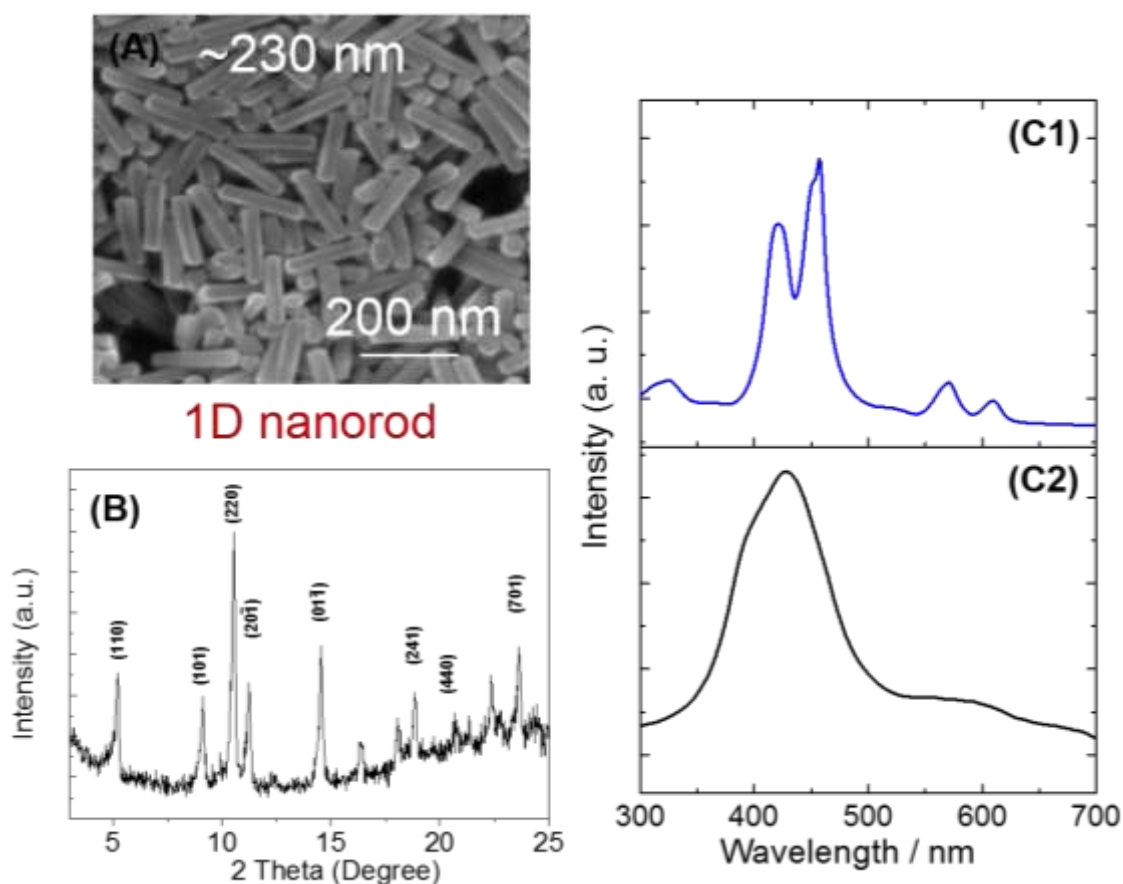


Fig. 2 (A) SEM image and (B) XRD pattern of ZnTPyP-CPPs nanorod structures; UV-vis spectroscopy of (C1) ZnTPyP monomer and (C2) Z- CPPs nanorod structures.

In order to synthesize metal-decorated Z-CPPs, ascorbic acid solution and AuCl_4^{2-} aqueous solution were added into Z-CPPs solutions. It is clearly shown that AuCl_4^{2-} complexes were reduced into Au nanoparticles on Z-CPPs nanorods under visible light illumination (Figure 2(A) and 2(B)). In our previous work, we confirmed that morphological transformation of Z-CPPs may occur by changing the solution pH, solution composition, temperature and so on.⁹ The final experimental condition was fixed by a series experiments. As shown in Figure 2(C) and 2(D), the mapping images for Au and carbon apparently revealed the gold nanoparticles formed on the surface of Z-CPPs nanorods.

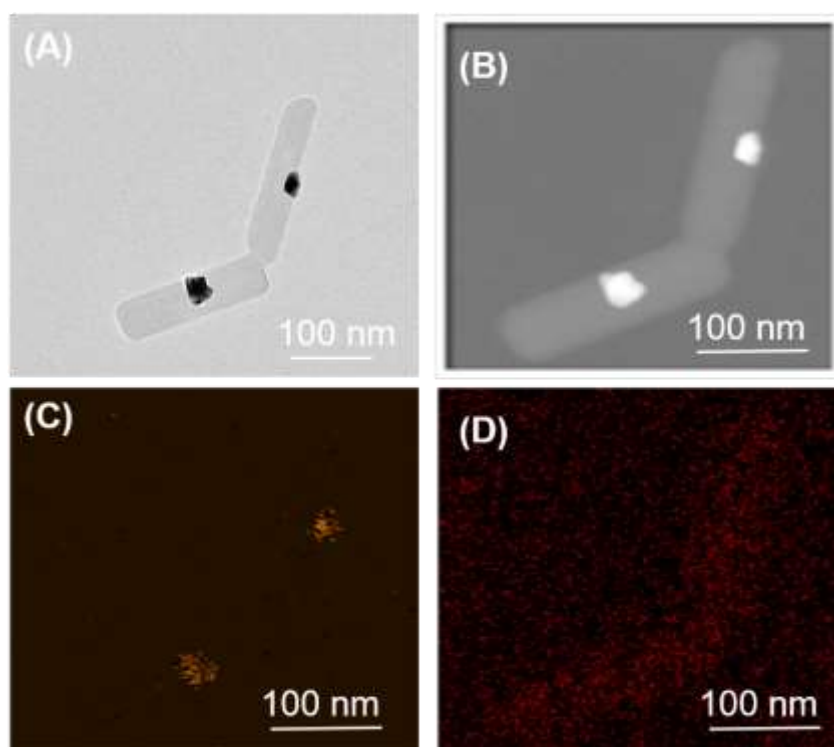


Fig. 3 (A) TEM image and (B) STEM image of Au-decorated Z-CPPs nanorod structures and elemental mapping data of (C) Au and (D) carbon.

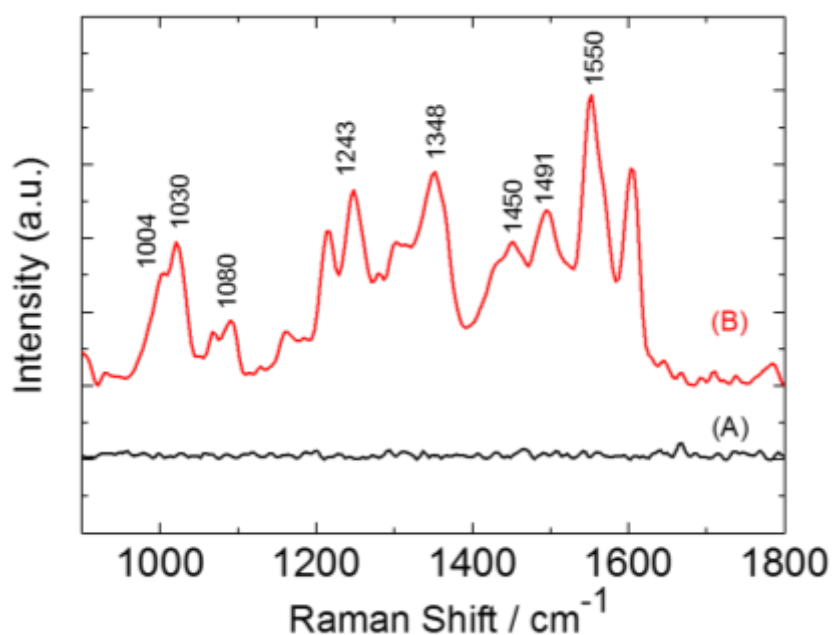


Fig. 4 Raman spectra of (A) Z-CPPs and (B) Au-decorated Z-CPPs.

Raman spectra of Z-CPPs and Au-decorated Z-CPPs are shown in Figure 4 (A) and (B) respectively. It clearly revealed that no Raman spectra were detected for Z-CPPs in aqueous solution. However, after Au decoration on the surface of Z-CPPs nanorods, all characteristic group contributions (fingerprint) consistent with ZnTPyP structures were identified, including 1004 cm⁻¹ [$\nu(\text{C}_\alpha\text{--C}_m)$], 1030 cm⁻¹ [pyrr $\delta(\text{C--H})$], 1080 cm⁻¹ [$\delta(\text{C}_\beta\text{--H})$], 1243 cm⁻¹ [$\nu(\text{C}_m\text{--Pyrr})$] as well as the ϕ stretch normal modes, 1384 cm⁻¹ [$\nu(\text{C}_\alpha\text{--H})$], 1450 cm⁻¹ and 1491 cm⁻¹ [$\nu(\text{C}_\alpha\text{--C}_\beta)$] and 1550 cm⁻¹ [$\nu(\text{C}_\alpha\text{--C}_\beta)$ and ($\text{C}_\beta\text{--C}_\beta$) stretch].^{4(a)}

4. CONCLUSION

In this work, we introduced and described a novel method to identify CPPs in aqueous solution. Z-CPPs with 1D nanorod structures were synthesized through a bottom-up strategy assisted by CTAB as surfactants. UV-vis spectra confirmed that J-type aggregation exists in Z-CPPs nanorod structures. However, no Raman shift was observed for Z-CPPs nanorod structures.

After surface metallization by gold nanoparticles, identification of Z-CPPs nanorod structures was successfully achieved by Surface-enhanced Raman Spectroscopy (SERS). All characteristic group contributions (fingerprint) consistent with ZnTPyP structures were identified.

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