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Surface-Enhanced Raman Spectroscopy of Metallotetraphenylporphyrins Adsorbed on Ag_2O and Silver Colloids

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Detailed abstract: The biological significance of porphyrins and metalloporphyrins has stimulated intensive investigations on these compounds for many years. On the other hand, porphyrins and metalloporphyrins also have extensive applications in many other fields such as chemical modified electrodes, organic photovoltaic devices and biomimetic catalysis. The adsorption behavior and chemical reactions of metalloporphyrins on surfaces or interfaces are very important for these applications. Surface-enhanced Raman spectroscopy has been used to investigate the physical and chemical processes of the porphyrins on surfaces in many scientific publications. Surface-reactions such as metalization, demetalization, aggregation, electrochemical redox and N-protonation of the porphyrins on colloids, electrodes or films have been revealed by SERS[1,2,6].

Although most SERS experiments were carried out on noble-metals such Ag, Cu and Au, enhanced Raman signals were also obtained from molecules adsorbed on transition metals and semiconductors[3~7]. Recently, enhanced Raman spectra were observed for pyridine, cyanine dyes, azobenzene and several other molecules adsorbed on silver oxide (Ag_2O)[6,7]. The charge-transfer (CT) mechanism was thought to be the major origin for Raman enhancements and small Ag_n^+ clusters on Ag_2O were believed to be active sites of SERS. It is known that silver oxide can catalyze a number of organic oxidation reactions. The oxidation and subsequent ring-openning of the porphyrins and their analog macrocycles are important for understanding the metabolism of relative prosthetic groups and cofactors in biological systems. Thus, the SERS studies of the porphyrins on Ag_2O may provide new insights to this natural process.

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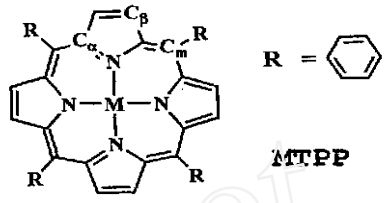
Here we report Raman scattering of four metallotetraphenylporphyrins (MTPP; M = Ag, Cu, Pd, Mg) adsorbed on Ag_2O colloids. The Ag_2O colloids were prepared by mixing aqueous solutions of sodium hydroxide and silver nitrate. Raman spectra were measured on a Labram-010 Raman spectrometer with the 488.0 nm line of an Ar^+ laser as the excitation source.



Normal resonance Raman spectra (Figure 1) of MTPP solid powders with 488 nm excitation are characterized with strong bands of ν_2 (1 532～1 560 cm^{-1}), ν_4 (1 339～1 360 cm^{-1}), ν_8 (330～338 cm^{-1}), etc. Frequencies of these three modes are known sensitively dependent on central metal ions. SERS of MTPP on Ag_2O colloids is dramatically different from the normal Raman spectra (NRS). As shown in Figure 2, the characteristic bands of AgTPP at 1 538 (ν_2), 1 339 (ν_4), 399 cm^{-1} (ν_8) almost completely vanished in the SERS of AgTPP on Ag_2O colloid, while new bands at 1 617, 1 530, 1 417, 947, 674, and 297 cm^{-1} dominate the spectra. Similar SERS spectra were also measured for other metallo-TPP and the free base on Ag_2O colloid. These spectral observations reveal that the adsorbents on the colloids undergo surface-reactions, which was considered to be the irreducible oxidation of the adsorbed MTPP. UV-visible spectra manifest that the final product of the irreducible oxidation has a strong absorption at 460 nm.

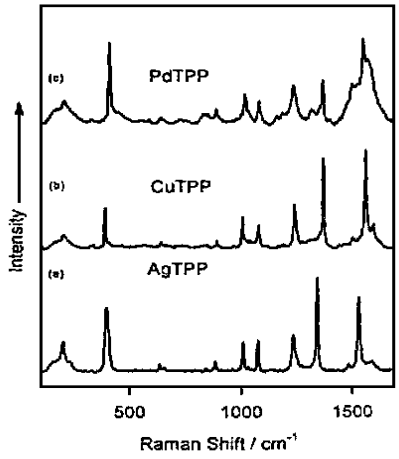


Fig. 1 Raman spectra of AgTPP, CuTPP and PdTPP solid powders

The Raman shifts in the SERS spectra of AgTPP, PdTPP and CuTPP on Ag colloid are very close to the corresponding NRS. For instance, structural sensitive bands (ν_2, ν_4, and ν_8) in SERS spectra were found well close to the corresponding NRS frequencies. Thus, SERS of AgTPP, PdTPP and CuTPP on Ag colloids (without OH^- modification) reveals negligible structural alteration or surface reaction. Slight frequency differences between SESR and NRS spectra may be attributed to the environmental difference of the molecule in solid and on surface.

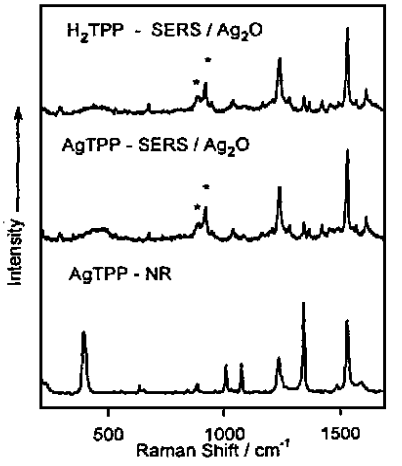


Fig. 2 SERS of AgTPP and H_2TPP adsorbed on Ag_2O colloid. Concentration of TPP: ～1 ×10^{-6} mol/L

Similar to those observed on Ag_2O colloid, dramatic spectral changes were also observed for MTPP adsorbed on hydroxyl-modified Ag colloid. Figure 3 displays the time evolution of the

488. 0 nm excited SERS spectra of AgTPP adsorbed on Ag colloid after addition of dilute aqueous solutions of sodium hydroxide. The characteristic Raman bands of AgTPP at 1 596, 1 579, 1535, and 1 340 cm^{-1} shift to 1 612, 1 566, 1 530, and 1 338 cm^{-1} respectively, accompanying dramatic enhance of Raman intensities. Besides, new Raman bands appear at 1 416, 1 358, 1 270, 946, 674 and 290 cm^{-1}, manifesting new species formation upon adsorption of AgTPP on hydroxyl-modified silver colloids. From the Raman frequencies and absorption spectra, it was concluded that this new species is identical to that observed on Ag_2O colloid.

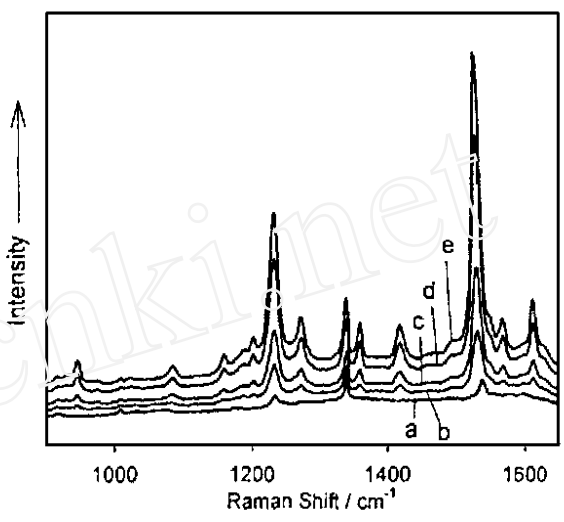


Fig. 3　SERS of AgTPP adsorbed on hydroxyl-modified Ag sols. Spectra recorded (a) 0, (b) 40, (c) 80, (d) 160, and (e) 200 after adding dilute NaOH solution. Concentration of AgTPP: ~1 $\times 10^{-6}$ mol/L

The above spectral changes were attributed to the ring-oxidation of TPP on methylene carbon (C_m) atoms. This irreducible oxidation is obviously catalyzed by the colloids. Based on Raman, NMR, and UV-visible absorption spectra, the product of irreducible oxidation was suggested having a structure similar to porphodimethene whose electronic conjugation extends over two adjacent pyrrole rings. This result is distinct from the irreducible oxidation of MTPPs by traditional chemical or photochemical methods, which usually leads to linear conjugated tripyrroles or tetrapyrroles as the main products.

Key words: SERS, Porphyrine, Silver oxide colloid

Acknowledgement:

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References:

[1] Woolley P, Keely B J, Hester R E. Surface-enhanced resonance Raman-spectra of water-insoluble tetraphenylporphyrin and chlorophyll-A on silver hydrisols with a dioxane molecular space[J]. Chem. Phys. Lett., 1996, 258: 501.

[2] Prochazka M, Mojzes P, Vlckova B, et al. Surface-enhanced resonance Raman-scattering from copper(Ⅱ) 5, 10, 15, 20-terakis(1-methyl-4-pyridyl) porphyrin adsorbed on aggregated and nonaggregated silver colloid [J]. J. Phys. Chem. 1997, B101: 3 161.

[3] Tian Z Q, Gao J S, Li X Q et al. Can surface Raman-spectroscopy be a general technique for surface science and electrochemistry[J]. J. Raman Spectrosc., 1998, 29: 703.

[4] Gao X P, He T J, Liu F C, et al. Surface-enhanced resonance Raman-scattering and enhanced fluorescence of dyes on silver chloridide sols[J]. Chem. Phys. Lett., 1984, 112: 465.

[5] Kuddelski A, Grochala W, Janik-Czachor M, et al. Surface-enhanced Raman-scattering (SERS) at copper(I) oxide[J]. J. Raman Spectrosco., 1998, 29: 431.

[6] Mou C, Chen D M, Liu F C et al. SERS and UV spectra of meso-tetrakis(4-sulfonatophenyl) porphyrin adsorbed on Ag_2O colloids[J]. Chem. Phys. Lett., 1991, 179: 237.

[7] Wang X Q, He T J, Liu F C et al. Surface-enhanced Raman-scattering from citrate, azobenzene, pyridine and cyanine dyes adsorbed on Ag_2O colloids. Spectrochimica Acta[J], 1997, A53: 411.

金属四苯基卟啉在氧化银和银胶体上的表面增强拉曼光谱研究

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摘要: 研究了四苯基卟啉金属配合物(MTPP; M = Ag, Cu, Pd, Mg)和游离碱(H_2TPP)在氧化银和银胶体中的表面增强拉曼光谱(SERS). 在 Ag_2O 胶体中 MTPP 和 H_2TPP 的 SERS 谱与其普通拉曼谱明显不同, 可知吸附分子在 Ag_2O 胶粒表面发生反应所引起, 况且产物于 460 nm 附近有一强烈吸收, 可知它含有共扼双吡咯发色团. 在 OH^- 修饰的银胶上也观察到类似的光谱变化.

关键词: 表面增强拉曼散射; 卟啉; 氧化银胶体