Supporting Information

Measurement of pH-dependent surface-enhanced hyper-Raman scattering at desired positions on yeast cells via optical trapping

Yasutaka Kitahama[1], Hiroaki Hayashi[1], Tamitake Itoh[2], and Yukihiro Ozaki[1]*
[1]Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan.
[2]Nano-Bioanalysis Research Group, Health Research Institute, National Institute of Advanced Industrial Science and Technology (AIST), Takamatsu, Kagawa 761-0395, Japan.
*To whom correspondence should be addressed.
E-mail: kitahama@kwansei.ac.jp; Fax: +81-79-565-9077; Tel.: +81-79-565-8349

The Ag colloidal dispersion with p-MBA, which prepared as written in the main text, was added to 0.01 M $Na_2B_4O_7$ (Tetraborate pH Standard Solutions; Nacalai Tesque, Kyoto, Japan) or 0.02 M NaCl aqueous solution in a ratio of 3:1 (v/v) in terms of the same kind and concentration of cation. The suspension was roughly adjusted to pH 9, 7, 2, or 1 by the addition of the pH Standard Solutions, the NaCl aqueous solution, H_2SO_4 aqueous solution (Wako, Osaka, Japan) whose final concentration at 0.05 or 0.005 M, respectively, in the suspension. The mixed dispersion was dropped on a washed conventional glass slide (S1112; Matsunami Glass, Osaka, Japan) and covered with another glass slide. The experimental setup is written in the main text.

Fig. S1 show the SEHRS spectra from the optically trapped AgNPs on the conventional glass slide in the suspension at different pH. At pH 9, the SEHRS peak at 1366 cm^{-1}, which is attributed to the $–COO^-$ of p-MBA, appears (Fig. S1a). At pH 7, the SEHRS peak was still observed in the Ag colloidal suspension with 0.005 M NaCl, (Fig. S1b). The SEHRS peak sometimes disappears at pH 2 (Fig. S1c). At pH 1, the SEHRS peak almost always disappears (Fig. S1d).

In our system, the SEHRS peak due to the $–COO^-$ tends to appear at lower pH than the previous results.[1,2] The reason may be the aggregation via Na cation and/or $–OH^-$ on the washed conventional glass slide. In conclusion, we confirmed the pH dependence of the SEHRS spectra of p-MBA in the present optical trapping system by using the continuous wave laser.

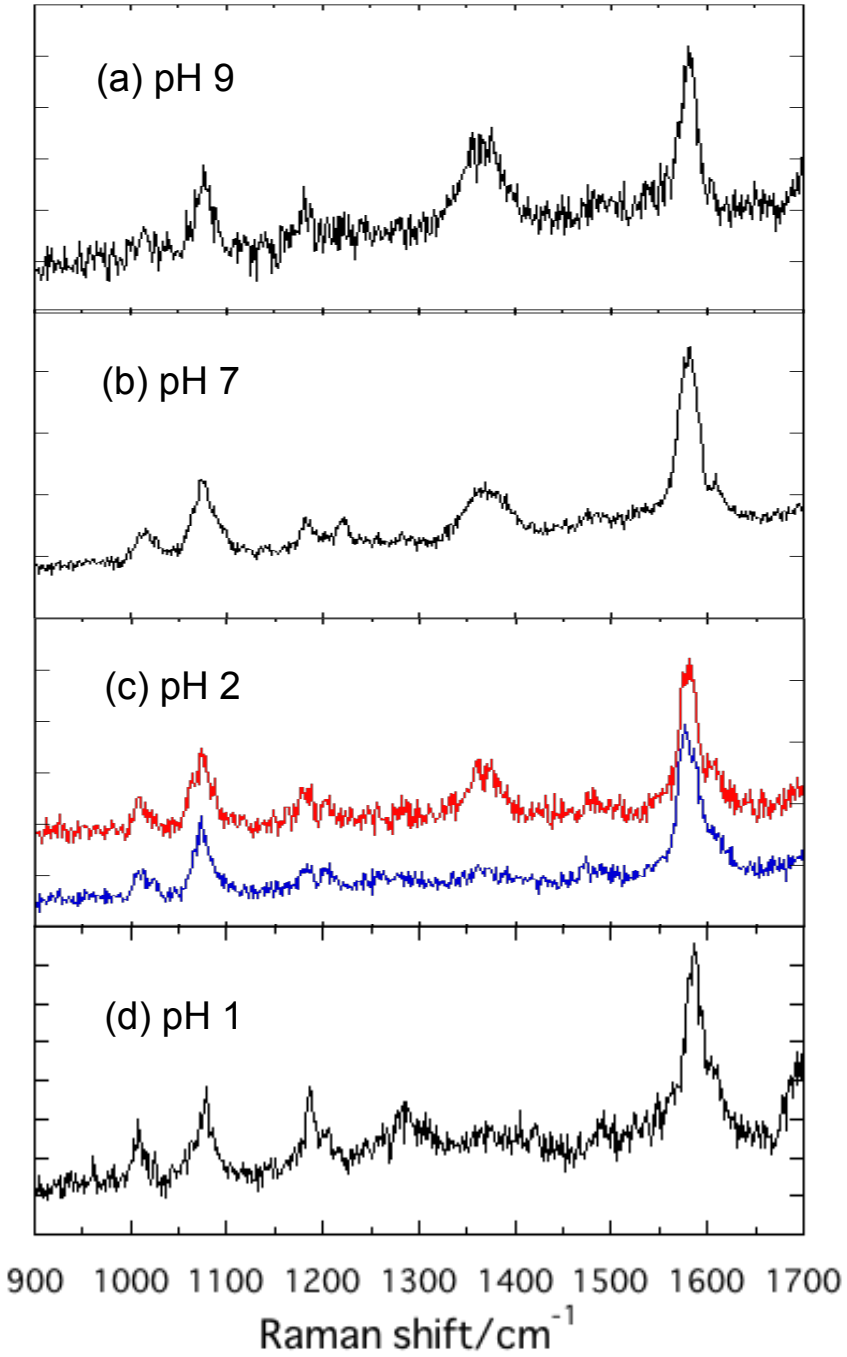

Fig. S1 SEHRS spectra from the optically trapped AgNPs adsorbed with p-MBA on the conventional glass slide in the suspension at pH (a) 9, (b) 7, (c) 2, (d) 1 by addition of (a) 0.01 M $Na_2B_4O_7$, (b) 0.02 M NaCl aqueous solution without and (c, d) with H_2SO_4 to the Ag colloidal suspension in a ratio of 1:3 (v/v).

References

1 J. Kneipp, H. Kneipp, B. Wittig and K. Kneipp, *Nano Lett.*, 2007, **7**, 2819.

2 M. Gühlke, Z. Heiner and J. Kneipp, *Phys. Chem. Chem. Phys.,* 2015, **17**, 26093.