

Electronic Supplementary Information for Chemical Science
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Supporting Information to:

Semiconductor-Driven “Turn-Off” Surface-Enhanced Raman Scattering Spectroscopy: Application in Selective Determination of Chromium(VI) in Water

Wei Ji,^a Yue Wang,^{a,b} Ichiro Tanabe,^a Xiaoxia Han,^b Bing Zhao,^{*b} and Yukihiro Ozaki ^{*a}

^a Department of Chemistry, School of Science and Technology, Kwansai Gakuin University, Sanda, Hyogo 669-1337, Japan. E-mail: ozaki@kwansai.ac.jp;

^b State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China. E-mail: zhaob@mail.jlu.edu.cn;

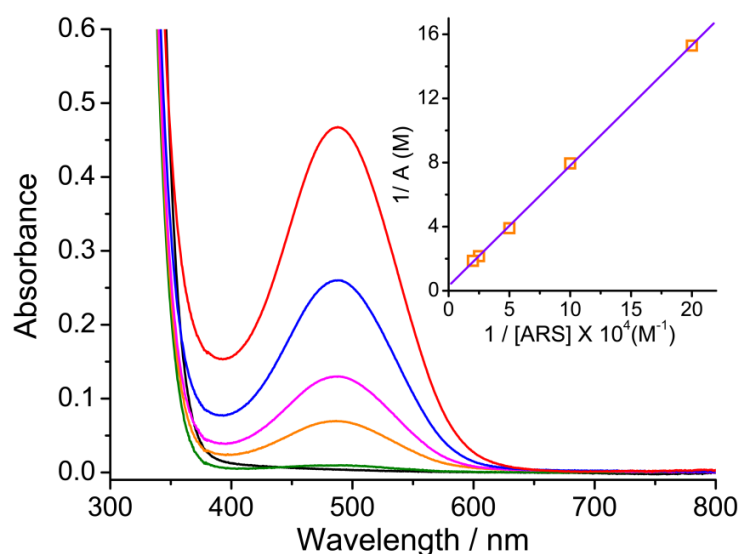


Fig. S1 ARS concentration-dependent changes in absorption spectra due to the formation of ARS-TiO₂ complexes. The concentration of ARS in the mixture from bottom to top is as follows: 0, 0.5, 5, 10, and 20 μM. The optical path length was 1 cm. Inset: Benesi-Hildebrand (B-H) plot for the 488 nm absorption of ARS-TiO₂ complexes system. For the case [TiO₂] >> [ARS-TiO₂], the functional relationship between the absorbance and the equilibrium constant (K_{ass}) of ARS-TiO₂ complex can be derived as:¹

$$\frac{1}{\Delta A} = \frac{1}{K_{ass} \Delta \epsilon_{CT} [ARS] [Ti_{surface}]_0} + \frac{1}{\Delta \epsilon_{CT} [Ti_{surface}]_0}$$

where $[Ti_{surface}]_0$ is the concentration of surface active sites for chelation and is proportional to [TiO₂]. $\Delta \epsilon_{CT}$ is the change in the molar absorptivity. Based on linear dependence of $1/\Delta A$ versus $1/[ARS]$, the equilibrium constant (K_{ass}) of the ARS-TiO₂ complexes has been determined to be $3.9 \times 10^3 \text{ M}^{-1}$. This strong binding affinity of enediol ligands with colloid TiO₂ NPs is well documented in the literature.^{2,3}

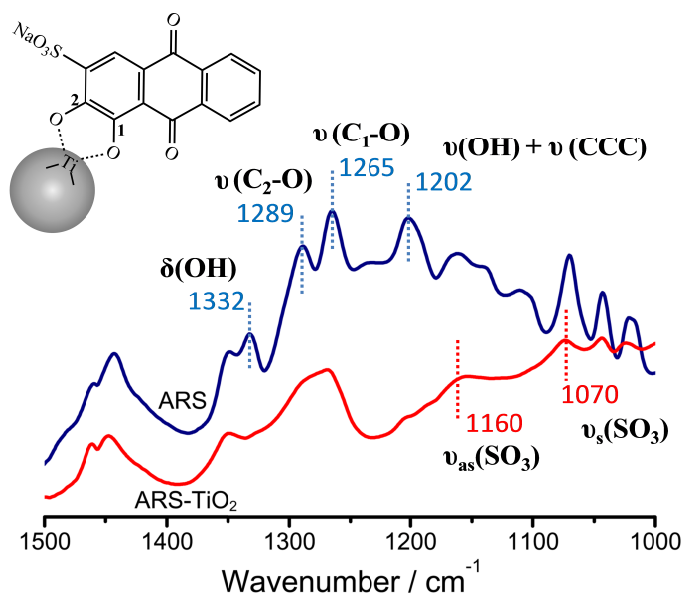


Fig. S2 Comparison of the IR spectra of ARS (blue line) and ARS adsorbed on TiO₂ NPs (red line). The IR spectra of ARS shows the characteristic bands at 1265 and 1289 cm⁻¹ due to the $\nu(\text{C}_1\text{-O})$ and $\nu(\text{C}_2\text{-O})$, respectively. The other two strong and wide bands at 1202 and 1289 cm⁻¹ are assigned to the stretching of hydroxyl (-OH) group. The adsorbed ARS on the surface of colloid TiO₂ NPs gave a significantly altered spectrum in the 1170-1350 cm⁻¹ region, while the sulfonic (-SO₃⁻) group absorption remained at 1070 and 1160 cm⁻¹. The decrease in the intensity of the $\nu(\text{C-O})$ and the absence of the $\nu(\text{-OH})$ band indicate that ARS is adsorbed on the surface using the two hydroxyl groups as a bidentate chelation mode.

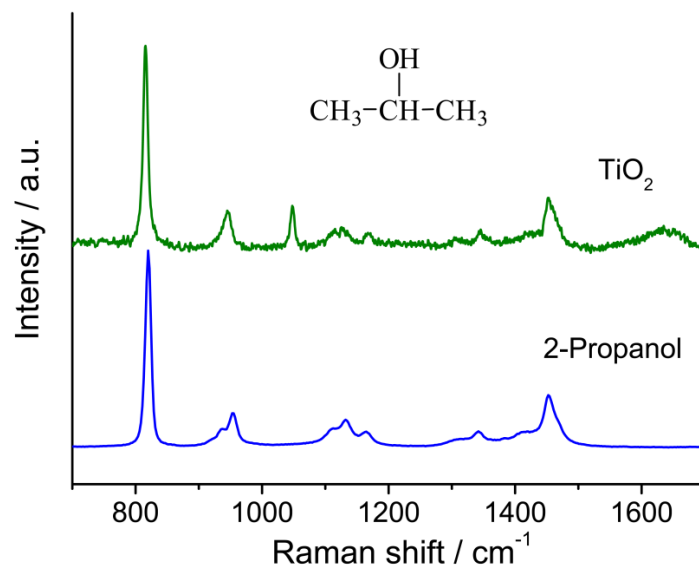


Fig. S3 Raman spectra of 2-propanol and colloid TiO₂ NPs. During sample preparation, 2-propanol was used as a solvent to dilute titanium(IV) butoxide. Thus, it was clearly found that the colloid TiO₂ NPs show a typical Raman spectrum of 2-propanol. Moreover, there is also a band at 1047 cm⁻¹ from NO₃⁻. The strong band at 816 cm⁻¹ is assigned to the stretching of hydroxyl (-OH) group, which was selected as an internal standard.

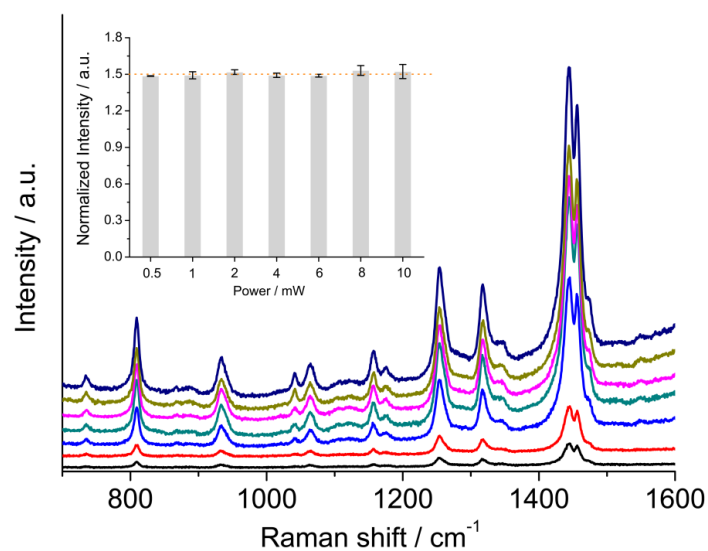


Fig. S4 SERS spectra of ARS-TiO₂ (0.1 mM ARS) measured by various laser power. The laser power from top to bottom was 10, 8, 6, 4, 2, 1, and 0.5 mW, respectively. Inset shows the normalized intensity at 1260 cm⁻¹. The intensity of the band was normalized to that of the signal from 2-propanol at 816 cm⁻¹. The Raman intensities increased with an increase in the laser power. However, the normalized intensities are negligibly different, indicating ARS could hardly be oxidized by 514.5 nm laser irradiation.

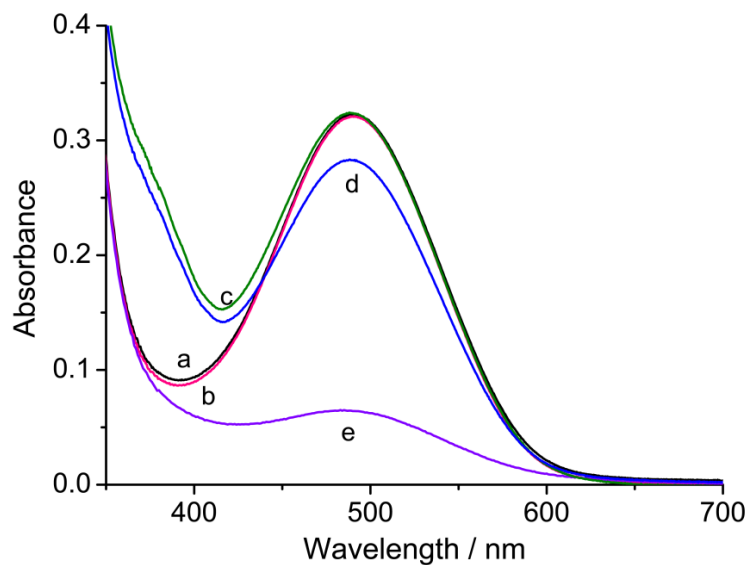


Fig. S5 UV-vis spectra of ARS-TiO₂ complexes without (a and b) and with (c, d and e) Cr(VI) concentration of 100 μM after exposure to visible light (514.5 nm) irradiation for different time. The exposure time was 0 (a and c), 10 (b and d) and 300 (e) min, respectively. Here, a halogen lamp (PCS-nHF150, COLDSPOT) equipped with a visible light-pass filter (OPTOSIGMA CWL= 514.5 nm) was used as the light source. The negligible difference in the absorption bands of ARS-TiO₂ complexes without Cr(VI) after 10 min visible light irradiation indicates the complexes process good stability. However, the absorption bands is obviously decreased after 10 min irradiation, indicating the ARS-TiO₂ can be degraded in the present of Cr(VI) upon 514.5 nm light irradiation.

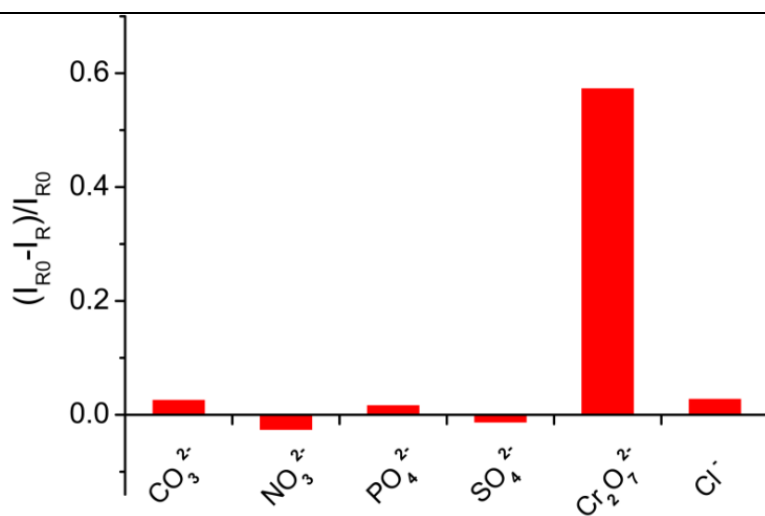


Fig. S6 Relative Raman intensity $[(I_{R0} - I_R)/I_{R0}]$ of ARS-TiO₂ complexes in the presence of environmentally common acid radical ions. The concentrations of Cr(VI) and each of the other anions were 20 and 50 μM , respectively.

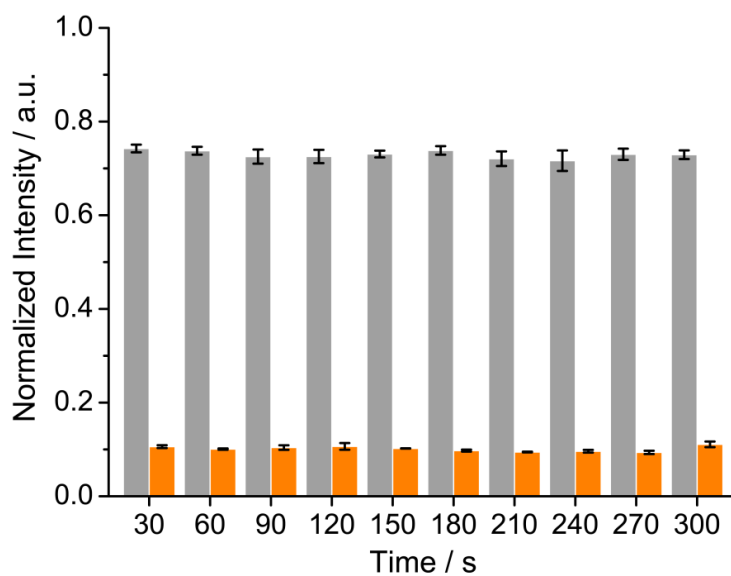


Fig. S7 Time-dependence of Raman intensities of ARS-TiO₂ complexes without (grey bar) and with (orange bar) the Cr(VI) concentration of 100 μM. The intensity of the band was normalized to that of the signal from 2-propanol at 816 cm⁻¹. The laser power used for the Raman spectra was much stronger compared to the halogen lamp, providing a more effective charge transfer process. Thus, Cr(VI)-induced SERS decrement was fast and reached equilibrium within 30 s.

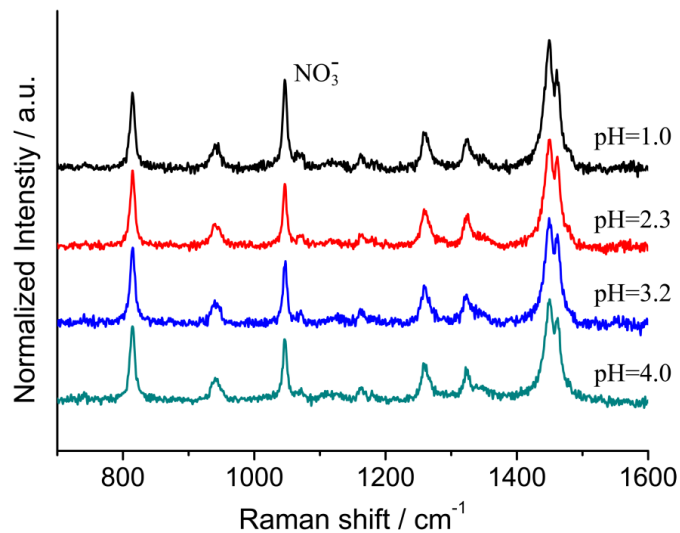


Fig. S8 SERS spectra of ARS-TiO₂ (50 μM ARS) with the Cr(VI) concentration of 10 μM at various pH values ranging from 1.0 to 4.0. The intensity of the band was normalized to that of the signal from 2-propanol at 816 cm⁻¹. The pH of the solution was turned by HNO₃ and NaOH. There is no obvious change in the Raman intensities except the vibrational band of NO₃⁻ ion.

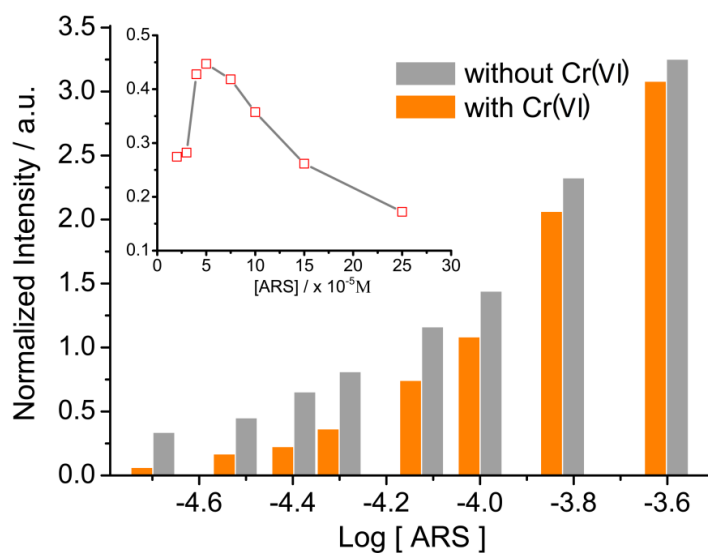


Fig. S9 Raman intensities of ARS-TiO₂ complexes at 1260 cm⁻¹ without and with Cr(VI) concentration of 20 μM under different ARS loading amount. Inset shows the difference between the intensities without Cr(VI) and with Cr(VI) under same ARS loading amount. The difference values represent the catalysis activity.

Table S1: IR and SERS Band Frequencies of Alizarin Red S.

IR		SERS		Assignments ^{a, b, c, d}
Bulk ^a	adsorbed on TiO ₂ ^b	adsorbed on Ag ^c	adsorbed on TiO ₂	
1665				v(C=O)
1634			1633	v(C=O)
1590				v(CC)
	1464	1480	1479	v(CC)
1459		1458	1462	v(CC)
1441		1446	1450	v(CC)
1350	1350	1340	1353	δ(CO)
1330	1330	1323	1323	v(C ₁ -O) + v(CC)
1289	1289	1295	1293	v(C ₂ -O) + v(CC)
1265	1265	1245	1260	v(CC) + v(C ₁ -O)
1235				Hydrous SO ₃
1203		1188	1183	δ(CH) + δ(CCC)
1160		1162	1163	v(SO ₃) assym
1068		1057	1073	v(SO ₃) sym

^{a, b, c}Data and assignments obtained from ref. [4], [5], [6], and [7], respectively. ^dApproximate description of the modes (v: stretching; δ: in-plane bending;).

It should be noted that ARS is adsorbed on the metal surface through the ketonic and hydroxyl groups, leading to the formation of a chelate complex as well.^{6, 8} But it is different with that on TiO₂ substrate, which is chelation through the two hydroxyl groups.⁶ In metal-enhanced Raman spectroscopy, both electromagnetic and chemical mechanisms contribute to the enhancement, and thus the SERS enhancement effect is better than that on TiO₂ substrate.¹ However, there are no obvious changes in Raman spectra except slight changes in the relative intensities of the ARS peaks. The changes in relative intensities may be due to the difference in adsorption model and chemical enhancement contribution.

Table S2: Recovery Data for the Determination of Cr(VI) in Cr(VI)-Spiked Pond Water Samples by Using Our Sensing System.

Cr(VI) added to the water sample [μM]	Cr(VI) detected [μM]	recovery
0.5	0.51	102.5%
1	0.98	98.1%
5	4.79	95.9%
10	9.6	96.7%

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