

Supporting Information for

**Enhanced Degree of Charge Transfer in Dye-sensitized Solar Cells
with a ZnO-TiO₂/N3/Ag Structure as Revealed by Surface-enhanced
Raman Scattering**

Xiaolei Wang,^a Peng Li,^a Xiao Xia Han,^a Yasutaka Kitahama,^b Bing Zhao,^{*,a} and Yukihiro Ozaki^b

^a. State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China.

^b. Department of Chemistry, School of Science and Technology, Kwansei Gakuin University, Sanda, Hyogo 669-1337, Japan

Chemical binding type in ZnO-TiO₂/N3/Ag system.

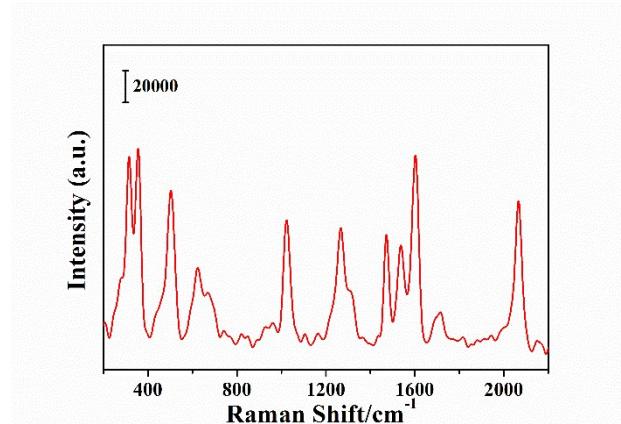


Figure S1. A Raman spectrum of N3 powders with the 532 nm excitation.

Based on the Raman spectrum of N3 powders (Figure S1) and the SERS spectra of TiO₂/N3, ZnO/N3, ZnO-TiO₂/N3, TiO₂/N3/Ag, ZnO/N3/Ag, and ZnO-TiO₂/N3/Ag (Figure 5-6) with the excitation wavelengths of 476.5 and 532 nm, the assignments of major bands are summarized in Table S1. As shown in Figure 5, the appearance of $\nu_s(\text{COO}^-)$ in the spectra of TiO₂/N3, ZnO/N3, and ZnO-TiO₂/N3 reveals that N3 binds to TiO₂, ZnO, and ZnO-TiO₂ via the carboxylic acid groups from bipyridine (bpy). And the Raman shifts of bpy ring stretch modes ($\nu(\text{C=C})$) in the spectrum of ZnO-TiO₂/N3 are similar to those in the spectrum of TiO₂/N3, meanwhile those in the spectrum of ZnO-TiO₂/N3 show ca. 4-8 cm^{-1} blue shifts compared to those in the spectrum of ZnO/N3. Thus, the chemical binding type of N3 to ZnO-TiO₂ is more similar to TiO₂ than ZnO via carboxylic acid groups. After introducing the Ag NPs to TiO₂/N3, ZnO/N3, and ZnO-TiO₂/N3, respectively, the peak due to $\nu(\text{C=N})$ from SCN groups appear, which can prove that Ag NPs participate in the absorption through the SCN groups from N3 molecule in TiO₂/N3, ZnO/N3, and ZnO-TiO₂/N3. Thus, N3 molecule works as a bridge to combine ZnO-TiO₂ via the carboxylic acid groups and Ag via SCN groups.

Table S1. Assignments of the major bands of N3, TiO₂/N3, ZnO/N3, ZnO-TiO₂/N3, TiO₂/N3/Ag, ZnO/N3/Ag, and ZnO-TiO₂/N3/Ag with excitation wavelengths of 476.5 and 532 nm.

	Excitation wavelength (nm)	Ring breathing (bpy)	$\nu_s(\text{COO}^-)$	$\nu(\text{C=N})$ (bpy)	$\nu(\text{C=C})$ (bpy)	$\nu(\text{C=C})$ (bpy)	$\nu(\text{C=N})$ (SCN)
N3	532	1024		1473	1537	1603	2067
TiO₂/N3	476.5	1027	1359, 1364	1474	1546	1613	
	532	1027	1377	1473	1545	1612	
TiO₂/N3/Ag	476.5	1024	1636	1475	1538	1606	2094
	532	1023	1361	1471	1538	1606	2136
ZnO/N3	476.5	1026	1359, 1390	1474	1543	1611	
	532	1024	1340, 1377	1470	1538	1608	
ZnO/N3/Ag	476.5	1024	1367	1475	1540	1607	
	532	1021	1637	1471	1539	1607	2136
ZnO-TiO₂/N3	476.5	1027	1363, 1390	1475	1545	1612	
	532	1026	1349, 1377	1472	1543	1611	
ZnO-TiO₂/N3/Ag	476.5	1023	1365	1474	1538	1606	2100
	532	1023	1363	1470	1536	1607	2144