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Supporting Information

Monitoring Catalytic Degradation of Dye molecules on the Silver-Coated ZnO Nanowire Arrays by Surface-Enhanced Raman Spectroscopy

Xinmei Zhao, [a,b] Baohua Zhang, [a,b] Kelong Ai, [a] Guo Zhang, [a,b] Linyuan Cao, [a,b] Xiaojuan Liu, [a,b] Hongmei Sun, [a,b] Haishui Wang,*[c] and Lehui Lu*[a]

[a] State Key Laboratory of Electroanalytical Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun, PR China
E-mail: lehuilu@ciac.jl.cn (Lehui Lu)

[b] Graduate School, Chinese Academy of Sciences, Beijing, PR China

[c] School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, PR China
E-mail: wanghsh@scut.edu.cn (Haishui Wang)

Experimetal

***Catalytic experiments of R6G*:** Catalytic degradation of R6G molecules was performed as follows. The silica wafer (1.0×1.5 cm) with ZnO nanowire arrays or silver-coated ZnO nanowire arrays was immersed in the aqueous solution of R6G (20 μM, 2.9 mL). After 10 min, a proper amount of the aqueous solution of $NaBH_4$ (10^{-2} M, 0.1 mL) was added into the above solution. The experiments were carried out in a quartz cell with a 10 mm light path for optical absorbance measurement.

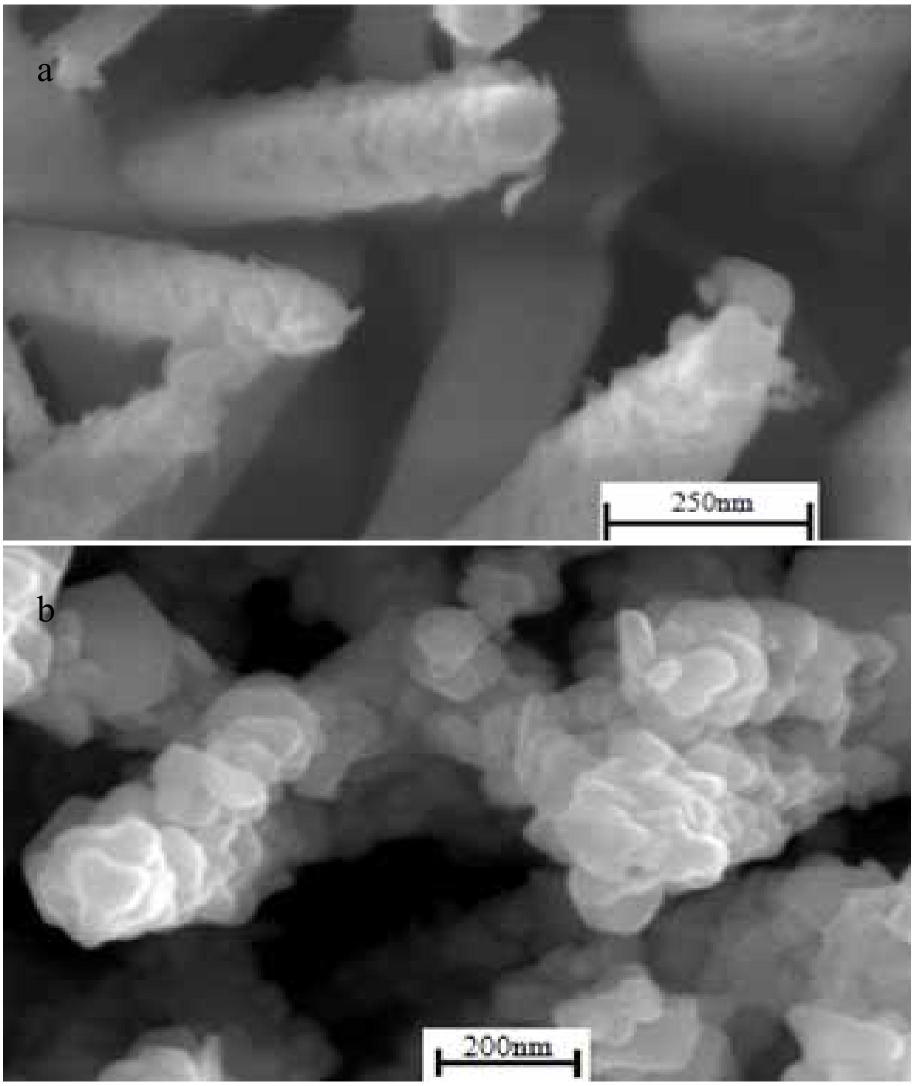


Fig. S1 (a) and (b) are the high-magnification SEM image of the samples shown in Figure 1C and 1D, respectively.

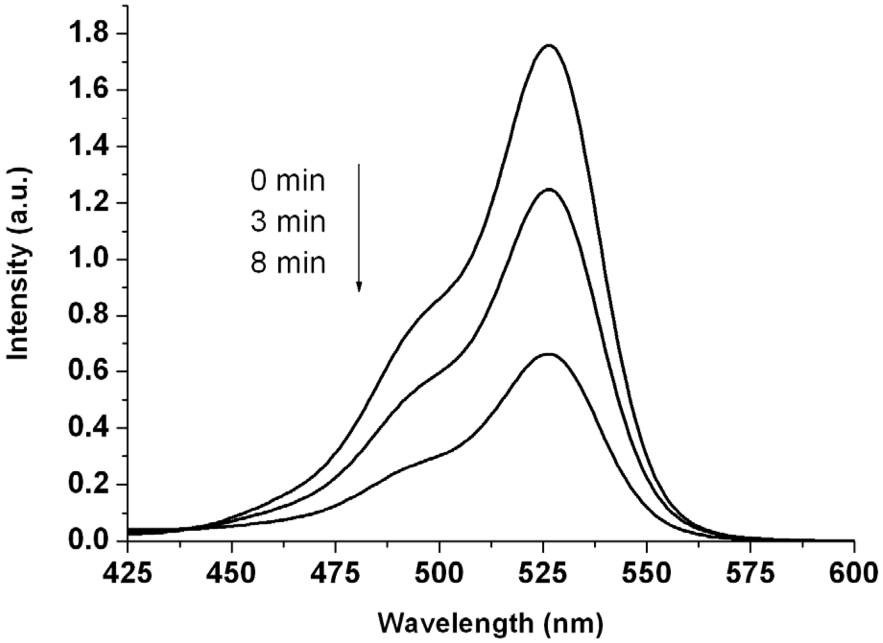


Fig. S2 UV-visible absorption spectra of R6G during different reaction-time.

In order to confirm that the SERS is superior to the UV-visible spectroscopy in monitoring the catalytic degradation of dye pollutants, we compared the UV-visible absorption spectrum and the SERS spectrum of R6G with low concentration (2.2×10^{-7} M). It is found that at low concentration, the UV-visible absorption spectrum is very weak, while the signals characteristic of R6G molecules in the SERS spectra are clear and unambiguous (as shown in Fig. S3).

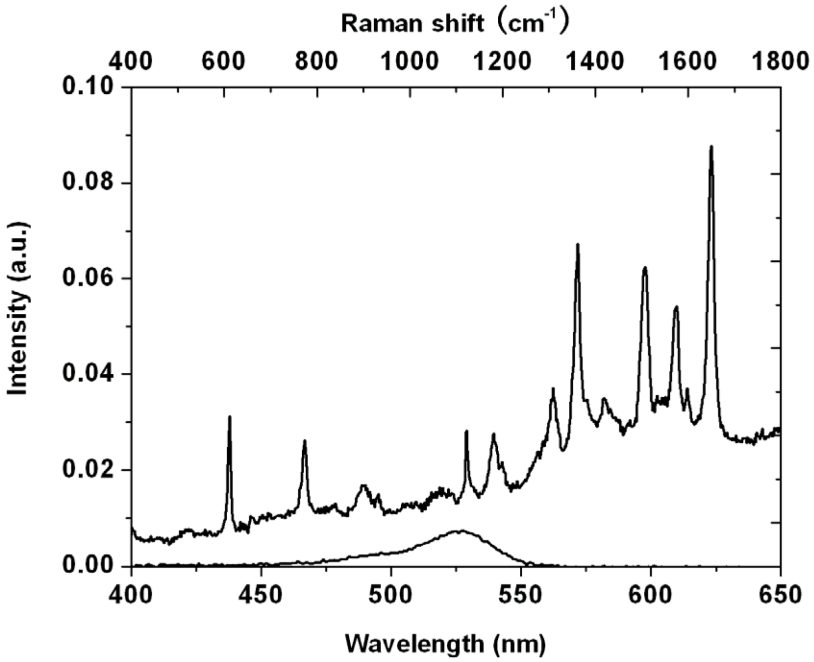
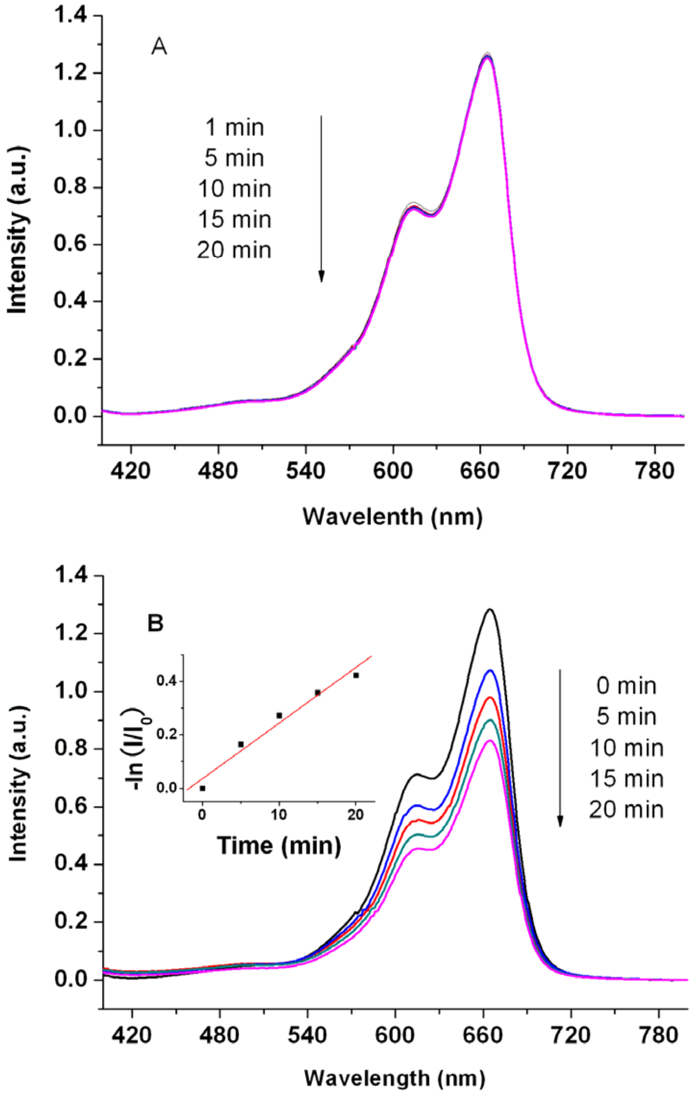


Fig. S3 UV-visible absorption spectrum and SERS spectra of R6G collected from the silver-coated ZnO nanowire arrays. [R6G] = 2.2×10^{-7} M.


A
1 min
5 min
10 min
15 min
20 min
Intensity (a.u.)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
420
480
540
600
660
720
780
Wavelenth (nm)
B
-ln (I/I$_0$)
0.4
0.2
0.0
0
10
20
Time (min)
0 min
5 min
10 min
15 min
20 min
Intensity (a.u.)
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.0
420
480
540
600
660
720
780
Wavelength (nm)

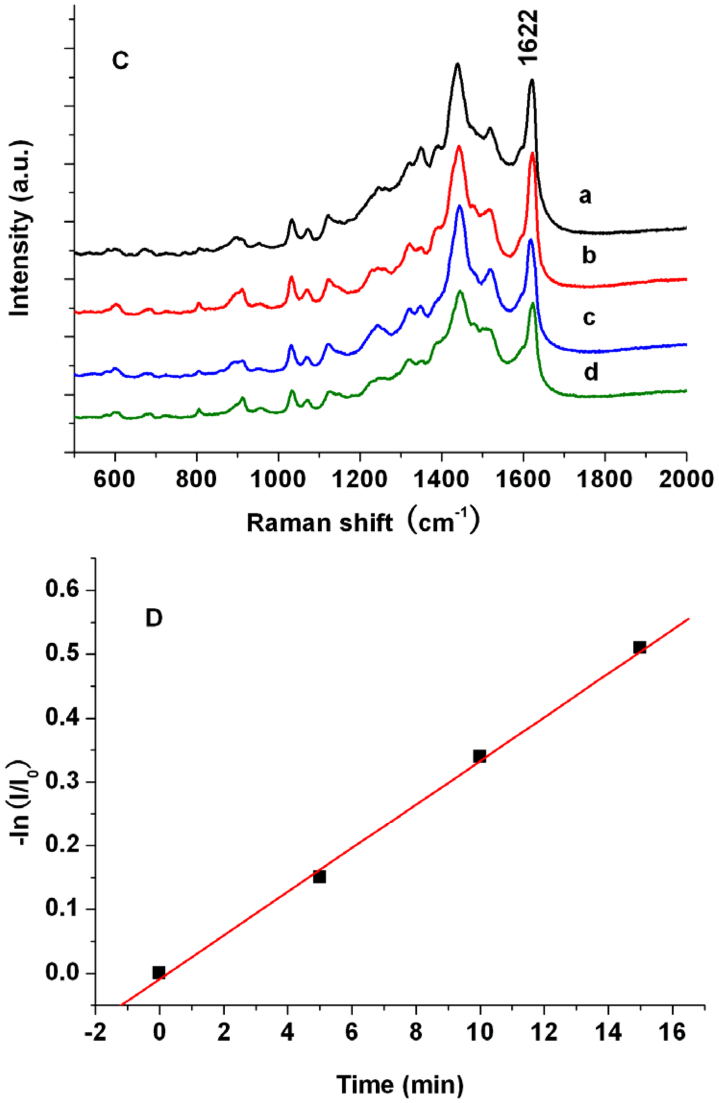


Fig. S4 Spectral variation of R6G in the reaction between R6G and $NaBH_4$ (A) in the absence of the as-prepared sample, and in the presence of (B) the silver-coated ZnO nanowire arrays. The inset figures in (B) is the corresponding kinetic degradation for MB. (C) Time-dependent SERS spectra of MB adsorbed on the silver-coated ZnO nanowire arrays during the degradation process: (a) 0 min, (b) 5 min, (c)10 min and (d) 15 min; (D) the corresponding linear relationship spectra of $-\ln(I/I_o)$ versus reaction-time acquired from SERS band 1622 cm^{-1}, respectively. Laser wavelength 514.5 nm. $[NaBH_4] = 10^{-2}$ mol/L, $[MB] = 2 \times 10^{-5}$ mol/L.

The same catalytic study of MB was performed (Fig. S4). In the absence of the as-prepared sample, the MB can be degraded about 17.3% in 20 min. But about 35.7% of MB was degraded in 20 min in the presence of silver-coated ZnO nanowire arrays. The rate constant is about 0.021 min^{-1} in the presence of silver-coated ZnO nanowire arrays. The cooresponding SERS spectra were shown in Fig. S4C. The rate constants calculated from the slops of the straight lines were 0.033 min^{-1} for SERS bands at1622 cm^{-1}.