

# Effect of TiO<sub>2</sub> Nanoparticles on the Improved Surface-Enhanced Raman Scattering of Polypyrrole Deposited on Roughened Gold Substrates

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We report here the first electrochemical oxidation–reduction cycle procedure to roughen gold substrates in 0.1 N HCl aqueous solution containing 1 mM rutile TiO<sub>2</sub> nanoparticles under the irradiation of UV light. It is encouraging to find that the oxidized peak in the anodic scan, which is responsible for the surface-enhanced Raman scattering, increases significantly due to the effect of adding TiO<sub>2</sub> under an electric field and UV irradiation. Moreover, the SERS spectrum of polypyrrole electrodeposited on the corresponding roughened gold substrate exhibits a 5-fold higher intensity compared to that without the contribution of TiO<sub>2</sub> nanoparticles.

## Introduction

Nanoscale titania is one of the most investigated oxide materials recently owing to its important applications in environmental cleanup,<sup>1</sup> photocatalysts,<sup>2</sup> and solar cells.<sup>3</sup> To increase its photocatalytic efficiency, many methods have been developed to prepare Au-coated TiO<sub>2</sub> nanocomposites.<sup>4,5</sup> For structural studies, Raman spectroscopy has recently been used to investigate heterogeneous individual and double-wall carbon nanotubes.<sup>6,7</sup> However, in collecting the Raman signals of organic compounds that are present in a system at very low concentration levels, surface-enhanced Raman scattering (SERS) was employed to enhance the detection.<sup>8,9</sup> In view of its unique sensitivity and excellent frequency resolution, SERS caused by roughened metal substrates provides a powerful means of obtaining vibrational information on adsorbate–surface interactions.<sup>10,11</sup> Among other techniques used to obtain roughened metals substrates,<sup>12,13</sup> a controllable and reproducible surface roughness can be generated through the electrochemical oxidation–reduction cycles (ORC).<sup>14,15</sup> Currently, some systems including metal/metal alloy colloids,<sup>16</sup> metal-coated metal colloids,<sup>17</sup> and metal/adsorbate/metal sandwiches<sup>18</sup> have been developed to further improve the SERS performance. To our knowledge, the effects of TiO<sub>2</sub> nanoparticles on the preparation of a roughened metal substrate and on the corresponding SERS effect have not yet been investigated. Since many nitrogen-containing heterocycles with five- or six-membered rings are known to give strong SERS spectral intensity, gold substrates are originally roughened by the ORC procedure in 0.1 N HCl aqueous solution containing 1 mM rutile TiO<sub>2</sub> nanoparticles under the irradiation of UV light. Then PPy films were

electrodeposited on the roughened gold substrates to examine the SERS enhancement in this study.

## Experimental Section

**Chemical Reagents.** Pyrrole (Py) was triply distilled until a colorless liquid was obtained, which was then stored under nitrogen before use. HCl and LiClO<sub>4</sub> were used as received without further purification. The reagents (p.a. grade) were purchased from Acros Organics. Rutile TiO<sub>2</sub> nanoparticles with particle sizes from 13 to 25 nm were purchased from Desunano Co., Ltd, Taiwan. All of the solutions were prepared using deionized 18 MΩ cm water.

**Preparation of Roughened Au Substrates.** All of the electrochemical experiments were performed in a three-compartment cell at room temperature, 24 °C, and were controlled by a potentiostat (model PGSTAT30, Eco Chemie). A sheet of polycrystalline gold foil with a bare surface area of 0.238 cm<sup>2</sup>, a 2 × 2 cm<sup>2</sup> platinum sheet, and a silver–silver chloride (Ag/AgCl) electrode were employed as the working, counter, and reference electrodes, respectively. Before the ORC treatment, the gold electrode was mechanically polished (model Minimet 1000, Buehler) successively with 1 and 0.05 μm of alumina slurry to a mirror finish. Then the electrode was cycled in a deoxygenated 0.1 N HCl aqueous solution containing 1 mM rutile TiO<sub>2</sub> nanoparticles from −0.28 to +1.22 V vs Ag/AgCl at 500 mV/s with 25 scans under the irradiation of 4-W UV light at 325 nm (this is called a modified roughened Au substrate). The durations at the cathodic and anodic vertexes were 10 and 5 s, respectively. After the ORC treatment, the roughened Au electrode was rinsed throughout with deionized water and finally dried in a vacuum-dryer in a dark atmosphere for 1 h at room temperature for subsequent use. For comparison, the roughened Au substrate without the additive of TiO<sub>2</sub> and the UV irradiation was also prepared by using the same roughening condition (this is called an unmodified roughened Au substrate).

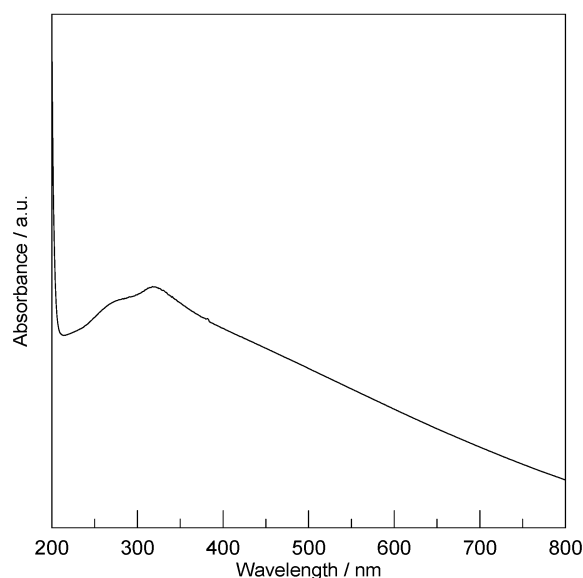
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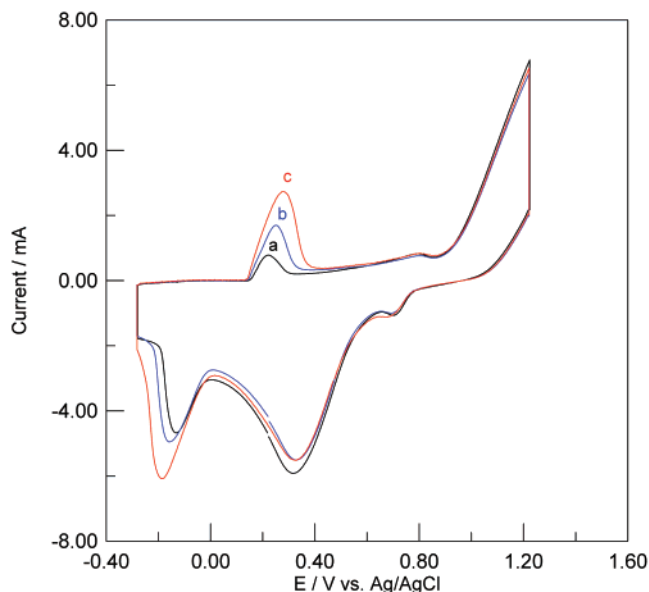
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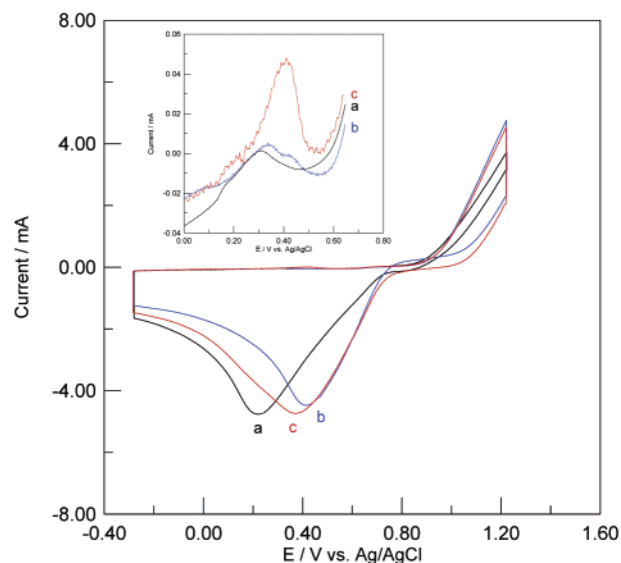
**Figure 1.** UV-vis spectrum of TiO<sub>2</sub> nanoparticles containing 0.1 N HCl aqueous solution.



**Figure 2.** Cyclic voltammograms at 500 mV/s of the 10th scan for electrochemically roughened gold substrates with predominant (111) orientation in different conditions: (a) 0.1 N HCl; (b) 1 mM TiO<sub>2</sub> and 0.1 N HCl; (c) 1 mM TiO<sub>2</sub>, 0.1 N HCl, and irradiation with UV light of 4 W at 325 nm in the roughening procedure.

**Electrodeposition of Polypyrrole on Roughened Au Substrates.** The electrochemical polymerization of polypyrrole (PPy) on the modified roughened Au substrate was carried out at a constant anodic potential of 0.85 V vs Ag/AgCl in a deoxygenated aqueous solution containing 0.1 M pyrrole and 0.1 N LiClO<sub>4</sub>. For comparison, PPy was also electrodeposited on the unmodified roughened Au substrate by using the same preparation conditions.

**Characteristics of Roughened Au and Electrodeposited PPy.** Raman spectra were obtained using a confocal microscope employing an Ar<sup>+</sup>–Kr<sup>+</sup> ion laser operating at 647.1 nm with an output power of 2.5 mW. The laser beam was focused down to a 5  $\mu$ m diameter (full width half max) by an objective lens (0.9 N.A.). The backscattered Raman signal was collected by the same objective lens and passed through an adjustable confocal hole to filter the unexpected stray-light noise. The



**Figure 3.** Cyclic voltammograms at 500 mV/s of the 10th scan for electrochemically roughened gold substrates with predominant (220) orientation in different conditions: (a) 0.1 N HCl; (b) 1 mM TiO<sub>2</sub> and 0.1 N HCl; (c) 1 mM TiO<sub>2</sub>, 0.1 N HCl, and irradiation with UV light of 4 W at 325 nm in the roughening procedure. The insert of the figure displays the differentiable oxidation phenomenon occurring on the roughened gold substrates in the range of 0–0.65 V vs Ag/AgCl.

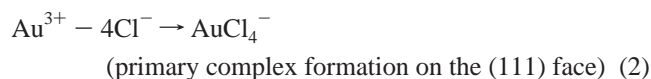
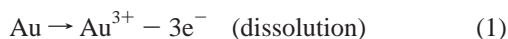
Raman signal was then sent to a monochromator (Triax 550) equipped with a 1200 grooves/mm grating (blaze wavelength at 630 nm) via an optical cable and collected by a liquid-nitrogen-cooled charge-coupled device (CCD, 1024  $\times$  256 pixels, 26  $\times$  26  $\mu$ m<sup>2</sup> per pixel). The complex SERS peaks were deconvoluted into component Gaussian peaks using a peak separation and analysis software (PeakFit v4.0, AISN Software Inc.). For the X-ray photoelectron spectroscopy (XPS) measurements, a Physical Electronics PHI 1600 spectrometer with monochromatized Mg K $\alpha$  radiation, 15 kV and 250 W, and an energy resolution of 0.1–0.8%  $\Delta E/E$  was used. To compensate for surface-charging effects, all XPS spectra were referred to the C 1s neutral carbon peak at 284.6 eV. Surface chemical compositions were determined from peak-area ratios corrected with the approximate instrument sensitivity factors. UV-vis absorption spectroscopic measurements were carried out on a Perkin-Elmer Lambda 25 spectrophotometer in 1-cm quartz cuvettes. The surface morphologies of roughened gold substrates were examined by a scanning electron microscope (SEM, model S-4700, Hitachi). The surface roughness of roughened gold substrates was obtained from atomic force microscopy (AFM, model Nanoscope III, Digital Instrument) experiments. The mean roughness was determined from the mean value of the surface relative to the center plane, which is automatically calculated from a program attached to the instrument.

## Results and Discussion

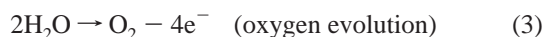
Figure 1 demonstrates the absorbance maximum of rutile TiO<sub>2</sub> nanoparticles, used in this study, appearing approximately at 325 nm. Therefore, the UV irradiation for TiO<sub>2</sub> nanoparticles was kept at 325 nm to promote their catalytic activities. Figures 2 and 3 show the results of the 10th scan of cyclic voltammograms for the dissolution and redeposition of Au substrates with predominant (111) and (220) orientations, respectively, in different conditions with and without the addition of TiO<sub>2</sub> nanoparticles and the irradiation of the UV light. As shown in a previous study,<sup>11</sup> the SERS spectrum of PPy deposited on roughened Au with predominant (111) orientation exhibits

higher intensity and better resolution than that deposited on roughened Au with predominant (220) orientation. The result was ascribed to the appearance of the anodic peak at ca. 0.2 to 0.4 V vs Ag/AgCl on Au with predominant (111) orientation (Figure 2), but it disappears on Au with predominant (220) orientation (Figure 3). Namely, the higher this anodic peak is the stronger the SERS signal of PPy is obtained. Furthermore, this anodic peak initially shows up at the 8th scan. Figure 2a displays similar phenomena to that of the previous study.<sup>11</sup> It is notable, as shown in Figure 2b, that the additive of TiO<sub>2</sub> nanoparticles under an electric field demonstrates a positive effect of increasing the anodic peak, which is responsible for the SERS enhancement of PPy. Certainly, with the supplemental UV irradiation at 325 nm, where TiO<sub>2</sub> nanoparticles exhibit the maximum absorption, the anodic peak should be further magnified, as shown in Figure 2c. This effect of increasing the anodic peak also slightly works on the Au substrates with predominant (220) orientation, as shown in the insert of Figure 3. In the ORC treatment, the chloride electrolyte was selected since this facilitates the metal dissolution-deposition process that is known to yield SERS-active roughened surfaces.<sup>19</sup> In the case of gold with predominant (111) orientation, Cl<sup>-</sup> is easily adsorbed on this (111) face.<sup>20</sup> The roughing procedure under the addition of TiO<sub>2</sub> and the irradiation of UV light can be summarized as follows.

In the anodic scan



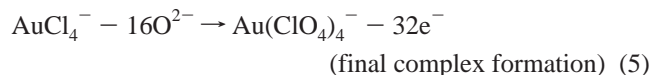
At the anodic vertex



In the cathodic scan

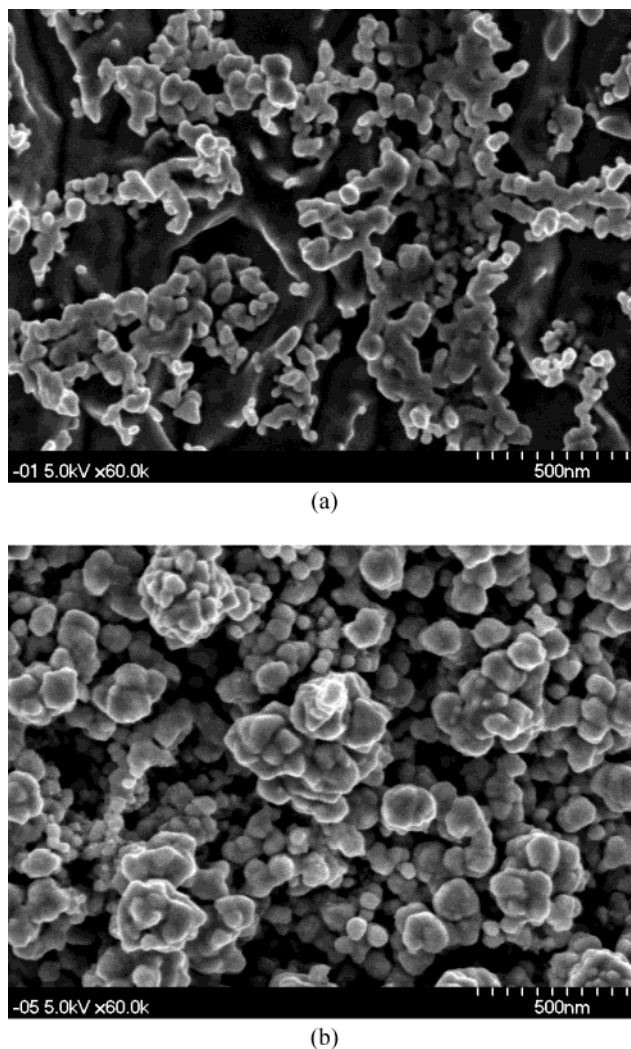


At anodic peak of ca. 0.2~0.4 V vs Ag/AgCl



By examination of the differences shown in Figures 2 and 3, one can see that the main contribution of TiO<sub>2</sub> nanoparticles to the roughening procedure is to promote the formation of the final complex Au(ClO<sub>4</sub>)<sub>4</sub><sup>-</sup>, as explicated in eq 5, which is the exact resultant responsible for the enhanced Raman scattering.<sup>11</sup> Further XPS analysis confirms that perchlorate was formed on the surface of the Au substrate after the substrate was roughened in a 0.1 N HCl aqueous solution containing 1 mM TiO<sub>2</sub> from -0.28 to +1.22 V vs Ag/AgCl with 25 scans under the irradiation of the UV light.

Figure 4 shows the SEM images of roughened Au substrates with and without the modification of TiO<sub>2</sub> nanoparticles. The surface morphology of the Au substrate roughened in 0.1 N HCl exhibits thin metal islands with good Raman activity, which results from a microstructure of <100 nm size.<sup>21</sup> With the addition of TiO<sub>2</sub> nanoparticles and the UV irradiation in the ORC treatment, the surface morphology of the Au substrate is dramatically changed into a thicker and more compact one (Figure 4b). Also, the mean roughness, as calculated from AFM experiments, are 40 and 143 nm for the unmodified and

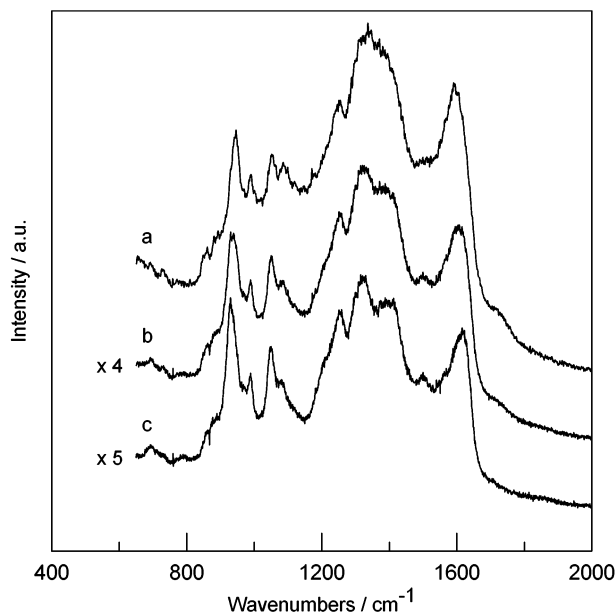


**Figure 4.** SEM images of different substrates: (a) electrochemically roughened gold; (b) electrochemically roughened gold modified with TiO<sub>2</sub> nanoparticles and irradiation with UV light of 4 W at 325 nm in the roughening procedure.

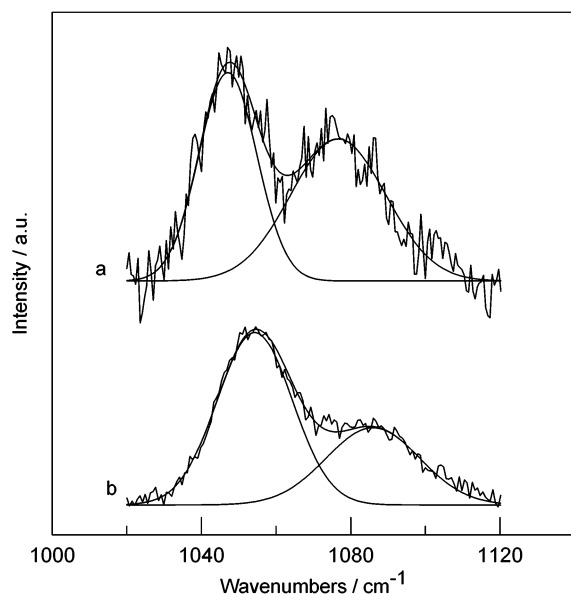
modified roughened Au substrates, respectively. Meanwhile, the mean roughness is 48 nm for the roughened Au substrate modified with TiO<sub>2</sub> nanoparticles in the absence of UV light in the roughening procedure. XPS analyses show that the content of TiO<sub>2</sub> nanoparticles in the modified roughened Au substrate is just about 3.2 mol %, ignoring the interference from the substrate of Au.

As shown in the previous report,<sup>22</sup> no meaningful information can be provided from the Raman spectroscopy of PPy deposited on an Au substrate without the ORC pretreatment. However, almost all of the scattering modes of PPy can be markedly demonstrated with sharp peaks, due to the SERS effect. Figure 5 shows the Raman spectra of PPy electrodeposited on the roughened Au substrates with and without the modification of TiO<sub>2</sub> nanoparticles and the UV irradiation. Obviously, a PPy spectrum obtained on the roughened gold caused by the treatment of TiO<sub>2</sub> nanoparticles and UV irradiation in the ORC procedure exhibits a magnified intensity of more than five times. This increase in intensity is significant in comparison with what was observed in the report of polyaniline chemically deposited on various rough metals by Baibarac et al.<sup>23</sup> The higher spectral intensity of PPy obtained on the modified roughened Au substrate can be attributed to the different contents of Au- and Cl-containing nanocomplexes formed on the Au substrates





**Figure 5.** SERS spectra of PPy electrodeposited on different substrates: (a) electrochemically roughened gold modified with TiO<sub>2</sub> nanoparticles and irradiation with UV light of 4 W at 325 nm in the roughening procedure; (b) electrochemically roughened gold modified with TiO<sub>2</sub> nanoparticles in the absence of UV light in the roughening procedure, the intensity was magnified 4-fold; (c) electrochemically roughened gold, the intensity was magnified 5-fold.



**Figure 6.** Raman doublet of the C–H in-plane deformation in the range of 1020–1120 cm<sup>-1</sup>, the same as shown in the Figure 5, of PPy deposited on different substrates: (a) modified roughened Au substrate; (b) unmodified roughened Au substrate.

during the roughening procedures<sup>11,24</sup> corresponding to different degrees of accompanying anodic peaks, as shown in Figure 2. Besides the enhanced SERS intensity of PPy, a much more oxidized PPy can also be observed on the Raman spectrum. As demonstrated in the previous study,<sup>25</sup> the peak at higher frequency of the doublet of ca. 1052 and 1083 cm<sup>-1</sup> in SERS is assigned to the C–H in-plane deformation of the oxidized PPy. The broad Raman peaks of PPy at 1020~1120 cm<sup>-1</sup> in

the present work have been deconvoluted into individual reduced and oxidized components, corresponding to the PPy films deposited on the roughened Au substrates with and without the contributions of TiO<sub>2</sub> nanoparticles and UV irradiation in the ORC procedure. Accordingly, the calculated oxidation degrees<sup>26</sup> are 0.53 and 0.36, respectively, for those oxidized PPy with and without the treatment of TiO<sub>2</sub> nanoparticles and UV irradiation in the ORC procedure. A greatly oxidized PPy can also be confirmed from the peak shift of the C=C backbone<sup>25</sup> from 1615.5 to 1591.7 cm<sup>-1</sup> due to the contributions of TiO<sub>2</sub> nanoparticles and the UV irradiation.

## Conclusions

In summary, we have presented a new pathway to prepare a roughened Au substrate by an ORC treatment facilitated with rutile TiO<sub>2</sub> nanoparticles and irradiation of UV light. This roughened Au substrate can be used to enhance the SERS intensity of PPy deposited on it. The method shown in the present work can be further extended to SERS studies for other materials that are present in a system at very low concentration levels.

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