

## 기계화학적 활성화에 의해 테이프에 자발적으로 환원된 은의 전기화학적 분석

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### Electrochemical Analysis of Spontaneous Reduction of Silver on Tape by Mechanochemical Activation

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**요약** : 본 연구는 기계화학적 활성화 된 스카치테이프가 금속 이온 수용액에서 유발하는 자발적 금속 나노입자 필름 형성의 구동력과 그 크기를 전기화학적 방법으로 분석했다. 은 필름이 형성된 테이프를 질산에 녹이고, 완충용액과 섞어 전기화학 측정용 샘플을 준비했다. 양극 벗김 전압전류법의 피크 신호를 통해, 은 입자의 자발적 환원에 소모된 전하량을 측정했다. 이를 검정 곡선에 대입하여, 환원된 은의 양을 구했다. 그 결과 은의 양이 선행 연구 대비  $10^6$ 배 많은 점, 수용액에서 전하를 가진 이온들의 짧은 수명을 참고하여, 자발적 반응의 구동력을 라디칼로 결론 냈다.

**주제어** : 기계화학적활성, 자발적환원, 전기화학, 라디칼, 양극 벗김 전압전류법

**Abstract** : We investigated the driving force and the required charges for spontaneous reduction of metal nanoparticles (NPs) on a scotch tape induced by mechanochemical activation. The charges were analyzed based on anodic stripping voltammetry (ASV) of silver, which is proportional to the number of charge identities on the tape. The results supported that the driving force is mechanochemical radicals rather than ions in the light of the high charge density on the tape.

**Keywords** : Mechanochemistry, Spontaneous Reduction, Electrochemistry, Radical, Anodic stripping voltammetry

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## 1. Introduction

The mechanochemical concept have been continuously established from Theophrastus of Ephesus in Greece philosopher[1]. The term 'mechanochemistry' was first called by W. Ostwald[2]. This phenomena consists of (1) breaking of intramolecular bonds by an external mechanical action and thus (2) having chemical potentials to evoke chemical reactions [3]. Two types of bond breaking can be induced by various mechanic stimulus, such as milling, grinding, shearing, cutting, stirring, pulling, and kneading. One is homolytic cleavage of covalent bond generating neutral radicals and another is heterolytic cleavage generating net charged ions[4]. These radicals and ions were used for chemical reactions, such as degrading polymer to desired molecular weight[5], generating  $H_2O_2$  in water/stressed polymer interface[4], and synthesizing nanoparticle[6]. Namely, mechanochemistry is one of methods for conversion from mechanical energy to chemical energy.

Recently, Bartosz group have reported spontaneous formation of various NPs on scotch tape in metal precursors by mechanochemical activation[7]. This phenomenon is induced by bond breaking of polyacrylic adhesive. The ions and radicals are generated on sticky side of scotch tape after peeling-off. The net charges by heterolytic breaking have not ability to cause chemical reaction because of rapid annihilation in aqueous precursor[8, 9]. Thus, they concluded that driving force for these NPs formation is mechanochemical radicals. By this method, several metals such as silver, gold, copper, and palladium can be easily formed after immersing activated tape into metal precursor for several days. These NP films can be used for antibacterial films on clothes and kitchen appliances, medical devices, electronic component and so on. Although the NP films have advantages such as increasing

conductance, selective patterning, and antibiotic properties[7], some controversies still exist. One is driving force for spontaneous NP formation. The strong candidate is radical. However, the radical is not clear in that reaction kinetic for NP formation is very slow. Another question is absence of charge density on driving identities. They only reported a few  $nC/cm^2$  measured by electrometer, which is not enough to form metal NP films on tape.

Herein we investigate the charge density and identity on the activated scotch tape using electrochemical method. The charges required for spontaneous reduction of metals on the tape are analyzed using anodic stripping techniques (ASV)[10]. We adopt AgNPs formed on the tape as a target material, because reduction of  $Ag^+$  is one electron reaction. Thus, the amount of silver is proportional to charge density of the activated tape by mechanochemistry.

## 2. Experimental Method

### 2.1. Materials

All reagents were purchased from Sigma-Aldrich.

### 2.2. Principle of anodic stripping voltammetry

Anodic stripping techniques (ASV) have been used in electrochemical analysis for recognizing selectively several metals[11]. The ASV method have powerful advantage for detection of very low concentration target materials[12] in that the method have high sensitivity, selectivity, analysis of a number of targets simultaneously, and low detection limit. The principle of ASV is shown in Figure 1. First, target ions are deposited on an electrode under constant cathodic potential larger than standard electrode potential for a few minutes. This preelectrolysis step function serve as concentrating target ions in solution to working electrode surface. After deposition step, the target is stripped (oxidation) from

electrode surface to solution by using voltammetric technique such as linear sweep voltammetry (LSV), differential pulse voltammetry (DPV), and square wave voltammetry (SWV). The concentration of target was calculated from integral of oxidation peak. This oxidation peak is less affected by charging current and impurity noise because of the pre-deposition step. This method is appropriate for detection of very dilute solutions (up to  $10^{-11}$  M) with low detection limits. The glass cell and electrode should be kept clean because the impurities adsorbed on electrode surface can interfere with diffusional transport of target[13]. A choice of working electrode is also important for this type electrochemical measurement. The noble metal electrodes, i.e. gold and platinum, are not suitable for ASV experiment because oxide layer formed on the noble metals cause reproducibility issue in some solutions[14]. The glassy carbon electrode is usually employed as working electrode in ASV, which has wide potential window to both cathodic and anodic directions. In this experiment, we adopt LSV mode as a voltammetry.

When the flux reaches maximum rate, peak current is represented by[15]

$$I_p = (2.69 \times 10^5) n^{3/2} A C D^{1/2} v^{1/2}$$

At 25°C, A is area in  $m^2$ ,  $D_O$  is diffusion coefficient  $cm^2/s$ ,  $C_O^*$  is concentration of Ox in mM, and  $v$  is scan rate in V/s.

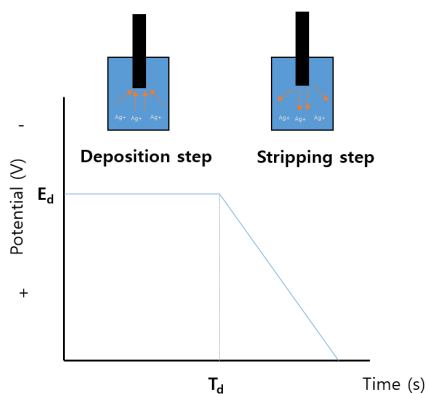


Fig. 1. Principle of anodic stripping voltammetry (ASV).

### 2.3. Sampling method and Electrochemistry

The AgNPs on the tape were prepared by cutting the tape in  $6.24 \text{ cm}^2$  and subsequent immersing in silver nitrate ( $\text{AgNO}_3$ ) electrolyte solution ( $2 \text{ mg/ml}$ ) for 92 h. After NP formation, the tape was washed with distilled water during 30 s and dried by nitrogen. Silver metals on the tape were dissolved by incubating in 1 ml nitric acid (50 %) for 30 min. The sample dissolved in nitric acid were transferred into 2 ml acetate buffer solution (pH 5.6).

The three-electrode system was used for ASV. A 3 mm diameter glassy carbon (GC, area:  $0.0706 \text{ cm}^2$ ), a platinum wire, and a Ag/AgCl electrode (sat'd KCl) were employed as working electrode, counter electrode, and reference electrode, respectively. The area of counter electrode was at least three times larger than area of GC. For preelectrolysis step, the GC was applied with  $-0.1 \text{ V vs. Ag/AgCl}$  for 600 s (deposition time). For stripping step, the LSV mode was chosen as a sweep method with  $50 \text{ mV/s}$  scan rate and potential range from  $-0.1 \text{ V}$  to  $+0.75 \text{ V}$ .

## 3. Results and Discussion

### 3.1. Anodic stripping voltammetry

Figure 3 shows representative anodic stripping voltammogram for dissolved Ag ion in the sampling solution. The peak has well defined and sharp shape compared with background current. The peak potential represents  $+0.35 \text{ V}$ . The peak current and peak area correspond to few  $\mu\text{A}$  and  $\mu\text{C}$  scales, respectively. The average peak current is  $5.90 \mu\text{A}$ , and the average charge is  $5.74 \mu\text{C}$ . These values represent approximate amount of reduction metal on the tape. Namely, ASV method can detect AgNPs on the scotch tape using above sampling method.

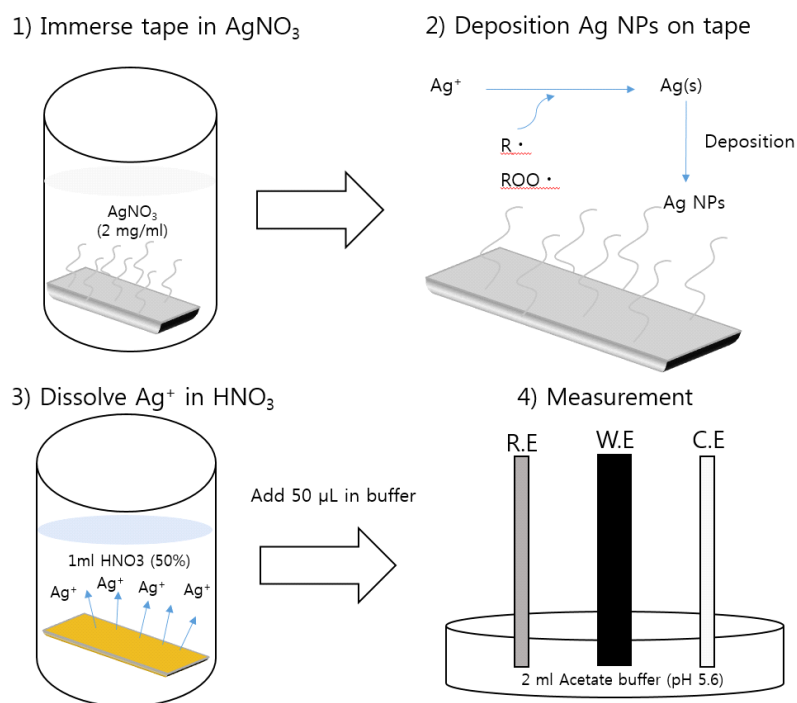


Fig. 2. Schematic illustration of measurement of silver on the tape. (1) Immersing a tape in  $\text{AgNO}_3$  solution for 92 h. (2) Deposition AgNPs on sticky side of tape. (3) Dissolving Ag in  $\text{HNO}_3$  (50%). (4) Electrochemical measurement using three-electrodes system. Deposition potential ( $E_d$ ):  $-0.1$  V vs.  $\text{Ag}/\text{AgCl}$  and deposition time ( $T_d$ ): 600 s. Electrolyte: dissolved silver ions in 0.2 M acetate buffer.

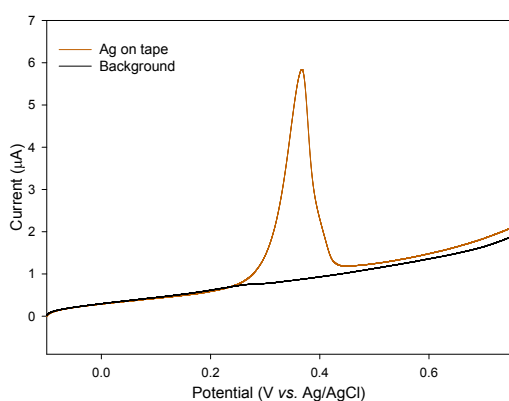


Fig. 3. Representative ASV of silver on the tape dissolved in 0.2 M acetate buffer (pH 5.6). Scan rate = 50 mV/s. Potential ranges from  $-0.1$  V to  $+0.75$  V.  $T_d = 600$  s at  $-0.1$  V  $E_d$ . Area of the activated tape is  $6.24$   $\text{cm}^2$ .

### 3.2. Cyclic voltammetry

Figure 4 shows cyclic voltammograms (CVs) for Ag ion in the solution under same conditions as anodic stripping mode, except for deposition step. This peak represents less sharp and high current than Figure 3. The absence of deposition time (preelectrolysis) cause low selectivity to target metals because of low concentrations of targets on the electrode compared with general ASV method. Thus, we selected ASV method to analyze Ag ions.

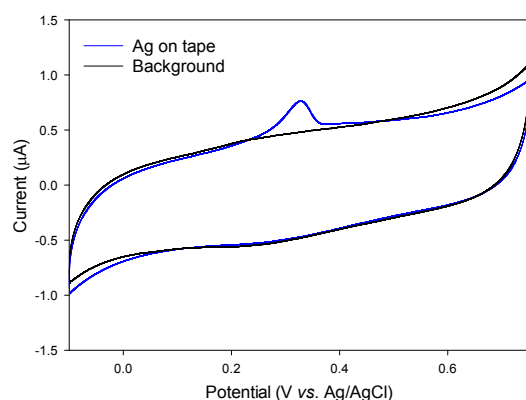


Fig. 4. Cyclic voltammety of silver on the tape dissolved in 0.2 M acetate buffer (pH 5.6). Scan rate = 50 mV/s. Potential ranges from +0.75 V to -0.1 V.

### 3.3. Quantitative Analysis of Experimental Data

Figure 5 represents calibration curve of Ag ion as  $-\log(\text{charge})$  versus  $-\log(\text{concentration})$ . The calibration curve was obtained by repeating ASV in standard solutions containing various  $\text{Ag}^+$  concentration. The unknown concentration of target can be calculated based on this curve.

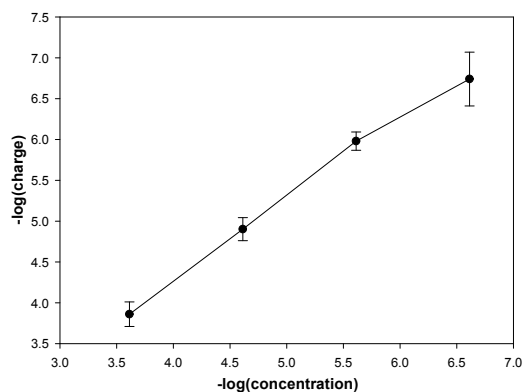


Fig. 5. Calibration curve of Ag concentration using silver standard solutions.

The silver standard solutions have similar composition with supporting electrolyte. The concentration range of standard solution is ca.  $10^{-7}$  to ca.  $10^{-4}$  M. The charge density calculated from ASV was applied to calibration

curve. The amount of reduced Ag by mechanochemistry is  $4.10 \times 10^{-4}$  M (from average charge) based on calibration curve. Thus, we can estimate precise concentration of Ag on scotch tape. The charge density on the activated tape is  $6.34 \times 10^{-3}$  C/cm<sup>2</sup>. This value is too high compared than previously reported  $10^{-9}$  C/cm<sup>2</sup> [7]. The charge density from deposited silver seems to be directly related with mechanochemical radicals, not ions. Because the ions generated by contact and separation are rapidly disappeared in metal electrolyte solutions. Thus, we have confirmed that radicals are strong candidate for spontaneous metal reduction of the scotch tape.

## 4. Conclusion

We electrochemically investigated driving force for spontaneous reduction of metal nanoparticle (NP) film on a scotch tape activated by mechanochemistry. The simple peeling-off generated mechanochemical ions and radicals on the surface, which have chemical potential. The both + and - ions on the tape alive for a short time in aqueous solutions, and thus can not induce formation of NPs. The electrochemical results demonstrated that radical is driving force for this spontaneous reaction in that silver has  $10^6$  times higher value than previously reported charge density of ions.

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