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Electrocatalytic Conversion of CO_2 and Nitrate Ions to Urea below -1.0 V vs Ag/AgCl by a TiO_2-Nafion® Composite Electrode

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Abstract

CO_2 and nitrate ions were successfully converted to urea by a TiO_2/Nafion® nanocomposite electrode under ambient conditions. The composite electrode was constructed by drop-casting the mixture of P-25 titania and Nafion® solution on an ITO electrode. When the electrode was electrolyzed in CO_2-saturated 0.1 M KNO_3 (pH 4.5) solution at -0.98 V vs. Ag/AgCl, urea was formed with a Faradaic efficiency of 40%. The other reduced products obtained were ammonia, CO, and H_2.

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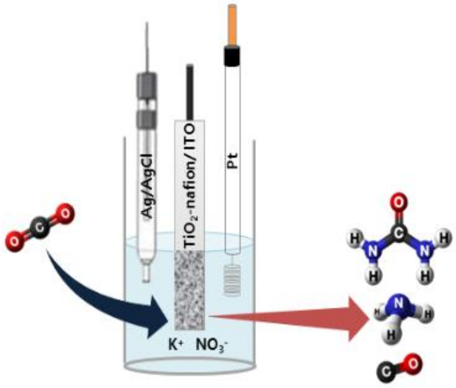
CO_2 and nitrate ions were converted to urea with a Faradaic efficiency of 40% using a TiO_2-Nafion® nanocomposite electrode as an electrocatalyst at -0.98 V vs. Ag/AgCl at room temperature and atmospheric pressure. The CO and ammonia precursors resulting from the simultaneous conversion of CO_2 and nitrate ions were adsorbed on TiO_2 and subsequently converted to urea.



Keywords: CO_2 conversion · electrocatalyst · modified ITO electrode · P-25TiO_2 · urea

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There have so far been few investigations of the photochemical conversion of CO_2 and nitrate to urea using TiO_2 and its derivatives at ambient conditions [1] . Shibata *et al*. have demonstrated the possibility of urea synthesis by electrochemical conversion of carbon dioxide and nitrate/nitrite ions by gas diffusion electrodes modified with variety of electroactive materials at ambient room temperature and atmospheric pressure [2]. The efficiency of urea formation on gas diffusion electrodes loaded with Cu or Zn was about 22 % and 37 % at -2.25 V and −1.75 V vs. SHE, respectively [2b]. These results imply the possibility of urea synthesis from CO_2 and ammonia at ambient conditions, in contrast to the temperatures of 150–200 °C and pressure of 100–200 atm used in the highly energy-intensive industrial urea synthetic process [3].

The chemical conversion of CO_2 to valuable products such as hydrocarbons, syngas, formate, and other chemical commodities is crucial to mitigate the greenhouse effect caused by CO_2 in the atmosphere [4]. Increasing concentrations of CO_2 in the atmosphere are a key cause of environmentally damaging phenomena such as global climate change and ocean acidification.[4] Electrochemical CO_2 conversion processes that can operate at room temperature present clean and sustainable methods to utilize CO_2, but systems that use metallic electrodes require a large overpotential [5]. Electrodes can be modified with suitable materials like inorganic nanomaterials, metal complexes with suitable ligand systems to reduce the required overpotential, increase their catalytic activity for CO_2 conversion, and allow kinetically fast and thermodynamically stable conversion[4].

As like CO_2, the pollutant nitrogen oxide also has significant impacts on the environment, and is also responsible for many human health problems, particularly in infants. Nitrogen oxide accumulates in water supplies from both the intensive use of synthetic fertilizers and industrial activity, and several technologies, including electro-reduction, have been developed to decrease the levels of nitrate contamination [6]. The electrochemical synthesis of urea from environmental CO_2 and nitrate in water under mild conditions would be a fascinating method for the utilization of CO_2 and nitrate pollutants. Urea is one of the most valuable industrial products derived from CO_2 because of its use as an important nitrogen source for fertilizers, which are produced worldwide at a scale of 100 million ton per year [4d]. In this study, we used commercially available P-25 TiO_2 nanoparticles with Nafion® as an electrocatalyst for the simultaneous conversion of CO_2 and nitrate to urea in aqueous solution at room temperature and pressure. The use of aqueous reaction conditions for the electrochemical conversion of CO_2 to urea is a significant improvement

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in this study, since the large-scale application of previous CO_2 conversion processes is limited by their use of undesirable expensive organic solvents.

We have recently demonstrated the successful conversion of CO_2 to CO and formate without any overpotential in neutral aqueous solution using bio- and synthetic electrocatalysts. We reported the highly selective electrocatalytic conversion of CO_2 to CO in aqueous solutions using the enzyme carbon monoxide dehydrogenase/acetyl-CoA synthase (CODH/ACS) and a synthetic Ni(cyclam) complex attached poly(allylamine)- catalysts [7]. We also converted CO_2 to formate with a current efficiency of 80–100 % by the acetogenic bacteria *Moorella thermoacetica* and *Clostridium formicoaceticum* in a neutral aqueous solution [8]. Encouraged by these works and related works on electrocatalytic conversion of CO_2, we extended our efforts to the conversion of CO_2 to CO and urea using nanoparticulate (P-25) titania. TiO_2 is a well-known catalyst for many chemical transformations because of the strong reducing power of its redox couple and its high electro-stability, chemical stability, excellent optical and electronic properties. TiO_2 is also readily prepared in different morphologies [9], which are used as the catalysts in several chemical processes. Recently, Kamat et al. reported the electrocatalytic reduction of CO_2 to methanol by nanostructured TiO_2 deposited on a glassy carbon electrode in acetonitrile [10]. TiO_2 and its derivatives are also already utilized for the photochemical activation of CO_2 [11] and nitrate reduction [12]. TiO_2 nanocrystals embedded in SiO_2 matrices were used as a photocatalyst for the conversion of CO_2 in different solvents and also for simultaneous reduction of CO_2 and NO_3^- for the formation of urea [1d&1e]. We are not aware of any existing reports on the electrochemical synthesis of urea using TiO_2, and thus report here the first instance of its use in urea synthesis. The industrial process for urea synthesis requires a significant amount energy to produce the required ammonia from hydrogen and nitrogen. The advantage of the system reported herein is that the urea synthesis is achieved by an energetically favorable process. In this study, we used commercially available P-25 TiO_2 nanoparticles with Nafion® as an electrocatalyst for the simultaneous conversion of CO_2 and nitrate to urea in aqueous solution at room temperature and pressure. The use of aqueous reaction conditions for the electrochemical conversion of CO_2 to urea is important since the large-scale application of previous CO_2 conversion processes is restricted by their use of costly organic solvents. The formation of urea from the simultaneous electrocatalytic conversion of CO_2 and nitrate on the P-25 TiO_2- modified electrode occurs at ambient temperature and pressure.

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Nafion®, a negatively charged perfluorinated polymer, can bind positively charged TiO_2, and forms a stable porous film on electrode surfaces. 5 % (v/v) Nafion® in water was used to make a composite with TiO_2. A planar tin-doped indium oxide (ITO) plate has been selected as an electrode to deposit TiO_2-nafion composite due to their promising characteristics such as good electrical conductivity, low background current over wide range of potentials at different pH values and its feasibility for size variations and durability. ITO electrode is inert up to -1.6 V vs SCE [13] (-1.55 V vs Ag/AgCl(3M KCl)) in 0.3 M Na_2SO_4 and -0.48 V vs RHE [14] (-1.091 V vs Ag/AgCl(3M KCl)) in 0.1 M NaAc at neutral pH 7. It should be noted that, in the acidic pH range, ITO electrode surface would be altered substantially due to segregation of indium or dissolution of tin during anodic potential sweeping [15]. The TiO_2-Nafion® composite (30 µL) was drop-cast on a plasma-treated indium tin oxide (ITO)-coated glass electrode. The modified electrode named as TiO_2-Nafion® modified ITO electrode, was then utilized for characterization and employed for further electrocatalytic CO_2 conversion.

A stable porous TiO_2-Nafion® film was observed on the ITO surface by scanning electron microscopy (SEM) as shown in Figure 1a. An X-ray diffraction (XRD) pattern of the TiO_2-Nafion® film on ITO is presented in the Supporting Information (Figure S1). The SEM image shows that the composite electrode exhibits a homogeneous porous structure.

Cyclic voltammograms of the modified electrode with TiO_2-Nafion® modified ITO were obtained in 0.1 M KNO_3 (pH 4.5) under both Ar and CO_2 atmospheres (Figure 2). Under Ar, an irreversible reduction wave is observed between −0.9 to −1.0 V vs. Ag/AgCl. The increase in the reduction current observed under CO_2 shows the occurrence of a catalytic reaction.The catalytic current observed for the TiO_2-Nafion®-modified ITO electrode suggests that TiO_2 can act as an electrocatalyst for CO_2 conversion, in addition to the known roles of TiO_2 and TiO_2-doped materials in the photocatalytic conversion of CO_2 [11]. The cyclic voltammogram of the blank ITO (Figure 2, blue) under CO_2 showed an electrochemical response at -0.8 V, which may be due to the reduction of Sn^{4+} or In^{3+} [15a].

CO_2-saturated solution containing 0.1M KNO_3 at pH 4.3, was electrolyzed under 1 atm CO_2 using the TiO_2-Nafion® modified ITO electrode at -0.98 V vs. Ag/AgCl for ~2 hours at RT, 25 °C.

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The electrolysis cell consisted of an H-type cell with two gas-tight compartments separated by a Nafion® 117 membrane (see the experimental section for full details). Since the maximum catalytic current was observed at -0.98V and this working potential has been chosen for electrolysis. The CO_2 saturation didnot cause any drastic change in the local pH of the solution, where the pH of the solution was altered from 4.5 to 4.3 after saturation of CO_2. The charge accumulation during electrolysis is shown in Figure 3. As shown in Figure 3, the TiO_2-Nafion®-modified ITO electrode affords a robust and linear charge build-up without significant loss of activity over the period.

In the presence of 0.1 M nitrate ions, the major CO_2 conversion products are found to be CO, ammonia, and urea. The formation of liquid products like formate was not found for this electrode at the potentials investigated. The Faradaic efficiency of the urea formation was ~40 %, and the Faradaic efficiencies for the formation of CO and ammonia were 27 % and 30 %, respectively. The total Faradaic efficiency was 99 %, including 2 % of an H_2 byproduct. The conversion of CO_2 by the TiO_2-Nafion modified electrode was found to occur at a rate of 1.95, 0.55 and 0.33 micromoles per hour for CO, ammonia and urea, respectively. When, TiO_2 modified electrode was subjected to electrolysis under the Ar atmosphere, the only product formed was ammonia at 0.30 micromole/h. However, the bare ITO electrode did not produce any of the above said products in the presence of CO_2. The modified electrode exhibited a current density of 0.18 and 0.02 mA/cm^2 in the presence of CO_2 and Ar atmospheres respectively. The pH of the solution after the electrolysis was checked and was found to be 5.2. The increase in pH from 4.3 to 5.2 after electrolysis did not cause any degradation in the electrode performance within the electrolysis time, as the repeated experiments with the same electrode retained almost the same efficiency and catalytic current. Already, Shchukin *et al.* reported the photocatalytic synthesis of urea at pH 5.5 (0.1 M $NaNO_3$) aqueous solution using TiO_2−PVA−PAH/PSS capsules [16]. These observations show that TiO_2 based catalysts exhibit a good stability even at pH 5.5. Also, it has been already demonstrated that the physically adsorbed TiO_2 on glass is stable up to pH 9 [17].

A blank test under CO_2 atmosphere was carried out using neat ITO plate at the same electrolysis potential as that of the modified electrode, -0.98 V vs Ag/AgCl(Figure S2). During the electrolysis, the ITO electrode turned opaque indicative of change in the In:Sn ratio by the reduction of either Sn^{4+} or In^{3+} [15]. The possible reduction product, ammonia was not found after electrolysis at the blank ITO electrode, which further evidences that the charge consumed during the electrolysis could be due to the reduction of Sn^{4+} or In^{3+}. Upon coating TiO_2-nafion composite

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on the ITO surface, the modified electrode exhibited excellent electrocatalytic properties along with remarkable stability. The ITO electrode was not found to undergo any deterioration after coating with TiO_2, which is attributed to the complete coverage of ITO with active TiO_2 particles. Control experiments showed that no CO formation occurred when CO_2 was electrocatalytically reduced with the nano TiO_2-Nafion® electrode in 0.1 M $KHCO_3$ buffer(Figure S3), and the reduction of nitrate ions in the absence of CO_2 by bulk electrolysis at -0.98 V vs. Ag/AgCl with the TiO_2-Nafion® nanocomposite electrode in 0.1 M KNO_3 produced ammonia as the sole product (Figure 2 and 3; green). These results indicate that electrons in the conduction band of TiO_2 have the capability to catalyze CO_2 and nitrate simultaneously. The corresponding Faradaic efficiencies are presented in Table 1.

The Faradaic efficiency for urea production of 40 %, achieved by the TiO_2-Nafion® modified electrode at −0.98 V vs. Ag/AgCl with an electrode surface area of 1.75 cm^2 and the other conversion products are CO, ammonia and hydrogen. In the present system produced urea with 40 % efficiency is better than the system reported by Shibata *et al*. [2b]. Gas diffusion electrodes with surface area of 12.6 cm^2 loaded with various metal catalysts were employed for the conversion CO_2 to urea, in which Zn and Cu-loaded gas diffusion electrodes [2b] are the best and the urea production was reported as, 37 % and 22 % at −1.75 V and −2.25 V vs. SHE (corresponding to −1.95 and −2.45 V vs. Ag/AgCl(3M KCl)) respectively. Along with urea, the Zn and Cu loaded gas diffusion electrodes produced CO, HCOOH, and ammonia. While comparing the performance of the TiO_2-Nafion® modified electrode in terms of potential with Zn and Cu loaded gas diffusion electrodes, TiO_2- Nafion® electrode produced urea at more positive potential, requiring an overpotential that was 1 V lower than the Zn gas diffusion electrode. The onset potential of the gas diffusion electrodes for urea formation is about -1.25 V Ag/AgCl(3M KCl) with current efficiency of around 15% whereas the Faradaic efficiency of 40 % was obtained at lower potential of -0.98 v vs Ag/AgCl(3M KCl) with our electrode. The cyclic voltammogram of TiO_2-Nafion® electrode in the presence of CO_2 reveals that the onset potential is -0.75 V and it is still possible to lower the overpotential. The Faradaic efficiency for CO by TiO_2-Nafion® electrode is 37 %. From the previous work [2], it is clear that the formation of urea is connected to the ability of formation of ammonia-like precursor by catalysts. To check the ability of the TiO_2-Nafion® modified electrode for the formation of ammonia-like precursor, the nitrate ions were reduced at -0.98 V vs. Ag/AgCl

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in the absence of CO_2 by the TiO_2-Nafion® nanocomposite electrode which produced ammonia with a Faradaic efficiency of 98 %.

Further, the electrocatalytic conversion of CO_2 to urea was carried out by following the same conditions adopted in the literature for gas diffusion electrode, i.e., in 0.2 M $KHCO_3$ containing 0.02M KNO_3 to check the performance of the modified electrode. The electrolysis was carried out using TiO_2-Nafion® modified electrode at a potential of -0.98 V vs Ag/AgCl in the presence of CO_2 for about 1 h (Figure S4). The current density and the charge consumed were similar to that of our present report (in 0.1 M KNO_3) and the conversion of CO_2 to urea was also found to be 36 %. This shows that our TiO_2 electrocatalyst exhibits reasonable activity towards the electrocatalytic conversion of CO_2 to urea at lesser potential of -0.98 V (compared to −1.95 and −2.45 V vs. Ag/AgCl of Zn and Cu gas diffusion electrodes respectively), both in the presence and absence of $KHCO_3$.

Urea formation depends on the capability of the catalysts which reduce CO_2 and nitrate simultaneously and produce CO and ammonia. Urea was formed by the in situ-generated intermediate precursors CO^- and ammonia, which were the products of the concomitant conversion of CO_2 and nitrate on the TiO_2-Nafion® electrode [2]. TiO_2 is highly active for the production of CO^- and ammonia-like precursors, and consequently, for the formation of urea. The CO^- and ammonia precursors could adsorb on the TiO_2 surface as CO and NH_2 molecules, which could then combine to form urea. A suggested pathway [2d] for urea formation on the TiO_2 surface is shown below:

One molecule of the two-electron reduction product CO can combine with two molecules of the eight-electron reduction product NH_2 to form urea as one possible product. The overall reaction requires 18 electrons and 18 protons to form urea in a high-energy consuming reaction. The nano TiO_2-Nafion® modified electrode presented in this paper can supply 18 electrons to effect the conversion of CO_2 and nitrate ions simultaneously and efficiently to obtain the urea product. This system is the first TiO_2-based electrocatalyst that shows successful electrocatalytic conversion of CO_2 to urea. We are optimizing the system to achieve maximum efficiency by varying the nitrate ion concentration, solution pH, and electrolysis potential to obtain a highly stable electrode to construct a CO_2 conversion system that shows good long-term stability. After optimising the

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conditions, a photoelectrochemical cell will be constructed with our composite electrode along with a suitable anode.

In conclusion, a combination of commercially available TiO_2 and Nafion® forms a stable film on ITO and is capable of converting CO_2 to urea with a combined reduction of nitrate in aqueous solution. This system shows a Faradaic efficiency of 40%, at lower overpotential than that observed in previous reports of similar systems.

Experimental Section

Materials. TiO_2 P-25 (anatase- 80 %, rutile 20 % with 50 m^2 g^{-1} surface area and 27 nm particle size, Degussa Corporation, Germany), Nafion® solution (5 wt.%), Nafion® 117 film (thickness 0.007 in), urease and Indium Tin Oxide (ITO) coated glass were purchased from Sigma-Aldrich and used without further purification. Potassium nitrate, potasium bicarbonate were purchased from Alfa Aesar. Deionized water (DI) water collected from Millipore Milli-Q plant were used for cyclic voltammetry and other studies.

Electrode modification. The ITO glass (0.5 × 5 cm) plates were cleaned by ultra-sonication for 30 min with 10% mucasol solution in deionized water, and treated with oxygen plasma for 10 min. A plasma cleaner module (Harrick Plasma Corporation PDC-32G) was used for the plasma cleaning of ITO. P-25 TiO_2 powder (2 mg) was dispersed in water (200 µL) and mixed with 80 µL of a 5 % v/v Nafion® solution and finally 120 µL water to make up the net volume 400 µL. The amount of TiO_2 present in the composite is 0.5 wt %. 30 µL of the TiO_2-Nafion® nanocomposite solution was drop-cast on ITO over 0.5 x 3.5 cm area (the apparent working area of the composite modified electrode was 1.75 cm^2), and the solvent was evaporated at RT. The final amount of TiO_2 on the electrode surface will be 0.15 mg (0.0375 wt %). This uniformly coated ITO electrodes were characterized and used for electrochemical experiments.

Characterization. The surface morphology of the as-prepared film on the ITO electrode was measured by field-emission SEM (JEOL LTD. JSM 890). X-ray diffraction (XRD) pattern for the TiO_2-Nafion$^@$ electrode was performed on a BRUCKER D8 Advance diffractometer, with monochromatic Cu Kα radiation (λ = 1.5418 Å) source.

Cyclic voltammetry and bulk electrolysis. Cyclic voltammetry measurements and bulk electrolysis experiments were carried out with a CHI 900 electrochemical analyzer (CH Instruments) in a three-electrode system comprising a modified ITO electrode as a working

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electrode, an Ag/AgCl (3 M KCl) reference electrode, and a coiled platimun wire auxiliary electrode. Ag/AgCl(3M KCl) was calibrated using potassium ferrocyanide and the half-wave potential of Ag/AgCl, $E°_{Ag/AgCl} = 0.197$ V vs NHE. All redox potentials were measured versus an Ag/AgCl electrode.

For bulk electrolysis, the TiO_2-nafion@ composite electrode was used in a custom-made gas-tight H-type cell (SI figure S5), in which coiled platinum wire electrode was placed in one compartment and connected through the Nafion$^{@}$ film to the working electrode compartment. The working electrode compartment contained 7.0 mL of 0.1 M KNO_3 (pH 4.5) with 7 mL of gas space. The electrolyte solution in the cathode compartment was purged with high purity CO_2 gas for 20 mins before the electrolysis. The oxygen produced at anode compartment was quenched by adding potassium ferrocyanide. The solubility of CO_2 in water is 36 mM / 1 atm at 25 °C.[18] Potassium ferrocyanide was added in the anode compartment in order to quench the oxygen. The electrolysis was perfomed at room temperature and ambient pressure. Nafion® 117 film was pretreated to remove organic impurities by reported procedure [19]. First, the membrane was boiled in H_2O_2 (3%, v/v) for 1 h and then boiled in deionized water for 1 h. Again, the membrane was boiled in 0.5 M H_2SO_4 for 1 h and finally once again boiled in deionized water for 1 h. The pretreated membrane was stored in deionized water.

Product analysis. Gas sampling was done through a rubber septum on the gas sampling port, and the interior pressure was adjusted by injecting CO_2 gas equivalent to the withdrawn sample volume before sampling. The effect of dilution on the gaseous products was included in calculations of the amount of the products. The gaseous products were quantified by chromatographic techniques, and the Faradaic efficiency was calculated by a method similar to those previously reported [7,8]. Carbon monooxide and hydrogen were analyzed by gas chromatography (HP 5890 SeriesII) using Porapak R80/100 packed column(Altech) with thermal conductivity detector. The operating conditions were: injection volume, 100 microlitre; oven temperature, 35 °C; carrier gas, nitrogen with flow rate of 10 mL/min. Ammonia produced was estimated by the indophenol method [20] using a spectrophotometer (Agilent 8453). The amount of urea produced was measured using the above method for ammonia after decomposition of the urea by urease into $CO_2 + 2NH_3$ (M_{urease}). The number of moles of urea produced (M_{urea}) was equal to ($M_{urease} - M_{ammonia}$)/2.

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Faradaic efficiency. The Faradaic efficiency of the TiO_2-Nafion$^@$ electrode was calculated in a custom made gas-tight H-type cell in 0.1 M KNO_3 (pH 4.5) at an applied potential of -0.98 V. The amount of products produced during constant potential bulk electrolysis for about 2 h, was in accordance with charge consumption, assuming that almost all of the current was used for the simultaneous conversion of CO_2 and nitrate. The bare ITO electrode did not produce any product at -0.98 V in 0.1 M KNO_3 (pH 4.5).

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Figure Captions

Figure 1. SEM image of the TiO_2-Nafion® modified ITO.

Figure 2. Cyclic voltammograms of a TiO_2-Nafion® modified ITO electrode (0.5 × 3.5 cm) in 0.1M KNO_3 (pH 4.5) under Ar (green),1 atm CO_2 (purple) and blank ITO plate under 1 atm CO_2 (blue) at scan rate of 50 mV s^{-1}.

Figure 3. Electrolysis of 0.1 M KNO_3 solution (pH 4.5) at -0.98 V vs. Ag/AgCl in the presence of 1 atm CO_2-saturated (purple) and absence of CO_2 (green), at RT with TiO_2-Nafion® modified ITO electrode; (a) plot of time *vs* current density and (b) plot of time *vs* charge density.

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Fig.1.

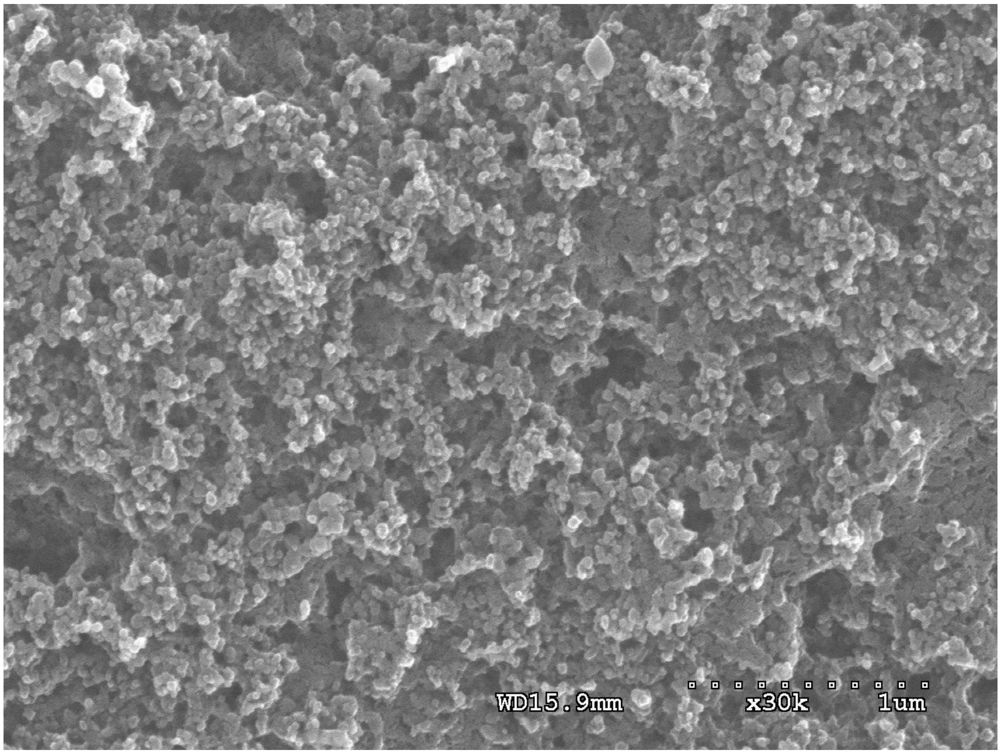

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Fig.2.

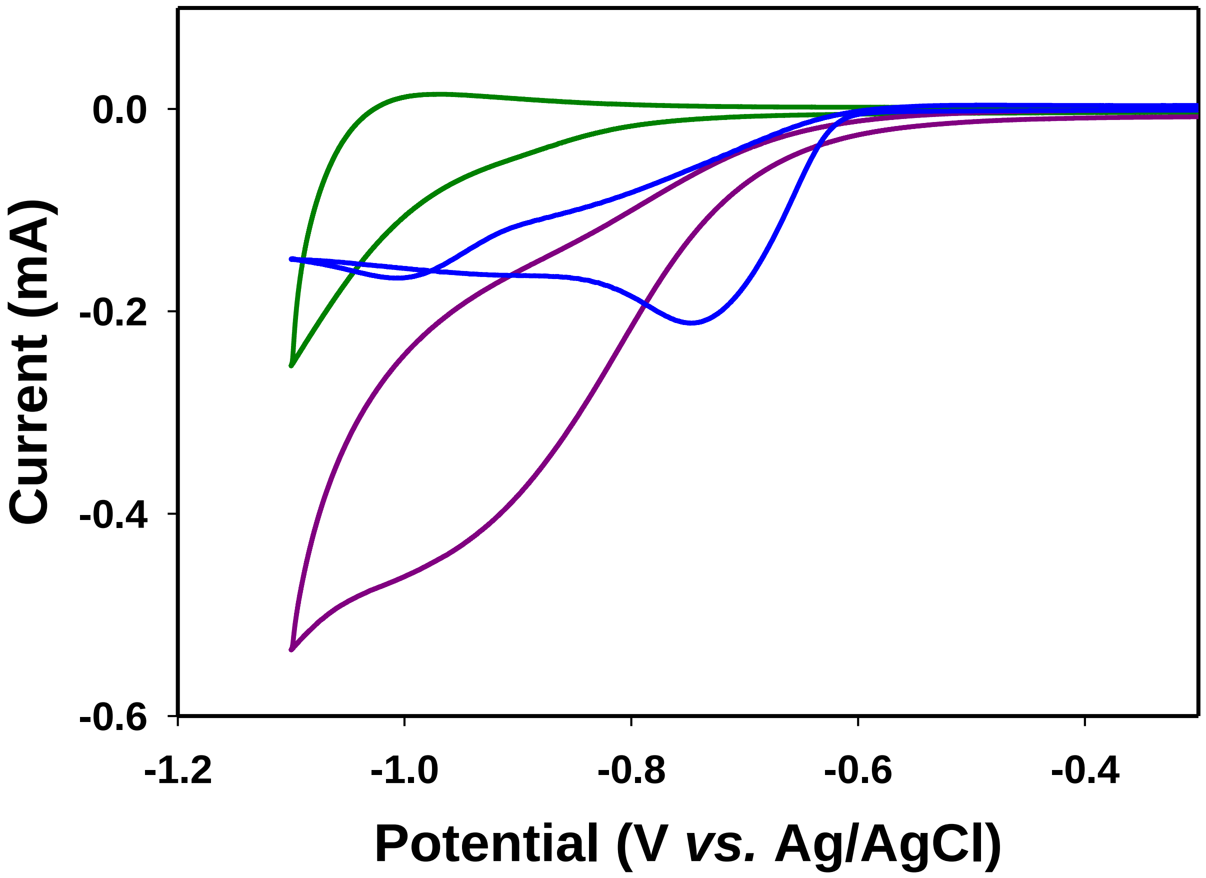

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Fig.3a & 3b.

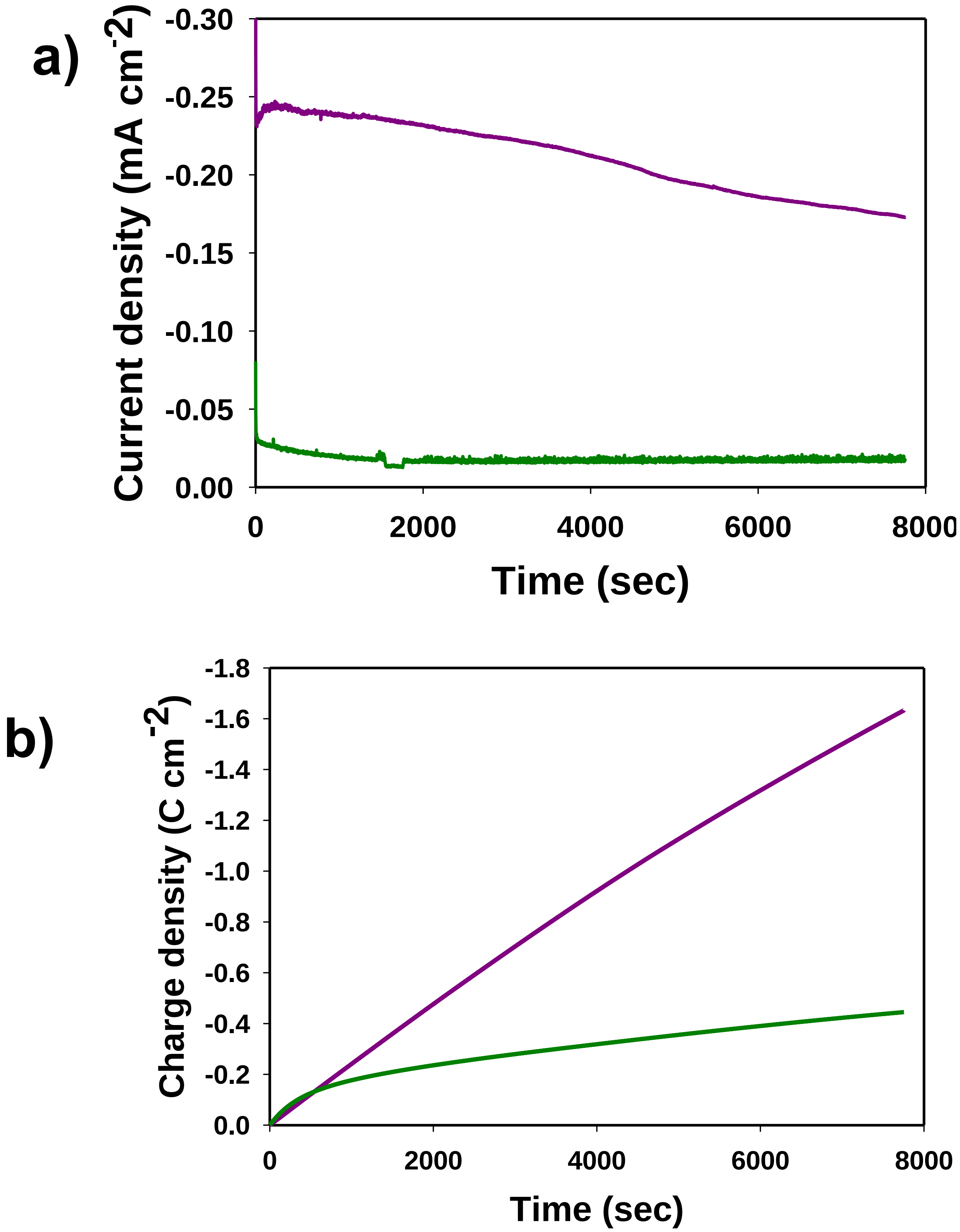

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Table

Table 1. Faradaic efficiencies (%)/concentrations(micromoles)/h of the conversion products[a]

Gas atmosphere	Urea	CO	NH_4^+	H_2
Ar	-	-	98/0.30	-
CO_2	40/0.33	27/1.95	30/0.55	2
Bare ITO	-	-	-	-

[a] Reaction conditions: Electrolyte : 0.1 M KNO_3, pH = 4.5 (under argon) and 4.3 (under CO_2 saturation), pressure = 1 atmosphere, temperature = RT (25 °C), electrolysis potential = -0.98V vs Ag/AgCl(3M KCl) and time = 2.15 h, current density = 0.18 mA/cm^2 under CO_2.

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Mechanism

$$CO_2 + 2e^- + 2H^+ \longrightarrow CO(\text{precursor}) + H_2O \qquad (1)$$

$$NO_3^- + 8e^- + 8H^+ \longrightarrow NH_2\ (\text{precursor}) + 3H_2O \qquad (2)$$

$$CO(\text{precursor}) + 2NH_2(\text{precursor}) \longrightarrow NH_2CONH_2 \qquad (3)$$

Net reaction:

$$CO_2 + 2NO_3^- + 18e^- + 18H^+ \longrightarrow NH_2CONH_2 + 7H_2O \qquad (4)$$

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