Notice

DESCRIPTION CN121737756A

Pulse electrodeposition of single-atom alloy catalysts and their application in air-to-fertilizer production

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[0001]

Technical Field

[n0001]

This invention relates to the field of electrochemical catalysis and environmental functional materials, specifically to pulse electrodeposition single-atom alloy catalysts and their application in air-to-fertilizer production.

[0003]

Background Technology

[n0002]

Nitrate contamination of groundwater is a widespread environmental problem that poses a significant threat to public health and ecosystems.

With the increase in agricultural runoff and waste discharge, nitrate pollution is becoming increasingly serious, endangering drinking water safety and damaging aquatic ecosystems, thus requiring effective remediation strategies.

The World Health Organization (WHO) and the U.S. Environmental Protection Agency (EPA) have set the maximum permissible concentrations of nitrates in drinking water at 50 mg L_NER1 (calculated as NO₃_NER3) and 10 mg L_NER4 (calculated as NO₃⁻-N), respectively.

Nitrate intake exceeding this limit was significantly associated with an increased risk of methemoglobinemia and gastrointestinal cancers in infants: for every 10 mg increase in nitrate concentration in drinking water (calculated as NONER8NER9), the risk of gastric cancer increased by 1.9 times (95% confidence interval: 1.09-3.33). These findings indicate that the continuous accumulation of nitrates in groundwater places long-term pressure on drinking water safety and aquatic ecosystems. Unlike traditional removal-oriented treatment methods, electrochemical nitrate reduction to ammonia (NO₃⁻RR) can achieve simultaneous pollutant reduction and nitrogen recovery in a single reactor and can be driven by renewable electricity. Within this framework, nonthermal plasma ionizes and activates air at room temperature, generating soluble nitrogen-oxygen anions (mainly nitrates) at the gas-liquid interface. These anions are then converted into ammonia via NO₃⁻RR, thus constructing an integrated "air-nitrate-ammonia" pathway. This strategy combines controllable external feedstock supply with mild operating conditions, demonstrating great potential in coupling environmental remediation and nitrogen resource recovery. Its process can be adapted to distributed and intermittent energy scenarios and provides a beneficial complement to the Haber-Bosch process in terms of energy consumption and carbon emissions.

[n0003]

Among the explored material systems, copper-based catalysts have attracted widespread attention due to their superior electronic structure and efficient mediating ability in multi-electron and multi-proton transfer processes.

However, its catalytic performance is limited by the dynamic balance of surface active hydrogen (*H). When the supply of *H is insufficient, the stepwise hydrogenation process of the *NO_x intermediate is hindered, leading to the accumulation of nitrite and the gradual deactivation of active sites. Conversely, when *H is in excess, it promotes the competitive reaction - the hydrogen evolution reaction (HER), which consumes electrons and protons, thereby reducing the activity and selectivity of NO₃⁻RR. To alleviate the above limitations, researchers have attempted to partially improve the availability of *H and regulate its release behavior at the catalytic interface by introducing a second metal to form an alloy or by introducing a hydrophilic phase. However, how the formation, spatial distribution, and lifetime of *H specifically affect the kinetics of the *NO_x hydrogenation reaction remains not fully elucidated. Although techniques such as in-situ spectroscopy and spin resonance have provided experimental evidence for the existence of *H, their results have rarely established quantitative correlations with kinetic or energetic descriptors. Such mechanistic uncertainties hinder the establishment of reliable design principles that organically link catalyst composition, electronic structure, and product selectivity, and also limit the universality of such principles in alloy catalyst systems. In addition, existing fertilizer production technologies mostly rely on the energy-intensive Haber-Bosch process, which generates large carbon emissions. There is an urgent need to develop new fertilizer production technologies that are low-energy and sustainable.

[0006]

Summary of the Invention

[n0004]

To alleviate or partially alleviate the above-mentioned technical problems, the solution of the present invention is as follows:

[n0005]

A pulse electrodeposition single-atom alloy catalyst, wherein the catalyst is an M-Cu single-atom alloy, wherein M is one of Ni, Co, Fe or Mn, and M exists in a dispersed form in the Cu lattice;

[n0006]

The catalyst is prepared using a three-electrode pulse electrodeposition method, comprising: using a copper sheet as the working electrode, a platinum foil as the counter electrode, and Ag /AgCl as the reference electrode; the electrolyte is a mixed electrolyte containing H₂SO₄ and Ni, Co, Fe or Mn metal sulfates, wherein Ni, Co, Fe or Mn metal sulfates are added respectively during the preparation of NiCu, CoCu, FeCu or MnCu alloys;

the molar ratio of Cu to M is controlled by adjusting the anode/cathode pulse time ratio ta/tc, wherein the value of ta/tc ranges from 1/10 to 10/10 s.

[n0007]

Preferably, ta/tc = 2/10s, the surface atomic percentage of Cu in the single-atom alloy is 77%, the surface atomic percentage of M is 23%, the metal atoms are in a single-atom dispersed state, and the coordination number is about 4.

[n0008]

Preferably, M is Ni.

[n0009]

Preferably, the deposition potential is 1.5V vs. anodic: 1.5V.

Ag/AgCl, cathode: -1.7V vs.

Ag/AgCl.

[n0010]

Preferably, the electrolyte is a mixed electrolyte containing 50 mM H₂SO₄ and 50 mM Ni, Co, Fe or Mn metal sulfates.

[n0011]

This solution also provides an application of the pulse electrodeposition single-atom alloy catalyst as described above, the catalyst being used in the electrochemical nitrate reduction to ammonia reaction.

[n0012]

Preferably, the catalyst is used in the electrochemical nitrate reduction to ammonia reaction to construct an integrated "air-nitrate-ammonia" air fertilizer system.

[n0013]

Preferably, the conditions for the electrochemical nitrate reduction to ammonia reaction are as follows: using an H-type electrochemical cell, with a Nafion 115 membrane as the separator, an electrolyte of 0.1M KOH + 0.1M KNO, and an operating potential range of 0 to -1.2 V vs.

RHE.

[n0014]

Further preferably, the operating potential is -0.6V vs.

RHE.

[n0015]

Preferably, the air-to-fertilizer system includes a non-thermal plasma air activation module, an electrochemical reduction module, and a CO₂capture module, and the module operates as follows:

[n0016]

Non-thermal plasma air activation module: Non-thermal plasma ionizes and activates air at room temperature and pressure, generating soluble nitrates at the gas-liquid interface;

[n0017]

Electrochemical reduction module: Nitrate enters the electrochemical reduction module and is electro-reduced to ammonia under the action of the single-atom alloy catalyst;

[n0018]

CO₂Capture Module: CO₂ is introduced into the ammonia-containing electrolyte to generate a mixed fertilizer of NH₄HCO₃ and KHCO₃.

[n0019]

The technical solution of this invention has the following beneficial technical effects:

[n0020]

Atomically dispersed alloys with tunable electronic structures were prepared by pulse electrodeposition. Under optimized conditions, NiCu achieved a Faraday efficiency of approximately 95% and a yield of 11.4 mg h⁻¹cm⁻².

[n0021]

When the catalyst catalyzes the NO₃-RR reaction in the air-to-fertilizer system, the ammonia faradaic efficiency is ⩾85%, with the NiCu catalyst exhibiting the highest ammonia faradaic efficiency of 95.4±2.8% and an ammonia yield of 11.4±0.7 mg h^{1} cm^{2}.

[n0022]

The catalyst was in 1.0 M KOH solution at -0.8 V vs.

The reactor operated stably for 30 hours under RHE and a flow rate of 0.25 mL min⁻¹.

[0026]

Attached Figure Description

[n0023]

Figure 1 shows the SEM images of NiCu, CoCu, FeCu, MnCu, and Cu;

[n0024]

Figure 2 shows the HR-TEM images of NiCu, CoCu, FeCu, MnCu, and Cu;

[n0025]

Figure 3 shows the EDS elemental mapping image of NiCu and the XRD pattern of M-Cu SAAs;

[n0026]

Figure 4 shows the AC-HAADF-STEM images highlighting the uniform contrast of the alloy and the AC-HAADF-STEM images with corresponding pixel intensity profiles.

[n0027]

Figure 5 shows the XPS spectra of Cu 2p and Ni 2p for the NiCu catalyst;

[n0028]

Figure 6 shows the normalized XANES spectra and Fourier transform k³weighted EXAFS spectra of Cu K-edge and Ni K-edge;

[n0029]

Figure 7 shows the structure of the NiCu catalyst and the Ni K-edge EXAFS spectrum fitting curves of the NiCu catalyst in k(b) and R(c, d) spaces;

[n0030]

Figure 8 shows the UV-Vis absorption spectrum and calibration curve for the determination of NH₃;

[n0031]

Figure 9 shows the NO₃⁻RR performance of the pulse electrodeposition M-Cu catalyst;

[n0032]

Figure 10 shows the ammonia Faraday efficiency of M-Cu SAAs;

[n0033]

Figure 11 shows the ammonia yield of M-Cu SAAs;

[n0034]

Figure 12 shows the long-term stability test results.

[0039]

Detailed Implementation

[n0035]

To make the objectives, technical solutions, and advantages of the present invention clearer, the technical solutions of the present invention will be clearly and completely described below with reference to the accompanying drawings. Obviously, the described embodiments are some embodiments of the present invention, but not all embodiments.

Based on the embodiments of the present invention, all other embodiments obtained by those skilled in the art without creative effort are within the scope of protection of the present invention.

[n0036]

Example 1

[n0037]

(1) Electrode pretreatment: The copper sheet was ultrasonically cleaned with 1M HCl for 10 min and ultrasonically cleaned with ultrapure water for 15 min in sequence, and then dried with nitrogen for later use; (2) Electrolyte preparation: When preparing NiCu alloy catalyst, a mixed electrolyte containing 50mM H₂SO₄ and 50mM NiSO₄ was prepared; (3) Pulse electrodeposition: A three-electrode system was adopted, with the copper sheet as the working electrode, the platinum foil as the counter electrode, and Ag/AgCl (3 M KCl) as the reference electrode, and the anode potential was 1.5V vs.

Ag/AgCl, cathode potential -1.7V vs.

Ag/AgCl, adjust ta/tc to 2/10s, and deposit at room temperature to obtain NiCu single-atom alloy catalyst; (4) Post-treatment: the deposited electrode is rinsed with ultrapure water 3 times, dried with nitrogen, and ready for use.

[n0038]

Example 2

[n0039]

(1) Electrode pretreatment: The copper sheet was ultrasonically cleaned with 1M HCl for 10 min and ultrasonically cleaned with ultrapure water for 15 min in sequence, and then dried with nitrogen for later use; (2) Electrolyte preparation: When preparing the CoCu alloy catalyst, a mixed electrolyte containing 50mM H₂SO₄ and 50mM CoSO₄ was prepared; (3) Pulse electrodeposition: A three-electrode system was adopted, with the copper sheet as the working electrode, the platinum foil as the counter

electrode, and Ag/AgCl (3 M KCl) as the reference electrode, and the anode potential was 1.5V vs.

Ag/AgCl, cathode potential -1.7V vs.

Ag/AgCl, adjust ta/tc to 2/10s, and deposit at room temperature to obtain CoCu single-atom alloy catalyst; (4) Post-treatment: the deposited electrode is rinsed with ultrapure water 3 times, dried with nitrogen, and ready for use.

[n0040]

Example 3

[n0041]

(1) Electrode pretreatment: The copper sheet was ultrasonically cleaned with 1M HCl for 10 min and ultrasonically cleaned with ultrapure water for 15 min in sequence, and then dried with nitrogen for later use; (2) Electrolyte preparation: When preparing FeCu alloy catalyst, a mixed electrolyte containing 50mM H₂SO₄ and 50mMM FeSO₄ was prepared; (3) Pulse electrodeposition: A three-electrode system was adopted, with the copper sheet as the working electrode, the platinum foil as the counter electrode, and Ag/AgCl (3 M KCl) as the reference electrode, and the anode potential was 1.5V vs.

Ag/AgCl, cathode potential -1.7V vs.

Ag/AgCl, adjust ta/tc to 2/10s, and deposit at room temperature to obtain FeCu single-atom alloy catalyst; (4) Post-treatment: the deposited electrode is rinsed with ultrapure water 3 times, dried with nitrogen, and ready for use.

[n0042]

Example 4

[n0043]

(1) Electrode pretreatment: The copper sheet was ultrasonically cleaned with 1M HCl for 10 min and ultrasonically cleaned with ultrapure water for 15 min in sequence, and then dried with nitrogen for later use; (2) Electrolyte preparation: When preparing the MnCu alloy

catalyst, a mixed electrolyte containing 50mM H₂SO₄ and 50mM MnSO₄ was prepared; (3) Pulse electrodeposition: A three-electrode system was adopted, with the copper sheet as the working electrode, the platinum foil as the counter electrode, and Ag/AgCl (3 M KCl) as the reference electrode, and the anode potential was 1.5V vs.

Ag/AgCl, cathode potential -1.7V vs.

Ag/AgCl, adjust ta/tc to 2/10s, and deposit at room temperature to obtain MnCu single-atom alloy catalyst; (4) Post-treatment: the deposited electrode is rinsed with ultrapure water 3 times, dried with nitrogen, and ready for use.

[n0044]

Example 5

[n0045]

The anodic deposition time mainly determines the amount of Cu²⁺ generated, thereby adjusting the Cu/M ratio in the cathode co-deposition process; parallel experiments were conducted by adjusting the anodic/cathode pulse time ratio (ta/tc) in Examples 1-4 to 1 /10 s, 5/10 s, 5/5 s, and 10/10 s.

[n0046]

Comparative Example 1

[n0047]

Single metal Ni, Co, Fe and Mn catalysts were deposited on graphite using their respective sulfates, while Cu catalysts were used as clean, untreated copper foil.

[n0048]

Example 6

[n0049]

The nitrate reduction activity of the prepared catalyst was tested in a sealed H-type electrochemical cell using a CHI 660E electrochemical workstation (CH Instruments, China) with a Nafion 115 membrane as the separator. Before all tests, a 3.5 cm × 3.5 cm Nafion 115 membrane was immersed in a 5 wt% hydrogen peroxide solution at 80 °C for 1 hour, and then immersed in ultrapure water at 80 °C for 1 hour.

A three-electrode electrochemical testing system was adopted, with a copper sheet (1×0.5cm²) loaded with catalyst directly used as the working electrode, and a saturated calomel electrode (SCE) and a graphite rod used as the reference electrode and counter electrode, respectively.

Before electrochemical measurements, pure argon gas was injected into 30 mL of electrolyte (0.1 M KOH + 0.1 M KNO3) for 30 minutes to remove oxygen from the solution.

At a given potential (0 to -1.2 V vs.

RHE (Optimal operating potential: -0.6 V vs. RHE)

The current-time (I-t) curves of NH4NER52- were recorded by chronoamperometry for 30 minutes of electrolysis at different constant potentials. The electrolyte after electrolysis was collected, and the amount of ammonia produced was quantitatively analyzed by indophenol blue method and ^{1}H NMR method. The yield and Faraday efficiency of NH4NER52- were calculated.

[n0050]

Example 7

[n0051]

Construction and application of an air-to-fertilizer system: This system integrates non-thermal plasma air activation, electrochemical reduction, and CO₂ capture modules. Air is activated by plasma to generate nitrates, which are then electro-reduced to ammonia under the action of a prepared single-atom alloy catalyst. Ammonia is then reacted with CO₂ to generate a mixed fertilizer, achieving a continuous conversion of "air - nitrate - ammonia - fertilizer". The module's working process is as follows:

[n0052]

Non-thermal plasma air activation module: Non-thermal plasma ionizes and activates air at room temperature and pressure, generating soluble nitrates at the gas-liquid interface;

[n0053]

Electrochemical reduction module: Nitrate enters the electrochemical reduction module and is electroreduced to ammonia under the action of the single-atom alloy catalyst. The reaction temperature is room temperature, the electrolyte is a 1.0 M KOH solution, the electrolyte flow rate is 0.25 mL min⁻¹, and the potential is -0.8 V vs.

RHE;

[n0054]

CO₂Capture Module: CO₂ is introduced into the ammonia-containing electrolyte to generate a mixed fertilizer of NH₄HCO₃ and KHCO₃. The flow rate of CO₂ is 5 sccm.

[n0055]

Figure 1 shows the SEM morphology and structure of M-Cu SAAs synthesized with Ni, Co, Fe and Mn under controlled pulse conditions. Uniform dendritic support was generated within the same parameter window. Figures 1(a)-(i) show the SEM images of NiCu-1/10 s; NiCu-2/10 s; NiCu-5/10 s; NiCu-5/5 s; NiCu-10/10 s; CoCu-2/10 s; FeCu-2/10 s; MnCu-2/10 s; and Cu-2/10 s, respectively. For NiCu, as shown in Figure 2, high-resolution TEM (HR-TEM) images show ordered lattice fringes corresponding to Cu(200), with an interplanar spacing of approximately 0.18 nm. The dendritic morphology and particle size distribution were consistent in the repeated samples. Figures 2(a)-(e) show the SEM images of NiCu-2/10 s, CoCu-2/10 s, and FeCu-2/10 s, respectively. TEM images of s, MnCu-2/10 s, and Cu-2/10 s, respectively. (f)-(j) in Figure 2 are HR-TEM images of NiCu-2/10 s, CoCu-2/10 s, FeCu-2/10 s, MnCu-2/10 s, and Cu-2/10 s, respectively.

[n0056]

The energy dispersive X-ray spectroscopy (EDS) mapping in Figure 3a confirms the uniform spatial distribution of Cu and Ni, with no clustering detected.

The X-ray diffraction (XRD) of Figure 3b did not show obvious Ni diffraction peaks, indicating that Ni is highly dispersed.

[n0057]

NiCu was further observed using a high-angle annular dark-field scanning transmission electron microscope.

As shown in Figure 4a, at the atomic scale, aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) images reveal a continuous copper lattice.

As shown in Figure 4b, based on the approximate correlation between the high atomic number enhanced dark field (HAADF) intensity and the atomic number, as well as the linear profile statistics, isolated scattering centers different from copper pillars were identified. These correspond to nickel atoms and are consistent with subsequent nickel K-edge coordination data, confirming that nickel exists in the copper lattice in an atomically dispersed form.

This evidence is consistent with the “anodic refresh-cathode reduction” mechanism of pulsed electrodeposition, which prevents cluster growth and thus ensures structural stability and atomic dispersion.

These combined characteristics provide a material basis for controlling surface hydrogenation kinetics.

[n0058]

Figure 5 shows the determination of surface chemical state and local coordination environment using XPS and X-ray absorption fine structure analysis (XAFS).

The 2p spectrum of Cu in Figure 5a shows peaks at approximately 932.8 and 952.5 eV, which are characteristic peaks of Cu⁰/Cu⁺, without obvious satellite features.

The 2p spectrum of Ni in Figure 5b shows a nickel (II) signal, which is attributed to surface oxidation that occurs during air exposure.

Figure 6 shows the Cu and Ni absorption edge position analysis in X-ray absorption near-edge structure (XANES)/extended X-ray absorption fine structure (EXAFS) analysis.

The K-side spectra of Cu indicate that it is mainly in the metallic state, and the R-space feature corresponds to Cu-Cu coordination at about 2.20 cm, with no Cu-O signal at 1.50 cm (Figure 6a and Figure 6b); as shown in Figure 6c, at the K-side of Ni, the metallic Ni foil shows a Ni-Ni feature at 2.18 cm, while NiO shows Ni-O and Ni-Ni signals at 1.68 and 2.58 cm, respectively.

In contrast, NiCu exhibits a dominant characteristic peak at approximately 2.15 cm, with no Ni-O or Ni-Ni signal, which is consistent with the coordination of the first layer of Ni-Cu (Figure 6c and Figure 6d).

The coordination and k-space residual diagrams of a-d in Figure 7 show that each nickel atom is coordinated by approximately four copper atoms (coordination number of approximately 4), a typical feature of single-atom alloys.

Importantly, although the Ni 2p spectrum showed some surface oxidation, the overall environment remained metallic, indicating that brief air exposure during sample processing led to the formation of a thin oxide layer on the single-atom alloy substrate.

[n0059]

Under 0.1 M KOH conditions containing 0.1 M KNO_NER64, we tested alloys synthesized under different pulse electrodeposition sequences, where t_a/t_c is the ratio of anodic to cathode pulse duration.

To calculate the FE and YR of ammonia produced during the NO₃⁻RR process, the specific concentration of ammonia in the electrolyte after electrolysis must first be determined using the indophenol blue colorimetric method.

As shown in Figure 8a, we prepared a series of ammonium sulfate solutions of different concentrations as standard solutions (concentrations of 0.0, 0.2, 0.5, 1.0, 2.0 and 3.0 μg mL⁻¹), and measured their UV absorption intensity curves in the wavelength range of 500 to 800 nm. We selected the absorbance at the peak and linearly fitted it to obtain the concentration-absorbance standard curve (Figure 8b).

[n0060]

Figure 9 shows the FE and YR thermal maps of NiCu, CoCu, FeCu, MnCu and pure Cu substrates at multiple potentials.

Figures 10 and 11 show the standard error plots of FE and YR obtained from three repeated experiments corresponding to this heatmap.

Under these test conditions, significant differences emerged between the different alloy catalysts.

NiCu and CoCu consistently exhibit higher Fermi levels and specific electrochemical reactivity than copper. Over a wide potential range and at t_a/t_c ratios, they form a continuous high FE region centered at a potential of -0.6 V (relative to the standard hydrogen electrode), while FeCu and MnCu do not show significant enhancement and in some cases even perform worse than Cu.

This activity sequence is consistent with the predictions of the Ψ (d-band) descriptor and is supported by evidence of single-atom dispersion and Ni-Cu coordination structure.

At an intermediate pulse ratio (t_a/t_c = 2/10 s) and -0.6 V, Cu had a FE of 68.4 ± 2.3%, YR was 10.4 ± 0.6 mg h⁻¹cm⁻², while NiCu reached 95.4 ± 2.8% and 11.4 ± 0.7 mg h⁻¹cm⁻², and CoCu reached 85.4 ± 3.0% and 9.7 ± 0.2 mg h⁻¹cm⁻² (Figure 9a-e).

These results indicate that the intermediate pulse ratio optimizes the supply balance of Cu and Ni and maintains a uniform atomic dispersion, thereby sustaining a high FE band near -0.6 V. However, excessively short or long anodic pulses disrupt this balance and reduce FE and YR.

[n0061]

The constructed continuous reaction platform, which integrates nonthermal plasma, flow electrolysis, and CO₂ trapping, enables the direct demonstration of catalytic performance on a macroscopic scale.

In this device, plasma activates air at room temperature and pressure to generate soluble nitrogen oxides. These nitrogen oxides are recycled into the catholyte and electrochemically reduced to ammonia on a single-atom alloy electrode.

Meanwhile, the CO₂ introduced upstream is captured by the generated ammonia to form ammonium carbonate and ammonium bicarbonate; any excess CO₂ reacts with KOH in the electrolyte to generate potassium carbonate and potassium bicarbonate, thereby preparing a mixed nitrogen and potassium fertilizer.

As shown in Figure 12, in a 1.0 M KOH solution, at -0.8 V vs.

Under RHE and a flow rate of 0.25 mL min_NER83, the reactor operated stably for 30 hours.

The current density remained at approximately -0.35 A, reflecting the dynamic balance between plasma-driven nitrate generation and cathode consumption.

The average ammonia yield and CO₂ absorption rate were approximately 0.53 mmol h⁻¹ and 20 mmol h⁻¹, respectively, confirming that continuous and coupled nitrogen-carbon conversion was achieved in this simple, robust, and renewable energy-compatible flow device.

[n0062]

In summary, this scheme prepares atomically dispersed alloys with tunable electronic structures through pulsed electrodeposition. Under optimized conditions, NiCu achieves a Faraday efficiency of approximately 95% and a yield of 11.4 mg h⁻¹cm⁻². The integrated plasma-electrocatalysis-capture continuous process can continuously convert air and water into nitrogen-potassium mixed fertilizer.

These results provide a mechanistic and scalable basis for guiding surface hydrogenation in nitrogen cycle electrocatalysis and sustainable fertilizer production.

[n0063]

To better illustrate the present invention, numerous specific details are provided in the above-described embodiments.

Those skilled in the art will understand that the present invention can be practiced even without certain specific details.

In some instances, methods, means, components, and circuits well known to those skilled in the art have not been described in detail in order to highlight the spirit of the invention.

[n0064]

The above description is merely a specific embodiment of the present invention, but the scope of protection of the present invention is not limited thereto. Any changes or substitutions that can be easily conceived by those skilled in the art within the scope of the technology disclosed in the present invention should be included within the scope of protection of the present invention.

Therefore, the scope of protection of this invention should be determined by the scope of the claims.
