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(54) FUNCTIONALIZED SILVER-COPPER CATALYSTS FOR ELECTROCHEMICAL CONVERSION OF CO2 TO SMALL MOLECULES

(57) The present invention belongs to the field of catalytic chemistry, and more specifically to catalysed reduction chemical reactions, preferably of CO_2 into small molecules.

The present invention relates to a new catalyst compound comprising a silver (Ag) layer and a copper (Cu) layer, wherein the copper layer is functionalized with at least one group of formula I: -S-R (Formula I), wherein R is an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S and its use thereof in a reduction chemical reaction, preferably in reduction of CO_2 into CO or other small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid). The invention also relates to the process of manufacture of said catalyst compound and to a process electrochemical conversion of CO_2 to small molecules.

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Description

Technical field

[0001] The present invention belongs to the field of catalytic chemistry, and more specifically to catalysed reduction chemical reactions, preferably of CO_2 into small molecules.

[0002] The present invention relates to a new catalyst compound comprising a silver (Ag) layer and a copper (Cu) layer, wherein the copper layer is functionalized with at least one group of formula I: -S-R (Formula I), wherein R is an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S and its use thereof in a reduction chemical reaction, preferably in reduction of CO_2 into CO or other small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid). The invention also relates to the process of manufacture of said catalyst compound and to a process electrochemical conversion of CO_2 to small molecules.

[0003] In the description below, references between **[]** refer to the list of references at the end of the examples.

Technical background

[0004] The release of carbon dioxide (CO_2) is a major concern for the environment. Its capture and recycling into small organic bricks such as carbon monoxide (CO), formic acid, methane or methanol could prove to be very advantageous.

[0005] Particularly, the conversion of CO_2 into small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid) is an attractive method as these molecules can be used as fuels or organic bricks for the production of longer hydrocarbon molecules **[1-3]**. Currently only copper-based catalysts (Cu) can convert CO_2 in small organic molecules but their efficiency is still limited - preventing its use in industrial process **[4,5].**

[0006] Therefore, there is a critical necessity to explore for an easier and cheaper way to produce small molecules such as gaseous hydrocarbons (methane, ethylene) or liquid molecules (ethanol, formic acid) from CO_2 in a cheap and environmental friendly procedure.

Detailed description of the invention

[0007] Applicant has developed a new catalyst compound that solves all of the problems listed above.

[0008] The present invention deals with a new catalyst compound, its manufacture process and its applications, such as a method to convert CO_2 into small molecules at room temperature and atmospheric pressure. Being able to produce such small molecules at room temperature and atmospheric pressure in large quantities is, to the knowledge of Applicant, something that was not observed in the art.

[0009] Applicant surprisingly found out that using a functionalized AgCu catalyst according to the invention gives very good yields in conversion of CO_2 into small molecules. Specifically, it was identified that the performance is considerably improved by grafting specific functional groups on the surface of inorganic electro-catalysts. The functional groups allow increasing the current density and improving the selectivity of the reaction towards the production of C2 molecules (mainly ethylene and ethanol) up to > 60 % at -1.2 V versus RHE.

[0010] The catalyst compound of the invention is based on copper (Cu) and silver (Ag) crystals grown on a conducting support (typically a commercial carbon support such as a gas diffusion electrode) via electrodeposition and then functionalized with various organic molecules. The catalyst compound of the invention may present a fern-like dendritic morphology.

[0011] A first object of the invention is a catalyst compound comprising a silver (Ag) layer and a copper (Cu) layer, wherein the copper layer is functionalized with at least one group of formula I:

-S-R Formula I,

wherein R is an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S. Preferably, 2 or 3 members of the ring are heteroatoms.

[0012] In particular, some advantages of the catalyst compound according to the invention are listed below:

- the catalyst compound according to the invention have increased current density and improved selectivity of the reaction towards the production of C_2 molecules (mainly ethylene and ethanol) up to -70 $mA.cm^{-2}$ and > 60 % at -1.2 V compared to -32 $mA.cm^{-2}$ and ~15 % for pristine non-functionalized Cu-based electrocatalyst when measured in a 3-electrode configuration;
- the catalyst compound according to the invention can be easily obtained by electrodepositing Cu and Ag metals in the form of a porous structure for larger active surface;

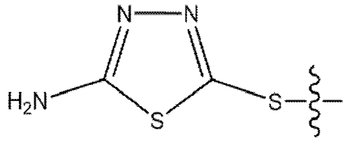
- the functionalization is easy and cheap as the molecules needed are very common and easily obtainable;
- the catalyst compound according to the invention allows the production of liquid and gaseous product, notably C_2 molecules with high added values
- the catalyst compound according to the invention have a total current density over 800 A m^{-2} at -1.2 V vs RHE in a 3-electrode configuration;
- the catalyst compound according to the invention have a specific current density over 300 A m^{-2} for ethanol for CO_2 at -1.2 V vs RHE, which means 0.7 L $m^{-2}h^{-1}$ (658 g $m^{-2}h^{-1}$) of ethanol;
- the electrode can be integrated in a 2-electrode electrolyser for continuous operation with a 40% selectivity for ethylene and 360 A m^{-2} at 4 V, which means 253 L $m^{-2}.h^{-1}$ (316 g $m^{-2}.h^{-1}$) of ethylene at atmospheric pressure.

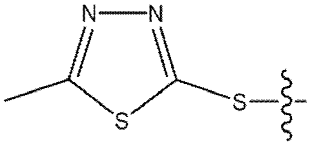
[0013] According to the invention, the copper and silver layers may be the result of a coating *via* sputtering or electrodeposition (usually on a conducting support) and may have a thickness from 1 to 2 μm.

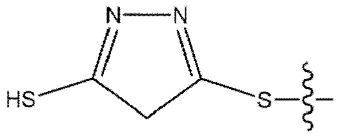
[0014] Advantageously, the compound according to the invention has a copper layer functionalized with at least one group of formula I as described above. R may be an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S. Preferably, 2 or 3 members of the ring are heteroatoms.

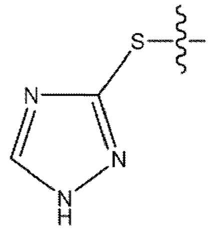
[0015] Advantageously, the R group may be an optionally substituted diazole, thiadiazole, triazole or triazine ring. The substituents may preferably be chosen in the group comprising an amine group (for example NH_2), a thiol group, an amide group (for example $CONH_2$), a carboxylic acid group and a short linear or branched C_1 to C_3 alkyl chain.

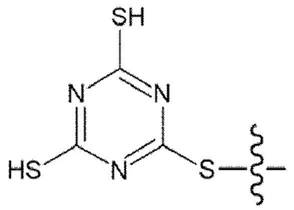
[0016] Advantageously, -S-R may be chosen in the group comprising:

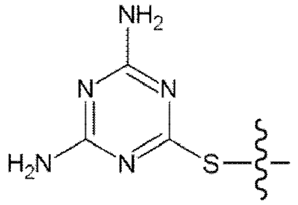








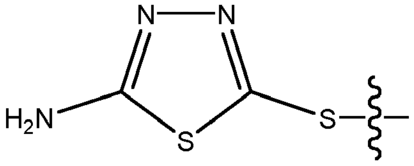


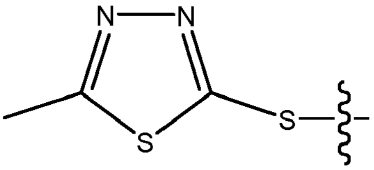


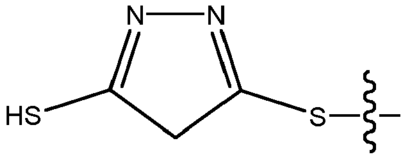
wherein

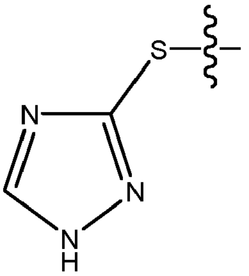
represents the point of attachment to the copper.

[0017] Advantageously, -S-R may be chosen in the group comprising:









wherein

represents the point of attachment to the copper.

[0018] Advantageously, the metal ratio of the compound according the invention may comprise from 50% to 95 at.% of copper atoms, preferably 70 at.% to 90 at.% of copper atoms, with regards to the total number of metal atoms (100 at.%) in the compound.

[0019] Advantageously, the metal ratio of the compound according to the invention may comprise from 5 to 50 at.% of silver atoms, preferably 10 at.% to 30 at.% of silver atoms, with regards to the total number of metal atoms (100 at.%) in the compound. The sum of silver and copper atoms gives 100 at.%.

[0020] Advantageously, the compound according the invention may comprise a S/Cu atomic surface ratio from 0.2 to 2, preferably from 0.35 and 1.2. It is meant by atomic surface ratio, the estimated S/Cu ratio (in number of atoms) from the top 5 nm of the surface of the compound and measured by X-ray photoelectron spectroscopy.

[0021] Advantageously, the compound according the invention may further comprise a conducting support. Preferably the conducting support may be a commercial carbon-based gas diffusion electrode. The catalyst compound according to the invention may thus be a functionalized AgCu electrode.

[0022] Advantageously, the compound according the invention can have a porous tree-like structure (or dendrite structure). This tree-like structure may be obtained by controlling the deposition current and the pulse parameters for the electrodeposition.

[0023] Advantageously, Ag and Cu may be successively electrodeposited using a current density comprised from 10 $mA.cm^{-2}$ to 20 $mA.cm^{-2}$, preferably from 12 $mA.cm^{-2}$ to 17 $mA.cm^{-2}$. The quantity of deposited Ag and Cu may be comprised from 15 $C.cm^{-2}$ to 35 $C.cm^{-2}$, preferably from 20 $C.cm^{-2}$ to 30 $C.cm^{-2}$. The silver may be grown in the form of a tree-like structure using a pulse deposition methods where the applied current is pulsed every 0.1 to 1 second, preferably every 0.25 second to 0.5 second and more preferably every 0.25 second.

[0024] The invention also relates to a process of manufacture of a catalyst compound according to the invention, comprising the steps:

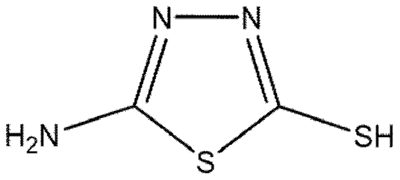
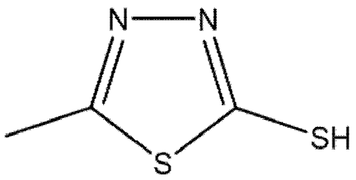
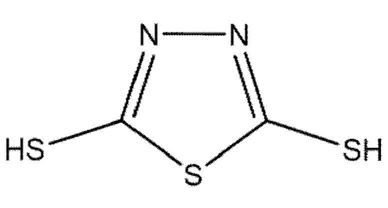
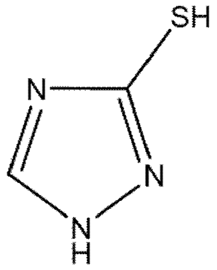
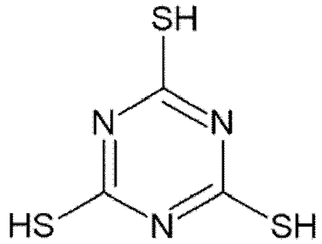
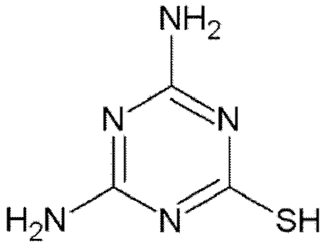
a) electrodeposition of the silver layer on a conductive support,
b) electrodeposition of the copper layer on the support obtained in step a), the copper being essentially deposited on the silver,
c) functionalization of the support obtained in step b) by contacting with molecule of formula II:

H-S-R Formula II,

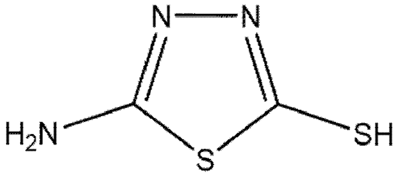
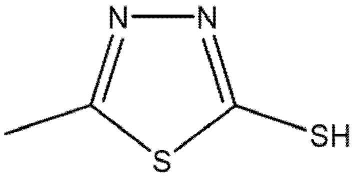
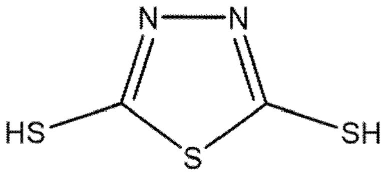
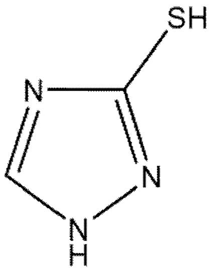
wherein R is an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S. Preferably, 2 or 3 members of the ring are heteroatoms.

[0025] Advantageously, the R group may be an optionally substituted diazole, thiadiazole, triazole or triazine ring. The substituents may preferably be chosen in the group comprising an amine group (for example NH_2), a thiol group, an amide group (for example $CONH_2$), a carboxylic acid group and a short linear or branched C_1 to C_3 alkyl chain.

[0026] Advantageously, H-S-R may be chosen in the group comprising:

[0027] Advantageously, H-S-R may be chosen in the group comprising:

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[0028] Advantageously, step a) and/or step b) of the process according to the invention may be conducted using a potentiostat.

[0029] Advantageously, the conductive support may be a commercial carbon-based gas diffusion electrode.

[0030] Advantageously, step a) and/or step b) of the process according to the invention may be conducted under a current density from 5 $mA.cm^{-2}$ and 50 $mA.cm^{-2}$, preferably from 10 $mA.cm^{-2}$ and 20 $mA.cm^{-2}$.

[0031] Advantageously, in step a) and/or step b) of the process according to the invention, the quantity of deposited Ag and Cu may be from 0.5 $C.cm^{-2}$ and 50 $C.cm^{-2}$, preferably between 15 $C.cm^{-2}$ and 35 $C.cm^{-2}$.

[0032] Advantageously, step a) and/or step b) of the process according to the invention may be done under pulse deposition methods. Preferably, the applied current is pulsed every 0.1 to 1 seconds, more preferably every 0.25 second to 0.5 second and even more preferably every 0.25 second.

[0033] Advantageously, in step a) of the process according to the invention, the source of silver (Ag) may be $AgNO_3$ or CH_3COOAg. The source of silver may be an electrolyte comprising $AgNO_3$, $(NH_4)_2SO_4$ and ethylene diamine.

[0034] Advantageously, in step a) of the process according to the invention, the electrodeposition of silver may be done using a carbon based-gas diffusion layer (GDL), a Pt plate, and Ag/AgCl (saturated with KCl) respectively as the working, counter, and reference electrodes, respectively. Alternatively, the process can be done using a 2-electrode configuration using a carbon based-gas diffusion layer (GDL) and a Pt plate respectively as the working and counter electrodes, respectively.

[0035] Advantageously, in step b) the source of copper (Cu) may be chosen in the group comprising $CuSO_4$, $CuCl_2$ and $CuBr_2$. The source of copper may be an electrolyte comprising H_2SO_4 and $CuSO_4$.

[0036] Advantageously, the step c) of the process according to the invention may be performed in an organic solvent. The concentration of the molecule of formula II in the organic solvent may be from 1 to 100 mM, preferably from 2 to 10 mM. For example, when HS-R is 5-amino-1,3,4-thiadiazole-2-thiol, the concentration may be 5 mM or when HS-R is 1,3,4-thiadiazole-2,5-dithiol , the concentration may be 2 mM.

[0037] Advantageously, the step c) of the process according to the invention may have a duration of from 5 seconds to 12 hours, preferably from 1 minutes to 30 minutes, more preferably 5 minutes to 15 minutes and even more preferably 10 minutes. Step c) may be performed at a temperature from 5 to 80 °C, preferably at room temperature (i.e. from 15 to 30 °C).

[0038] Advantageously, the process according to the invention may further comprise a step d) of washing the obtained catalyst compound with an organic solvent, preferably ethanol.

[0039] The invention further relates to the use of the catalyst compound according to the invention as a catalyst, preferably to convert CO_2 into small molecules. It is meant by small molecules, molecules such as C_2H_4, C_2H_5OH, CO, formic acid, as well as small amount of H_2

[0040] The invention further relates to a process of conversion of CO_2 into small molecules comprising a step of contacting CO_2 (gas) with a catalyst compound according to the invention. The conversion reaction of CO_2 may be done under atmospheric pressure and at room temperature.

Brief description of the figures

[0041]

Figure 1 represents the SEM images of different atomic ratios of AgCu (a) 10at.%AGCu, (b) 15at.%AGCu, (c) 25at.%AGCu and (d) 50at. %AGCu.

Figure 2 represents SEM images of non-functionalized 15at.%AgCu (a), N2C-15at.%AgCu (b), N2S-15at.%AgCu (c), N2N-15at.%AgCu (d) and N3S-15at.%AgCu (e), respectively.

Figure 3 represents the dark field (a) and bright field (b) TEM images of 15at.%AgCu. The bright field TEM image allow the identification of the Ag and Cu domains.

Figure 4 represents the SEM images and the corresponding EDX mappings of 15at.%AgCu showing the presence of the Ag, Cu and C atoms.

Figure 5 represents the proposed interaction mechanism between thiol and pristine material (15at.%AgCu).

Figure 6 represents the Faradaic efficiencies for each CO_2 reduction reaction product and H_2 on non-functionalized 15at.%AgCu (A) and different functionalized 15at.%AgCu electrodes (B: N2C, C: N2S, D: N2N and E: N3S) at various potentials ranging from -0.3 to -1.2 V versus RHE in 0.5M $KHCO_3$.

Figure 7 represents the evolution of the total current density (a), and the specific current density for the production of C_2: C_2H_4, ethanol and C_2H_6 (b), the specific current density for the production of C_1: CH_4, CO, formiate (c) and hydrogen (d) of different atomic ratios AgCu catalysts.

Figure 8 represents the evolution of the total current density (a), and the specific current density for the production of C_2: C_2H_4, ethanol and C_2H_6 (b), the specific current density for the production of C_1: CH_4, CO, formate (c) and hydrogen (d) of various functionalised 15at.%AgCu catalysts (respectively N2C, N2S, N2N and N3S) vs. non-functionalised 15at.%AgCu catalyst.

Figure 9 represents the ratio of the specific current density for C2+ and C1: $J_{C2}+/J_{C1}$ for the pristine and various functionalized 15at.%AgCu (respectively N2C, N2S, N2N and N3S). Ratio values (JC_2/JC_1) as a function of potential vs. RHE (V).

EXAMPLES

Example 1: Preparation of a catalyst compound 1 according to the invention

[0042] The electrodeposition of Cu and Ag were conducted using a potentiostat.

[0043] Firstly, to electrodeposit Ag, an electrolyte composed of 0.01 M $AgNO_3$ (99%, CAS: 7761-88-8), 0.6 M $(NH_4)_2SO4$ (99%, CAS: 7783-20-2), and 0.04 M ethylene diamine (99.5%, CAS: 107-15-3) was prepared. To electrodeposit Cu, an electrolyte composed of 1.5 M H_2SO_4 (CAS: 7664-93-9) and 0.2 M $CuSO_4$ (CAS: 7758-98-7) was prepared. A carbon based-gas diffusion layer (GDL), Pt plate, and Ag/AgCl (saturated with KCl) were used as the working, counter, and reference electrodes, respectively.

[0044] Ag and Cu were successively electrodeposited on the support by controlling the voltage or the current density in order to control the morphology of the deposited. Ag and Cu were successively electrodeposited using a current density comprised between 10 $mA.cm^{-2}$ and 20 $mA.cm^{-2}$, preferably between 12 $mA.cm^{-2}$ and 17 $mA.cm^{-2}$. The loading of Ag and Cu are comprised between 15 $C.cm^{-2}$ and 35 $C.cm^{-2}$, preferably between 20 $C.cm^{-2}$ and 30 $C.cm^{-2}$. A traditional electrochemical workstation (potentiostat/galvanostat) was used for the deposition. Good performances are obtained when the silver is grown in the form of a tree-like structure using a pulse deposition methods where the applied current is pulsed every 0.25 seconds (Figure 1). The source of Ag and Cu used for the electrodeposition are $AgNO_3$ (CAS: 7761-88-8) and $CuSO_4$ (CAS: 7758-98-7).

[0045] A series of electrodes where prepared with Ag:Cu atomic ratios varying from 10 up to 50 at.% were prepared following the procedure described above (see table 1 below and the electrocatalytic performance have been systematically recorded. Theses electrodes are not functionalized and thus are comparative examples. By comparing the performance in term of selectivity of the reaction (FE), the results showed that 15 at.% of Ag (15at.%AgCu) gives the highest performance with 18.3 % of C2 products (ethylene and ethanol) at a potential of -1.2 V vs. Reversible Hydrogen Electrode (RHE) (Table 2).

Table 1	**Potentials (V vs. RHE)**					
	-1,2 V			**-1,1 V**		
	C_2	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
10%AgCu	14.1%	97.2%	59.9%	12.3%	92.1%	56.9%
15%AgCu	18.3%	90.4%	38.2%	14.7%	82.0%	35.7%
25%AgCu	10.7%	93.8%	44.2%	9.5%	89.1%	40.7%
50%AgCu	8.0%	91.0%	42.0%	7.7%	88.1%	37.0%

	-1,0 V			**-0,9 V**		
	C_2	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
10%AgCu	11.1%	87.5%	52.2%	6.8%	79.9%	47.3%
15%AgCu	12.4%	76.5%	34.2%	8.2%	73.7%	32.6%
25%AgCu	8.5%	90.0%	39.8%	7.1%	88.9%	36.5%
50%AgCu	7.1%	89.1%	35.5%	4.7%	88.6%	32.4%

	-0,8 V			**-0,7 V**		
	C_2	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
10%AgCu	4.1%	78.2%	42.7%	2.8%	76.6%	34.9%
15%AgCu	4.7%	74.0%	42.8%	2.5%	74.6%	52.8%
25%AgCu	4.5%	95.4%	35.6%	3.6%	95.9%	48.4%
50%AgCu	4.3%	93.9%	36.8%	0.9%	93.5%	43.3%

	-0,6 V			**-0,5 V**		
	C_2	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
10%AgCu	1.2%	81.1%	49.8%	0.0%	85.9%	61.2%
15%AgCu	1.8%	78.0%	63.5%	0.0%	82.8%	73.8%
25%AgCu	0.0%	93.3%	58.8%	0.0%	87.4%	65.3%
50%AgCu	0.0%	96.7%	54.5%	0.0%	96.1%	62.6%

	-0,4 V			**-0,3 V**		
	C_2	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
10%AgCu	0.0%	89.7%	75.1%	0.0%	89.0%	85.9%
15%AgCu	0.0%	90.3%	85.9%	0.0%	95.7%	93.9%
25%AgCu	0.0%	89.2%	75.1%	0.0%	90.5%	80.6%
50%AgCu	0.0%	93.2%	68.3%	0.0%	90.7%	77.0%

Table 2	**Potentials (V vs. RHE)**					
	-1,2 V			**-1,1 V**		
	J_{tot}	**J_{EtOH}**	**J_{C2H4}**	**J_{tot}**	**J_{EtOH}**	**J_{C2H4}**
10%AgCu	-35.6	-0.9	-3.9	-32.6	-0.6	-3.2
15%AgCu	-37.2	-1.1	-5.4	-34.8	-0.9	-4.2
25%AgCu	-25.4	-0.3	-2.4	-22.1	-0.2	-1.8
50%AgCu	-22.9	-0.3	-1.4	-19.0	-0.4	-1.0

	-1,0 V			**-0,9 V**		
	J_{tot}	**J_{EtOH}**	**J_{C2H4}**	**J_{tot}**	**J_{EtOH}**	**J_{C2H4}**
10%AgCu	-28.3	-0.4	-2.2	-25.2	0	-1.6
15%AgCu	-31.2	-0.7	-3.0	-25.4	-0.4	-1.5
25%AgCu	-17.4	-0.2	-1.2	-14.4	-0.2	-0.8
50%AgCu	-14.1	-0.3	-0.6	-11.3	-0.1	-0.5

	-0,8 V			-0,7 V		
	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
10%AgCu	-21.1	0	-0.8	-16.5	0	-0.4
15%AgCu	-22.0	-0.1	-0.8	-14.1	0	-0.4
25%AgCu	-10.6	0	-0.5	-7.8	0	-0.3
50%AgCu	-8.8	-0.1	-0.2	-6.2	0	-0.1

	-0,6 V			-0,5 V		
	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
10%AgCu	-9.9	0	-0.1	-6.2	0	0
15%AgCu	-8.1	0	-0.2	-5.1	0	0
25%AgCu	-6.2	0	0	-4.5	0	0
50%AgCu	-4.3	0	0	-2.7	0	0

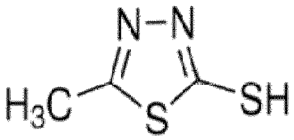
	-0,4 V			-0,3 V		
	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
10%AgCu	-3.2	0	0	-1.4	0	0
15%AgCu	-3.4	0	0	-1.2	0	0
25%AgCu	-2.5	0	0	-1.0	0	0
50%AgCu	-1.9	0	0	-0.9	0	0

Tables 1 and 2: Summary of the electrocatalytic performance for pristine 10 to 50at.%AgCu (CO_2RR = CO_2 reduction reaction).

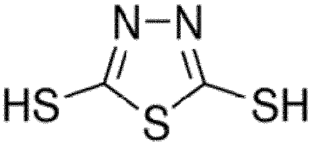
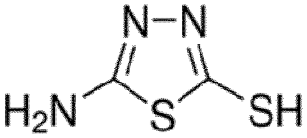
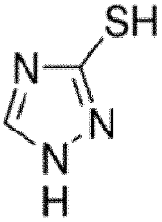
Example 2: Performances of the catalyst compounds (functionalized 15at.%AgCu electrodes) compared to pristine 15at.%AgCu electrodes (comparative example)

[0046] 15at.%AgCu electrodes as prepared above were then functionalized with various functional groups to obtain catalyst compound according to the invention. The structure of the Ag and Cu layers are not modified after the functionalization reaction (Figures 2, 3). Various -S-R groups were attached on the electrodes, essentially on the copper atoms (Figure 4, 5). The various HS-R molecules that have been tested are shown table 3 below. The functionalization of the 15at.%AgCu electrodes was performed in ethanol at a concentration of 5 mM. The total time for each reaction was about 10 minutes at room temperature. The electrodes were washed with ethanol and dried with Ar. The S/Cu measured by XPS analyses after the functionalization reaction is presented in Table 3, below.

Table 3: Label, code, HSR molecule and S/Cu ratio of catalyst compounds of example 2.

Label	Code	S-R-Molecule	S/Cu ratio
A		Non-functionalized	0
B	N2C	 5-Methyl-1 ,3,4-thiadiazole-2-thiol (N_2C)	0.98

(continued)

Label	Code	S-R-Molecule	S/Cu ratio
C	N2S	 1,3,4-Thiadiazole-2,5-dithiol (N_2S)	1.02
D	N2N	 5-Amino-1,3,4-thiadiazole-2-thiol (N_2N)	1.2
E	N3S	 1H-1,2,4-Triazole-3-thiol (N_3S)	0.62

[0047] The results obtained with the functionalized 15at.%AgCu electrodes are shown in tables 4 and 5 below:

Table 4	**Potentials (V vs. RHE)**					
	-1,2 V			**-1,1 V**		
15%AgCu	**C_2**	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
Non Fct	18.3%	90.4%	38.2%	14.7%	82.0%	35.7%
N2N	55.3%	95.9%	24.3%	50.3%	96.2%	21.1%
N2C	53.7%	92.6%	24.7%	45.7%	85.7%	19.6%
N2S	63.3%	104.4%	26.0%	54.3%	102.2%	23.2%
N3S	59.7%	90.8%	21.5%	54.5%	89.2%	19.4%

	-1,0 V			**-0,9 V**		
15%AgCu	**C_2**	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
Non Fct	12.4%	76.5%	34.2%	8.2%	73.7%	32.6%
N2N	45.1%	95.8%	18.4%	39.9%	91.0%	15.9%
N2C	36.7%	78.5%	16.5%	25.0%	73.9%	14.8%
N2S	45.1%	93.2%	19.7%	36.8%	85.1%	16.7%
N3S	49.7%	89.6%	17.0%	41.0%	86.0%	15.1%

	-0.8 V			**-0.7 V**		
15%AgCu	**C_2**	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
Non Fct	4.7%	74.0%	42.8%	2.5%	74.6%	52.8%
N2N	35.5%	88.3%	13.6%	26.4%	88.1%	18.9%
N2C	19.3%	67.3%	12.9%	14.5%	70.9%	19.4%
N2S	29.7%	80.5%	15.0%	26.0%	88.4%	21.5%
N3S	39.0%	88.2%	12.8%	28.5%	88.1%	16.5%

	-0.6 V			**-0.5 V**		
15%AgCu	**C_2**	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
Non Fct	1.8%	78.0%	63.5%	0.0%	82.8%	73.8%
N2N	20.6%	81.4%	26.8%	14.9%	75.3%	32.4%
N2C	10.1%	77.6%	37.9%	3.7%	79.9%	49.1%
N2S	18.5%	84.1%	35.0%	10.1%	79.0%	45.4%
N3S	22.5%	80.9%	22.5%	13.1%	73.3%	30.7%

	-0.4 V			**-0.3 V**		
15%AgCu	**C_2**	**CO_2RR**	**H_2**	**C_2**	**CO_2RR**	**H_2**
Non Fct	0.0%	90.3%	85.9%	0.0%	95.7%	93.9%
N2N	8.0%	70.4%	38.9%	4.0%	63.3%	41.5%
N2C	1.0%	81.4%	63.9%	0.0%	88.0%	78.2%
N2S	7.3%	82.2%	54.7%	2.8%	76.5%	60.9%
N3S	7.3%	65.4%	37.5%	2.5%	62.2%	42.5%

Table 5	**Potentials (V vs. RHE)**					
	-1.2 V			**-1.1 V**		
15%AgCu	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
Non Fct	-37.2	-1.1	-5.4	-34.8	-0.9	-4.2
N2N	-71	-17.61	-20.38	-64.3	-15.17	-16.72
N2C	-45.4	-12.39	-11.49	-41.6	-9.94	-8.9
N2S	-55.3	-20.07	-14.43	-48.2	-15.38	-10.56
N3S	-60.2	-15.71	-18.9	-52.4	-12.94	-14.78

	-1.0 V			**-0.9 V**		
15%AgCu	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
Non Fct	-31.2	-0.7	-3.0	-25.4	-0.4	-1.5
N2N	-55.6	-11.89	-13.07	-47.8	-9.32	-9.75
N2C	-36.2	-7.02	-6.26	-29.5	-5.16	-4.31
N2S	-39.5	-10.43	-7.39	-34.2	-7.35	-5.23
N3S	-45.2	-10.35	-11.98	-37.9	-6.94	-8.6

	-0.8 V			**-0.7 V**		
15%AgCu	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
Non Fct	-22.0	-0.1	-0.8	-14.1	0	-0.4
N2N	-38.2	-6.88	-6.65	-29.1	-3.64	-4.04
N2C	-21.8	-3.2	-2.25	-14.5	-1.54	-1.26
N2S	-26.7	-4.89	-3.04	-17.8	-2.97	-1.66
N3S	-29.1	-5.24	-6.11	-20.2	-2.65	-3.11

	-0.6 V			**-0.5 V**		
15%AgCu	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
Non Fct	-8.1	0	-0.2	-5.1	0	0
N2N	-20.7	-1.95	-2.32	-13.4	-0.8	-1.19
N2C	-11.6	-1.03	-0.65	-4.9	-0.33	-0.16
N2S	-14.4	-1.69	-1.34	-5.4	-0.32	-0.23
N3S	-13.2	-1.14	-1.83	-6.7	-0.39	-0.49

	-0.4 V			**-0.3 V**		
15%AgCu	J_{tot}	J_{EtOH}	J_{C2H4}	J_{tot}	J_{EtOH}	J_{C2H4}
Non Fct	-3.4	0	0	-1.2	0	0
N2N	-8.7	-0.2	-0.49	-5.6	-0.02	-0.2
N2C	-3.4	-0.08	-0.05	-2.8	-0.008	-0.02
N2S	-4.3	-0.19	-0.12	-3	-0.051	-0.033
N3S	-4.8	-0.12	-0.23	-3.2	-0.006	-0.074

Tables 4 and 5: Summary of the electrocatalytic performance for pristine and functionalized 15at.%AgCu (CO_2RR = CO_2 reduction reaction).

[0048] The electrodes were functionalized using the same optimized conditions in order to compare the performance of the different functional groups and the performances were recorded under the exact same conditions (electrolyte, temperature, time). The results shown in tables 3 and 4 demonstrate that both the current density and the Faradaic efficiency are both strongly improved after functionalization. Triadiazole and triazole groups gave the best results and the selectivity towards the formation of C2 can reach 60% at -1.2 V vs. RHE compare to < 16 % for pristine 15at.%AgCu (Figure 6). By taking into account the current density, the results show that the specific current density for ethylene and ethanol can be as high as 20.38 mA cm^{-2} and 17.61 mA cm^{-2} respectively from 15at.%AgCu-N2N (Figure 7). These values correspond to a production of ~ 32 mL of ethanol and 21 L of ethylene per m^2 per hour of electrode for an applied potential of -1.2 V vs. RHE. C2 products are detected at potential as low as -0.3 V vs. RHE with a Faradaic efficiency as high as 5 % towards C_2H_4.

[0049] Importantly the functionalization of 15at.%AgCu translates into 1) high activity (higher current density), 2) higher efficiency towards the conversion of CO_2, 2) High activity towards the production of C2 products (C_2H_4, ethanol and C_2H_6) over C1 as demonstrated by the ratio of the specific current density for C2+ and C1 (Figures 9).

[0050] The catalysts according to the invention prepared and tested in the example allowed improving the performance towards the production of C2 molecules (notably ethanol and ethylene) at room temperature and atmospheric pressure. Compared to pristine 15at.%AgCu electrocatalyst, the specific current density for C2 products (C_2H_4, ethanol and C_2H_6) is increase by a factor of 7. The new electrocatalysts according to the invention are more energy efficiency.

List of references

[0051]

[1] Whipple D T, Kenis P J A. Prospects of CO2 utilization via direct heterogeneous electrochemical reduction[J]. The Journal of Physical Chemistry Letters, 2010, 1(24): 3451-3458.
[2] Xia C, Zhu P, Jiang Q, et al. Continuous production of pure liquid fuel solutions via electrocatalytic CO2 reduction using solid-electrolyte devices[J]. Nature Energy, 2019, 4(9): 776-785.
[3] Hernandez S, Farkhondehfal M A, Sastre F, et al. Syngas production from electrochemical reduction of CO2: current status and prospective implementation[J]. Green Chemistry, 2017, 19(10): 2326-2346.
[4] Hori Y, Wakebe H, Tsukamoto T, et al. Electrocatalytic process of CO selectivity in electrochemical reduction of CO2 at metal electrodes in aqueous media[J]. Electrochimica Acta, 1994, 39(11-12): 1833-1839.
[5] Bagger A, Ju W, Varela A S, et al. Electrochemical CO2 reduction: a classification problem[J]. ChemPhysChem, 2017, 18(22): 3266-3273.

Claims

1. A catalyst compound comprising a silver layer and a copper layer, wherein the copper layer is functionalized with at least one group of formula I:

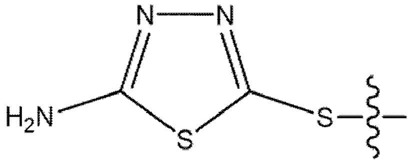
   -S-R Formula I,

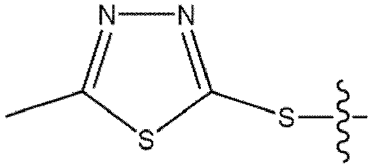
   wherein R is an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S.

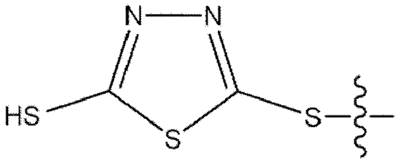
2. The compound according to claim 1 having a fern-like dendritic morphology.

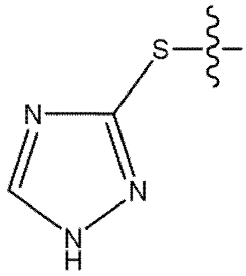
3. The compound according to claim 1 or 2 wherein R is an optionally substituted diazole, thiadiazole, triazole or triazine ring, the substituents being preferably chosen in the group comprising an amine group, a thiol group, an amide group, a carboxylic acid group and a short linear or branched C_1 to C_3 alkyl chain.

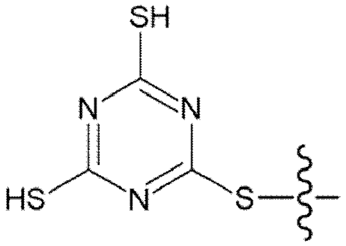
4. The compound according to the preceding claim, wherein -S-R is chosen in the group comprising:

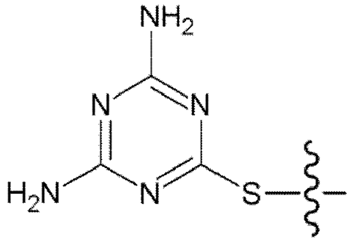












wherein

represents the point of attachment to the copper.

5. The compound according to any of preceding claims, comprising from 70 to 90 at.% of copper atoms, preferably 85 at.%.

6. The compound according to any of preceding claims, comprising from 10 to 30 at.% of silver atoms, preferably 15 at.%.

7. The compound according to any of preceding claims, wherein the S/Cu atomic surface ratio is from 0.2 to 0.6.

8. The compound according to any of preceding claims, further comprising a conducting support, preferably a commercial carbon-based gas diffusion electrode.

9. Use of the compound according to any of preceding claims as a catalyst, preferably to convert CO_2 into small molecules, preferably C_2H_4, C_2H_5OH, CO, formic acid, as well as small amount of H_2.

10. A process of manufacture of a catalyst compound comprising a silver layer and a copper layer, wherein the copper layer is functionalized with groups of formula I:

-S-R Formula I,

wherein R is an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S,
comprising the steps:

a) electrodeposition of silver on a conductive support,
b) electrodeposition of copper on the support obtained in step a), the copper being essentially deposited on the silver,
c) functionalization of the support obtained in step b) by contacting with molecule of formula II:

H-S-R Formula II,

wherein R is an optionally substituted, four-, five- or six-membered aromatic ring comprising at least one heteroatom chosen in the group comprising N and S.

11. The process according to the preceding claim, wherein step c) is performed in an organic solvent.

12. The process according to claim 10 or 11, wherein the concentration of the molecule of formula II in the organic solvent is from 1 to 100 mM.

13. The process according to any of claims 10 to 12, wherein step c) lasts from 5 seconds to 12 hours, and is preferably done at room temperature.

14. The process according to any of claims 10 to 13, further comprising a step d) of washing the catalyst compound with an organic solvent, the solvent preferably being ethanol.

15. A process of conversion of CO_2 into small molecules comprising a step of contacting CO_2 (gas) with a catalyst compound according to any of claims 1 to 8.

16. The process according to the preceding claim, wherein the conversion reaction of CO_2 is done under atmospheric pressure and at room temperature.

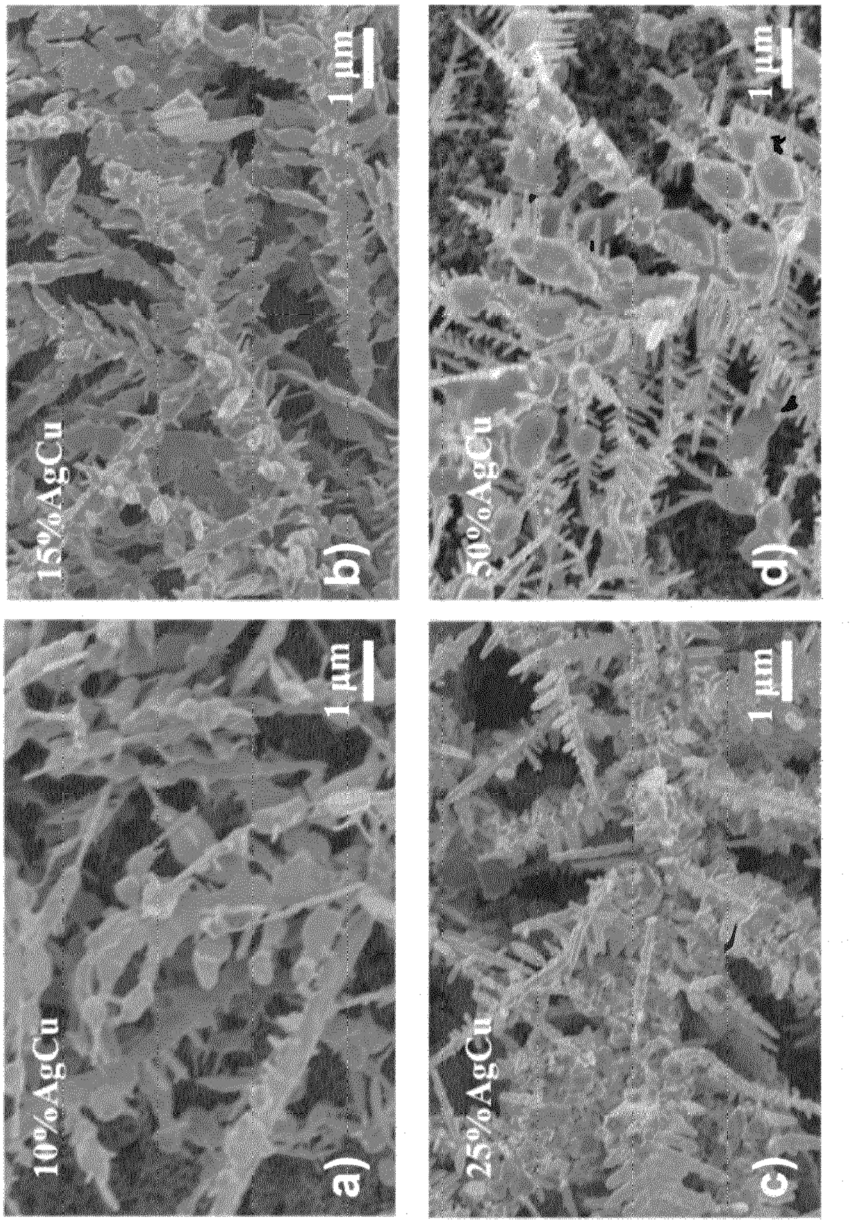


Figure 1

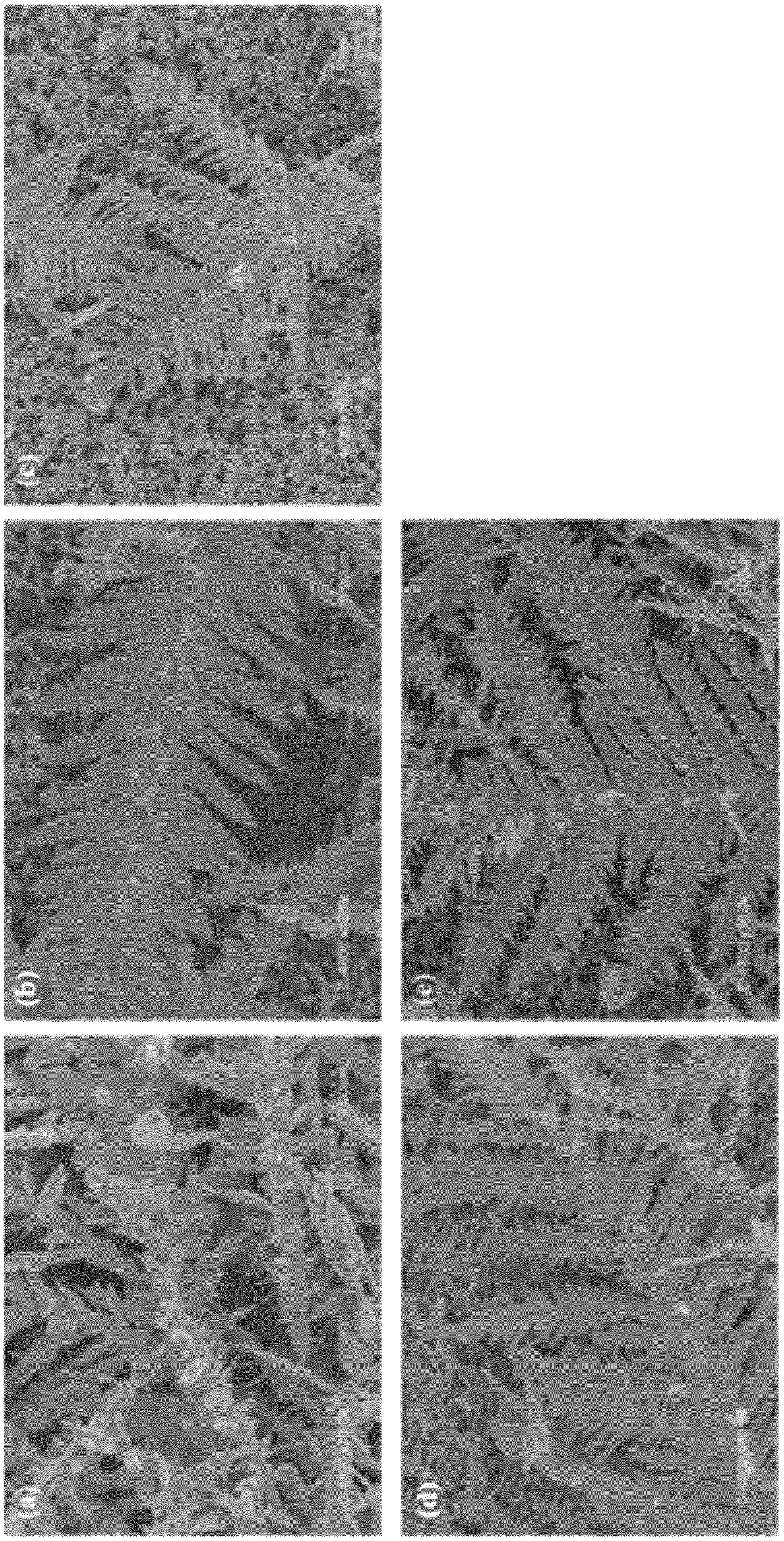


Figure 2

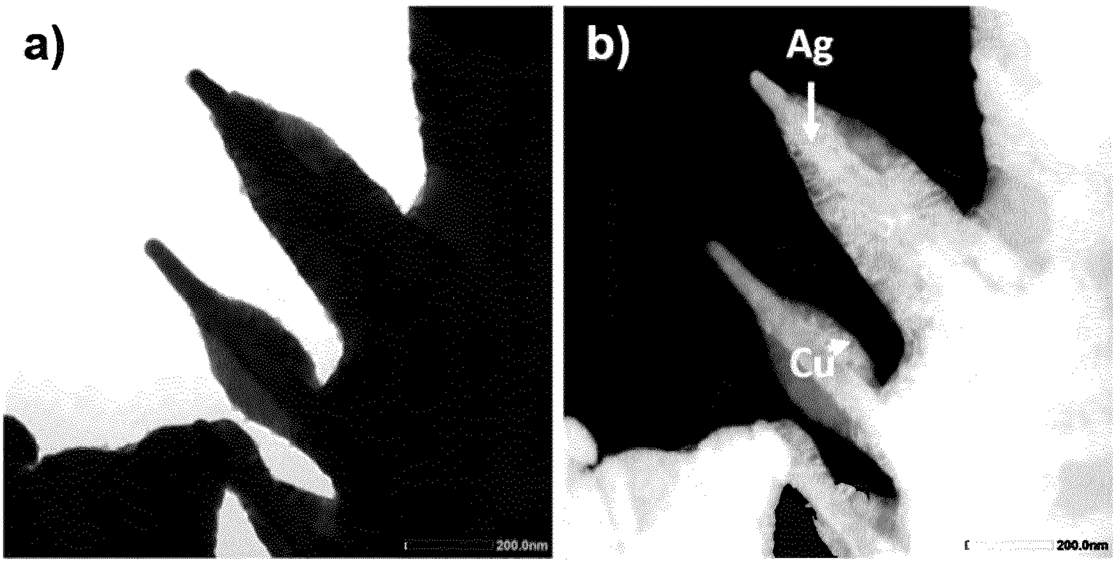


Figure 3

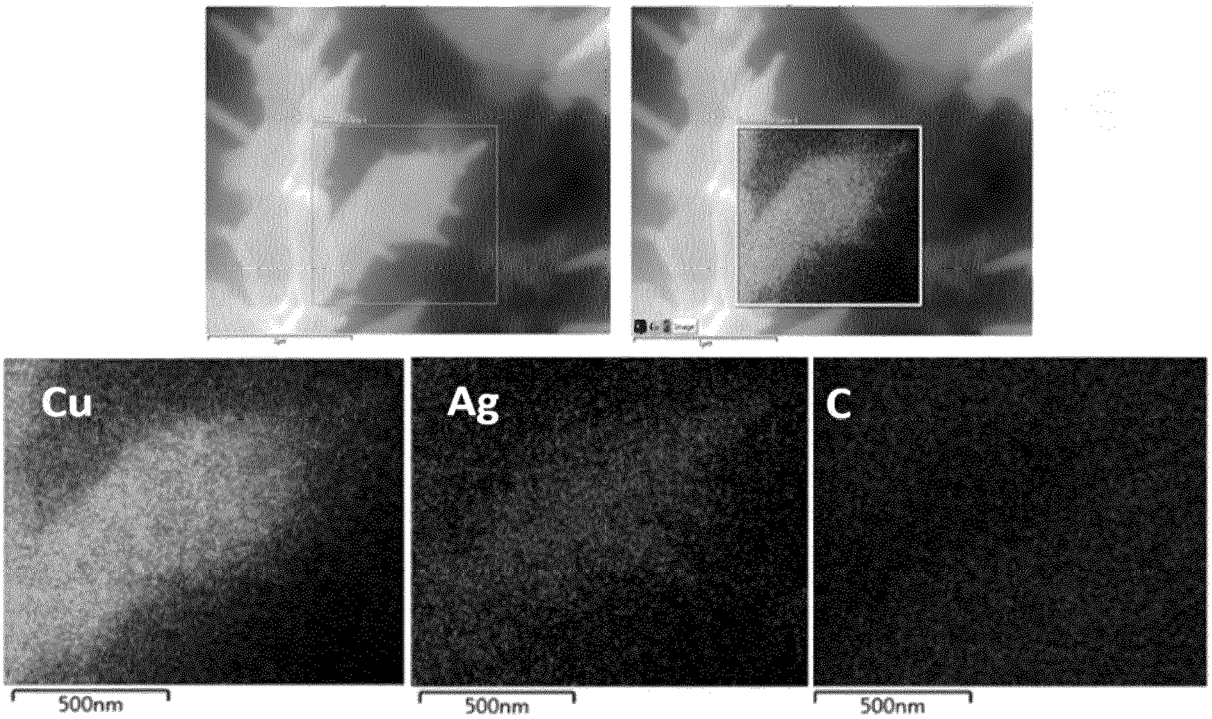


Figure 4

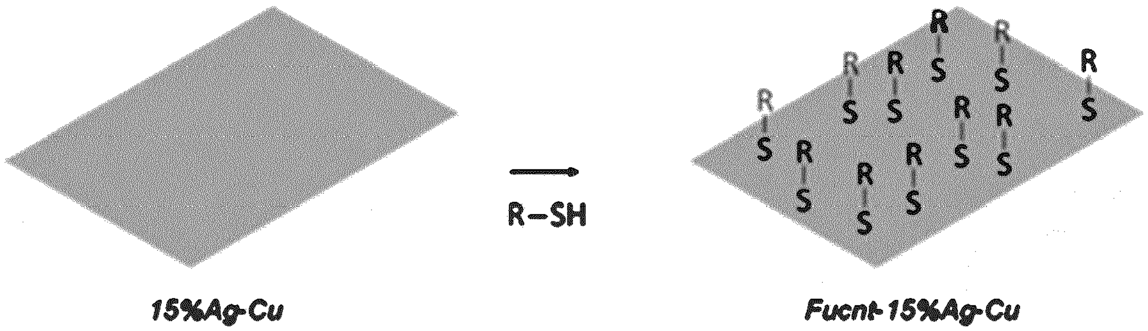


Figure 5

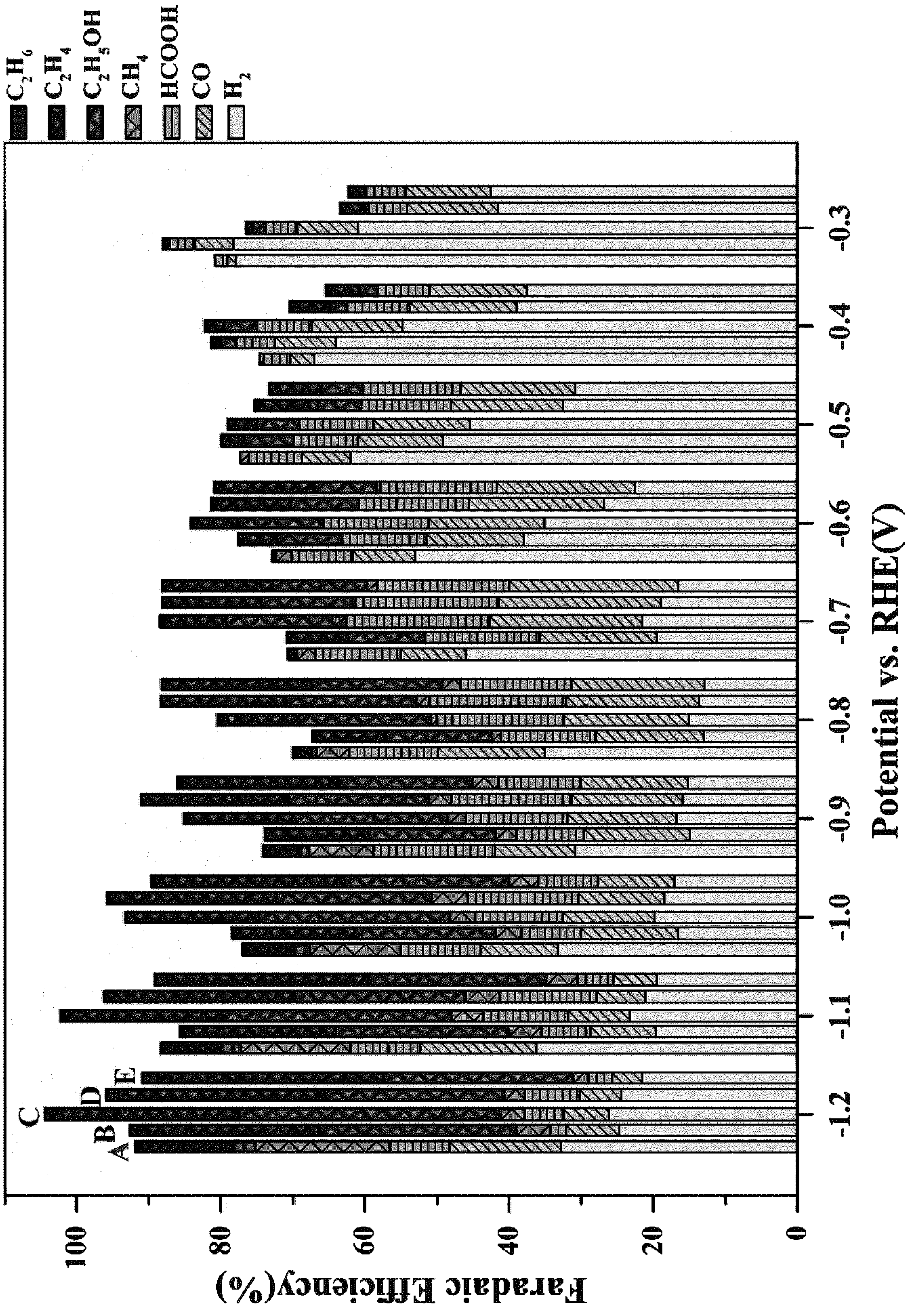

C_2H_6
C_2H_4
C_2H_5OH
CH_4
HCOOH
CO
H_2
A
B
C
D
E
Faradaic Efficiency(%)
0
20
40
60
80
100
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
-0.3
Potential vs. RHE(V)

Figure 6

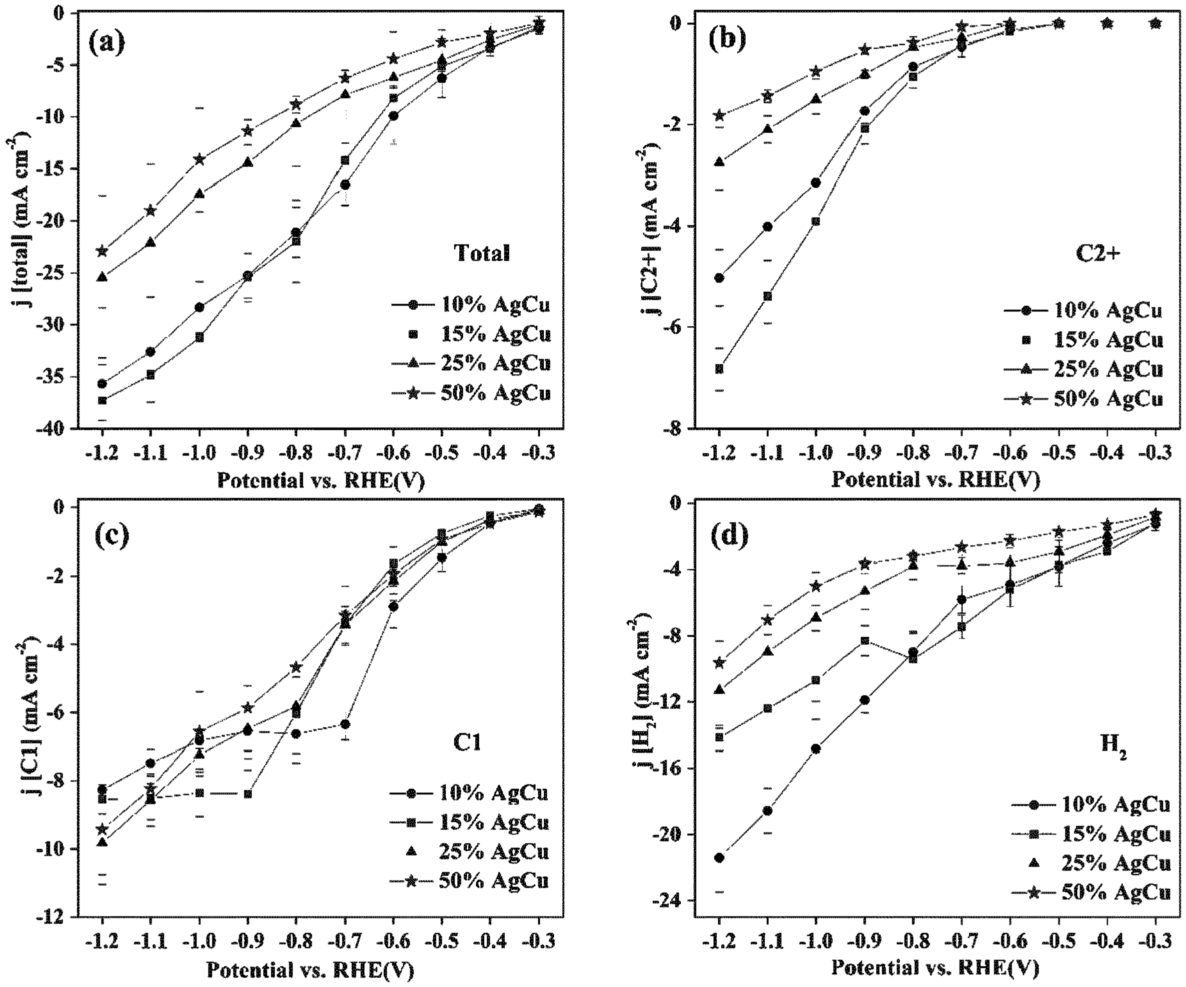

(a)
Total
j [total] (mA cm^{-2})
0
-5
-10
-15
-20
-25
-30
-35
-40
-1.2 -1.1 -1.0 -0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3
Potential vs. RHE(V)
10% AgCu
15% AgCu
25% AgCu
50% AgCu
(b)
C2+
j [C2+] (mA cm^{-2})
0
-2
-4
-6
-8
-1.2 -1.1 -1.0 -0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3
Potential vs. RHE(V)
10% AgCu
15% AgCu
25% AgCu
50% AgCu
(c)
C1
j [C1] (mA cm^{-2})
0
-2
-4
-6
-8
-10
-12
-1.2 -1.1 -1.0 -0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3
Potential vs. RHE(V)
10% AgCu
15% AgCu
25% AgCu
50% AgCu
(d)
H$_2$
j [H$_2$] (mA cm^{-2})
0
-4
-8
-12
-16
-20
-24
-1.2 -1.1 -1.0 -0.9 -0.8 -0.7 -0.6 -0.5 -0.4 -0.3
Potential vs. RHE(V)
10% AgCu
15% AgCu
25% AgCu
50% AgCu

Figure 7

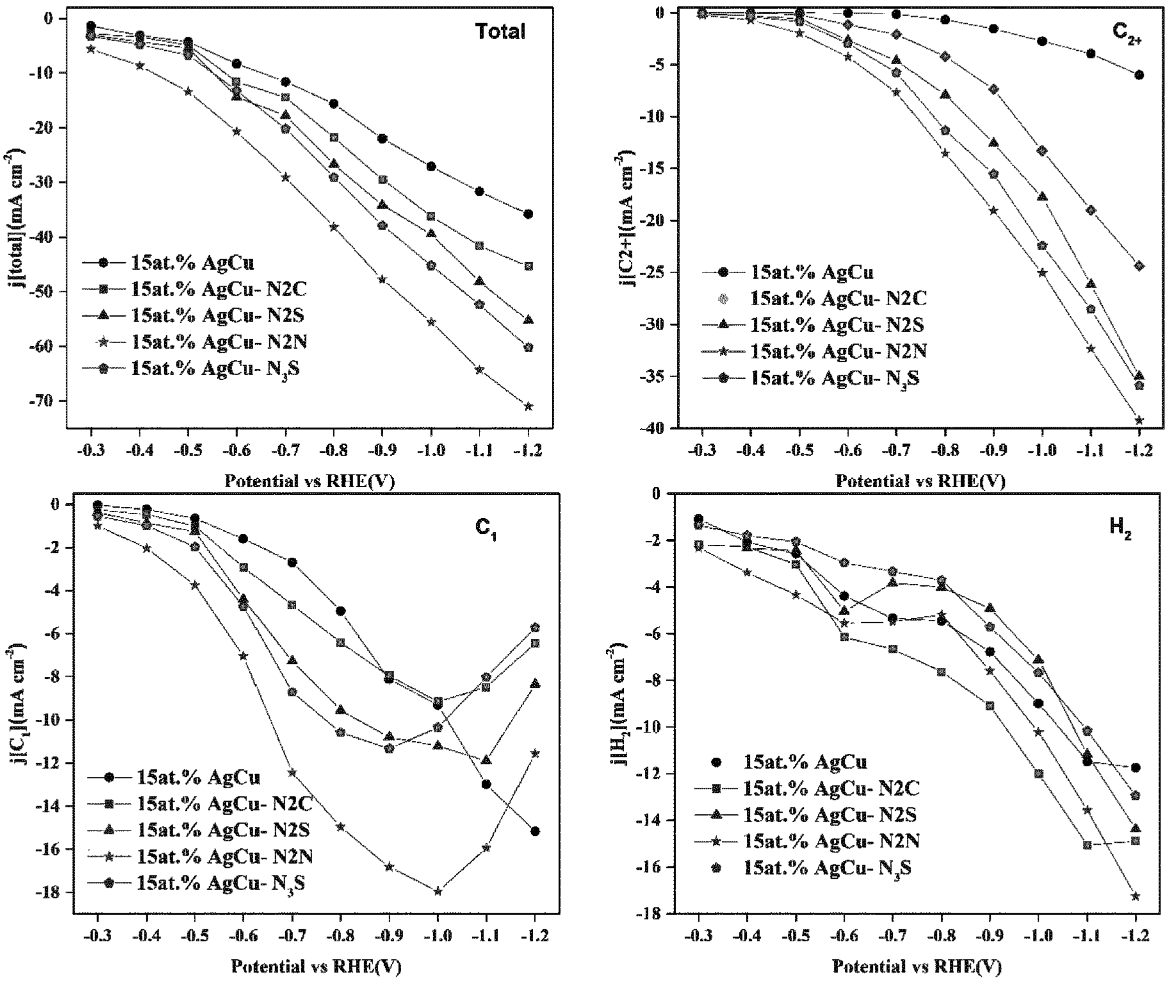

Total
j[total](mA cm^{-2})
0
-10
-20
-30
-40
-50
-60
-70
15at.% AgCu
15at.% AgCu- N2C
15at.% AgCu- N2S
15at.% AgCu- N2N
15at.% AgCu- N$_3$S
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
Potential vs RHE(V)
C$_{2+}$
j[C2+](mA cm^{-2})
0
-5
-10
-15
-20
-25
-30
-35
-40
15at.% AgCu
15at.% AgCu- N2C
15at.% AgCu- N2S
15at.% AgCu- N2N
15at.% AgCu- N$_3$S
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
Potential vs RHE(V)
C$_1$
j[C$_1$](mA cm^{-2})
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
15at.% AgCu
15at.% AgCu- N2C
15at.% AgCu- N2S
15at.% AgCu- N2N
15at.% AgCu- N$_3$S
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
Potential vs RHE(V)
H$_2$
j[H$_2$](mA cm^{-2})
0
-2
-4
-6
-8
-10
-12
-14
-16
-18
15at.% AgCu
15at.% AgCu- N2C
15at.% AgCu- N2S
15at.% AgCu- N2N
15at.% AgCu- N$_3$S
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
Potential vs RHE(V)

Figure 8

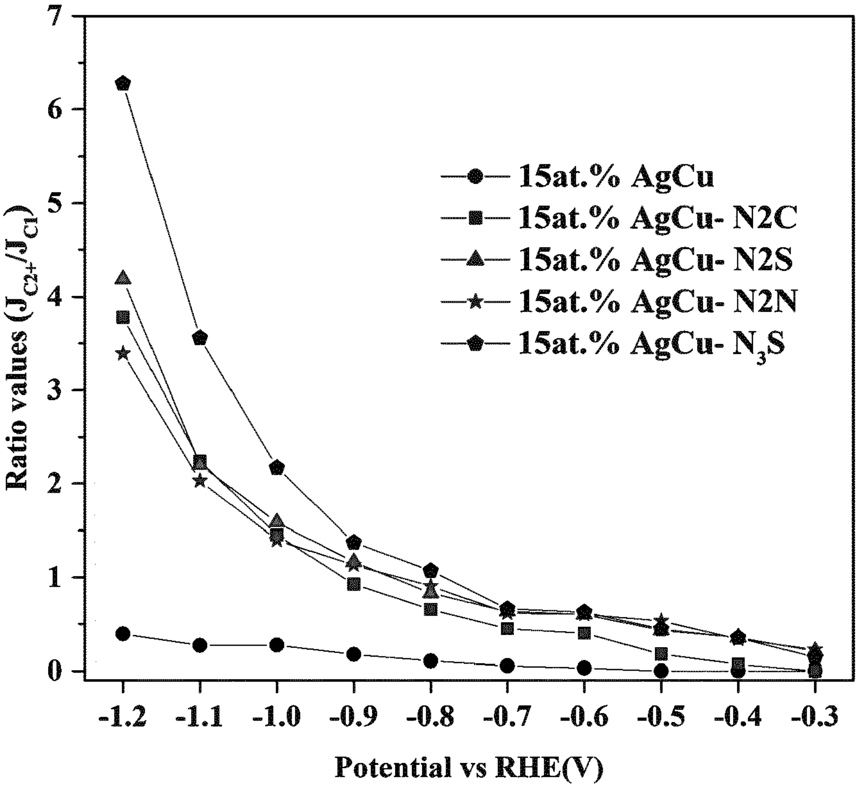

Ratio values (J_{C2+}/J_{C1})
Potential vs RHE(V)
0
1
2
3
4
5
6
7
-1.2
-1.1
-1.0
-0.9
-0.8
-0.7
-0.6
-0.5
-0.4
-0.3
—●— 15at.% AgCu
—■— 15at.% AgCu- N2C
—▲— 15at.% AgCu- N2S
—★— 15at.% AgCu- N2N
—⬟— 15at.% AgCu- N_3S

Figure 9

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EUROPEAN SEARCH REPORT

Application Number
EP 20 30 6391

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C25B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	26 March 2021	Ritter, Thomas

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CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 20 30 6391

26-03-2021

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