

ing the inside of the detection chip **20** to remove the label binding substance **190** may be further performed after the labeling process. For example, ethanol and purified water can be used for the washing.

[0163] In the oxidation reduction current/electrochemiluminescence detection method for an analyte according to the present embodiment, the operation may be performed so as to form a label binding substance in the labeling process as shown in FIG. **8** in place of labeling the analyte **S** using the label binding substance **190** to which the labeling substance **193** is bound in advance in the labeling process.

[0164] In FIG. **9D**, taking the case where the light is measured as an example, the process is illustrated. When the labeling substance **193** is the labeling substance which generates oxidation reduction current when a voltage is applied, the labeling substance **193** is excited to generate electrons. The generated electrons move to the working electrode **60**. As a result, current flows between the working electrode **60** and the counter electrode **66**. Then, the current flowing between the working electrode **60** and the counter electrode **66** is measured by the ammeter **14** of the detector **1**. The current value measured by the ammeter **14** correlates with the number of the labeling substance. Therefore, the analyte can be quantified based on the measured current value.

First Example

[0165] Hereinafter, the present invention will be described in detail with reference to Examples, however, the present invention is not limited thereto.

Preparation Example 1-1

[0166] 1% by volume of 3-aminopropyltriethoxysilane (APTES), i.e., a silane coupling agent, was added to toluene to prepare a solution A.

Preparation Example 1-2

[0167] Acetonitrile and ethylene carbonate were mixed at a volume ratio of 2:3 to prepare an aprotic polar solvent. As an electrolyte salt, tetrapropylammonium iodide was dissolved in the aprotic polar solvent at a concentration of 0.6 M. As an electrolyte, iodine was dissolved in the obtained solution at a concentration of 0.06 M to prepare an electrolytic solution.

Preparation Example 1-3

[0168] A counter electrode of a 200-nm thick platinum thin film (conductive layer) was formed on the substrate body of silicon dioxide (SiO₂) by the sputtering method to obtain a counter electrode substrate. The counter electrode lead for connecting to the ammeter was connected to the counter electrode. Thus, the counter electrode substrate was obtained.

Test Example 1-1

(1-1) Production of DNA Binding Ferritin

[0169] In order to bind DNA to be used as a binding substance or linker to the outside of ferritin (a support composed of polypeptide), the 86th serine residue located outside was modified to a cysteine residue having high reactivity with a maleimide group by the gene-recombination technology using a kit for mutagenesis of a horse ferritin subunit [trade name: QuikChange Site-Directed Mutagenesis kit, manufactured by Stratagene] to obtain a recombinant ferritin subunit.

[0170] Then, the recombinant ferritin subunit was self-associated to obtain a spherical shell-shaped ferritin. The spherical shell-shaped ferritin thus obtained [see **111** in FIG. **11B**] was bound to maleimidized DNA [manufactured by Japan Bio Services Co., LTD., SEQ ID NO: 1] in 1 mM ethylenediaminetetraacetate-containing 20 mM phosphoric acid buffer at 50° C. The maleimidized DNA is DNA of 41 bases in which the 3' terminal is modified with maleimide. The maleimidized DNA has a sequence [the italicized sequence in FIG. **10A**] complementary to CK19 DNA (SEQ ID NO: 5) which is the analyte **S** being as a target and a sequence to which a labeling substance-retaining DNA to be described later is bound [the sequence indicated by boldface in FIG. **10A**].

[0171] The obtained product was subjected to gel filtration chromatography to purify the DNA-binding ferritin. The DNA-binding ferritin (conjugate) [see **110a** in FIG. **11B**] was assumed to have a structure in which about 12 DNAs were bound to the spherical shell-shaped ferritin based on SDS-PAGE. In FIG. **11**, in order to make the description easy, as for the DNA-binding ferritin **110a** (conjugate), a part of DNA bound to the spherical shell-shaped ferritin is omitted.

(1-2) Production of Label Binding Substance

[0172] 100 nM of a labeling substance-retaining DNA [manufactured by Hokkaido System Science Co., Ltd., SEQ ID NO: 2, see **115** in FIG. **10B** and FIG. **11C**] and 1 μM of AlexaFluor750-labeled DNA [manufactured by Japan Bio Services Co., LTD., SEQ ID NO: 3, see **117** in FIG. **11C**] were incubated in 1×MES hybridization solution (manufactured by Affymetrix) at 45° C. for 1 hour to obtain a labeled form [see **110b** in FIG. **11C**].

[0173] A labeling substance retaining DNA **115** has six sequences which hybridize with an AlexaFluor750-labeled DNA **117** [the underlined sequence in FIG. **10B**]. Further, The labeling substance retaining DNA **115** has a sequence which hybridizes with maleimidized DNA in the DNA-binding ferritin [the italicized sequence in FIG. **10B**] at the 3' terminal. The AlexaFluor750-labeled DNA **117** has a sequence which hybridizes with the labeling substance-retaining DNA **115** [see FIG. **10C**]. Both ends of DNA (linker) [see **116** in FIG. **11C**] included in the AlexaFluor750-labeled DNA **117** were labeled with AlexaFluor750 (labeling substance) [see **113** in FIG. **11C**].

(1-3) Production of Working Electrode Substrate

[0174] A working electrode composed of a thin film (about 200 nm in thickness) of tin-doped indium oxide was formed on the surface of the substrate body **30a** composed of silicon dioxide (SiO₂) by the sputtering method. The thin film serves both as the conductive layer and the electron accepting layer. Subsequently, a working electrode lead for connecting to the ammeter was connected to the working electrode.

[0175] Then, the surface of the working electrode was brought into contact with the solution A obtained in Preparation example 1-1 to provide an amino group on the surface of the working electrode.

[0176] A DNA solution containing 10 μM of CK19 DNA-trapping DNA (the trapping substance **81**) [SEQ ID NO: 4, see FIG. **10D**] and a crosslinking reagent [trade name: microarray crosslinking reagent D, manufactured by GE Healthcare] were mixed at a volume ratio of 1:9. The obtained mixture was dropped onto the working electrode. Thereafter,