論 文 の 内 容 の 要 旨

論文題目　Copper-oxide-based semiconducting nanostructures for electrochemical solar water splitting and glucose sensing
（太陽光による電気化学水分解とグルコース検知のための酸化銅系半導体ナノ構造）

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The photoelectrochemical (PEC) water splitting using sunlight offers a sustainable means to produce hydrogen without relying on any fossil fuels. Cu_2O is one of the most promising photocathode materials with respect to cost, abundance, light absorption, and energy band position, although the application of Cu_2O is limited because of a negative onset potential and self-reduction in electrolyte under illumination. A new and low-cost fabrication method was introduced to synthesize Cu_2O microcrystalline films with high photoactivity. The two-step fabrication method consists of the synthesis of $Cu/Cu(OH)_2$ nanowires and their subsequent transformation into Cu_2O at 500^{o}C under a vacuum. The growth of the Cu_2O microcrystalline film was driven by the outward diffusion of Cu ions from the Cu substrate via Cu vacancies to the oxide surface and reacts with the oxygen from the gas phase. By controlling the annealing time, the photoactivity and stability of the films can be tuned. Photoelectrochemical evaluation of the Cu_2O films performed under chopped simulated AM 1.5G illumination reveals that the sample annealed at 500 ^{o}C for 2 h exhibited the highest photocurrent of 4.07 mA/cm^2 at 0 V/RHE.

Although the obtained Cu_2O film exhibits a high photoactivity, the Cu_2O surface layer was reduced to Cu and lost its activity quickly during the stability test. To preclude the self-reduction and increase the photovoltage of the Cu_2O photocathode in solar water splitting, we introduce a Ga_2O_3 thin layer as a buffer layer between the Cu_2O sunlight absorber layer and the TiO_2 protective layer. This

buffer layer decreases the conduction band discontinuity at the Cu_2O/buffer layer interface and thus increases the photovoltage of the structure, thus shifting the onset potential positively and improving the efficiency. The TiO_2 protective layer inhibits the Cu_2O self-reduction efficiently and the TiO2/electrolyte interface is favorable for electron transport due to the narrow depletion region at TiO2 surface. The fabricated Pt/TiO_2/Ga_2O_3/Cu_2O structure achieves a large shift of the onset potential toward positive values and a stable photocurrent over at least two hours. The observed onset potential of 1.02 V vs. RHE and the relatively large photocurrent generated at low applied biases demonstrate the potential of this structure for developing superior photoelectrodes for use in high-efficiency tandem cells.

The detection of glucose in analytical applications such as clinical diagnostics, food processing and environment protection has been the subject of much attention by analytical researchers in recent years. Among the metal-oxide materials used for glucose sensing, CuO is a promising candidate toward high performance glucose sensor both in enzymatic and non-enzymatic glucose sensing because of its high isoelectric point (IEP) and good electrochemical activity. The CuO nanoporous structure with a high crystal quality is synthesized by annealing the Cu/$Cu(OH)_2$ nanowires at 500^{o}C under a O_2/Ar atmosphere. The presence of O2 during the annealing results in the formation of CuO at the outer surface of the oxide layer and the CuO porosity is enhanced by using nanowires as the starting material for the growth of the outer layer. The obtained Cu/Cu_2O/CuO structure is used as an efficient electrode for glucose sensing and exhibits good sensitivity both in enzymatic and non-enzymatic glucose sensing schemes. The high surface area of nanoporous layer and the enhanced electron transfer facilitated by a Schottky barrier at the Cu/Cu_2O interface are likely responsible for the high performance glucose sensing.

Considering that the surface area plays a great role in the electrooxidation of glucose, a CuO nanowire/microflower structure with a high electrochemically active surface area is synthesized by annealing the previously grown $Cu(OH)_2$ nanowires/CuO flowers. The obtained CuO nanowire/microflower structure exhibits a high sensitivity of 1943 $\mu A/mM/cm^2$, a wide linear range up to 4 mM and a low detection limit of 4 μM in a non-enzymatic glucose sensing scheme. With the help of a second consecutive growth of CuO nanowires on the microflowers, the sensitivity of the obtained CuO nanowire/microflower/nanowire structure further increase to 2424 $\mu A/mM/cm^2$, benefiting from an increased density of

electrochemically active sites. A performance comparison between the CuO nanowire/microflower/nanowire, CuO nanowire/microflower, CuO nanowire and Cu_xO film electrode was systematically conducted to demonstrate the significant role of surface area in the electrocatalysis of glucose. Moreover, the fabricated electrode presents a good selectivity towards interference species (ascorbic acid, uric acid and chloride anions), indicating great potential of the proposed electrode for applications in electrochemical devices. The main advantage of the presented structure is to provide a structure with well controlled interfaces using simple and low-cost fabrication techniques, without resorting on materials in the form of powders. Thus, the reported CuO nanowire/microflower/nanowire structure, which is fabricated directly from a Cu foil, provides a simple and economic way towards high performance CuO glucose sensors.