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Short Communication

New Green Soft Chemistry Route to Ag-Cu Bimetallic Nanomaterials

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Ag-Cu bimetallic nanomaterials were synthesized by an environmental-friendly liquid phase reduction method with sodium hypophosphite reducing the mixed aqueous solution of cupric acetate silver nitrate and sodium hexametaphosphate. Nitric acid was used to adjust the pH and sodium hexametaphosphate performed as the surfactant. The Ag-Cu bimetallic nanomaterials were characterized with powder X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and X-ray spectroscopy (EDS). The result showed that Ag and Cu are not mechanical mixing but the combination at the atom scale and lattice level. The reaction parameters such as the molar ratio of Ag/Cu, reaction time and temperature were investigated. The ultraviolet-visible absorption spectra (UV-vis) and electrochemical properties of the samples were explored and it was found that the sample shown high electrochemical activity and excellent performance of hydrogen evolution.

Keywords: Ag-Cu bimetallic, Soft chemistry, Electrochemical property

1. INTRODUCTION

As the increasing development in intelligent electronic device, the demand for low cost, high performance and miniaturization of electronic devices become more and more important. Recently, bimetallic nanomaterials draw focus attention for its excellent properties and wide application prospect. Compared to single metal, bimetallic nanoparticles possess more excellent properties both in electrical and optical aspect [1, 2]. Thus bimetallic nanomaterials are more promising than single metal materials [3, 4]. Normally, bimetallic nanomaterials are prepared by using sol-gel method [5], hydrothermal method [6], total reduction method [7, 8], continuous reduction method [9-11], microemulsion method [12], electrodeposition method [13-15] and microwave heating method [16, 17]. However, most of these methods exists some shortcomings such as high energy consumption, high

cost of reactants, cumbersome steps, long reaction time or using hydrazine hydrate, formaldehyde and other toxic reagent in the process. Therefore, it's of great importance to find a convenient for industrialization, low cost and environmentally friendly method for the preparation of bimetallic nanomaterials.

Among single nanometals, copper nanometal has high strength and super plasticity at room temperature [18]. In the treatment process of automobile tail gas, nanometer copper powder can be used as a catalyst to turn CO into CO_2, which replaces noble metals such as platinum and ruthenium [19]. Besides, nanocopper can be used in the manufacture of conductive frame material (conductive rubber, magnetic conductive adhesive, etc.). Copper nanometals are widely applied in microelectronics industry, encapsulation and connections, which play important roles in the miniaturization of microelectronic device. Silver nanomaterials, as an important part of the noble metal nanometer materials, not only retained their good properties such as electroconductivity, but also have important applications in the field of antibacterial, catalytic, optical and biological. Colloid nano-scale silver has good surface enhanced Raman scattering activity [20]. The DNA probes labeled with silver nanoparticles have good accuracy and high reliability, which can be applied to biological medicine field [21]. However, both copper nanometal and silver nanometal have some disadvantages. Nano copper can be oxidized or generate electromigration easily. At the same times, the cost of silver is high. Therefore, if copper nanometal combined with silver nanometal, it will not only overcome the shortcomings of copper [22], but also can reduce the cost.

In this work, liquid phase reduction method is used to produce Ag-Cu bimetallic nanomaterial. The optical and electrochemical performances of the as-prepared Ag-Cu nanomaterials are explored. This route is convenient, low cost, environmental friendly and suitable for industrial production.

2. EXPERIMENTAL

2.1 Materials

Cupric acetate ($Cu(CH_3COO)_2 \cdot H_2O$, silver nitrate ($AgNO_3$), anhydrous ethanol (C_2H_5OH), sodium hexametaphosphate ($(NaPO_3)_6$, SHMP), sodium phosphite ($NaH_2PO_2 \cdot H_2O$) and nitric acid (HNO_3) were purchased from Chongqing Chuandong chemical company. All the reagents used in this experiment were of analytical grade and used without any further purification. In the experiment, ionized water was used.

2.2 Preparation

In this experiment, Ag-Cu bimetallic nanomaterials were prepared in aqueous solution by using sodium hypophosphite reducing copper acetate and silver nitrate. The main preparation process is shown in Figure 1. At first, 0.49 g $Cu(CH_3COO)_2 \cdot H_2O$, 0.68 g $AgNO_3$ and 0.5 g $(NaPO_3)_6$ were mixed in a beaker containing 40 ml de-ionized water. Then, the mixture was stirred at room temperature for 10 min to obtain a blue solution A. Meanwhile, 0.95 g $NaH_2PO_2 \cdot H_2O$ and 10 ml de-ionized water were

mixed in a beaker to gain solution B. Then, B was poured into A and the mixture was heat at 50℃ for 0.5 hours with continuous stirring. After the reaction, the products were washed with de-ionized water and ethanol for several times by high-speed centrifuge. Finally, the products were dried in a vacuum at 60 ℃ for 12 h.

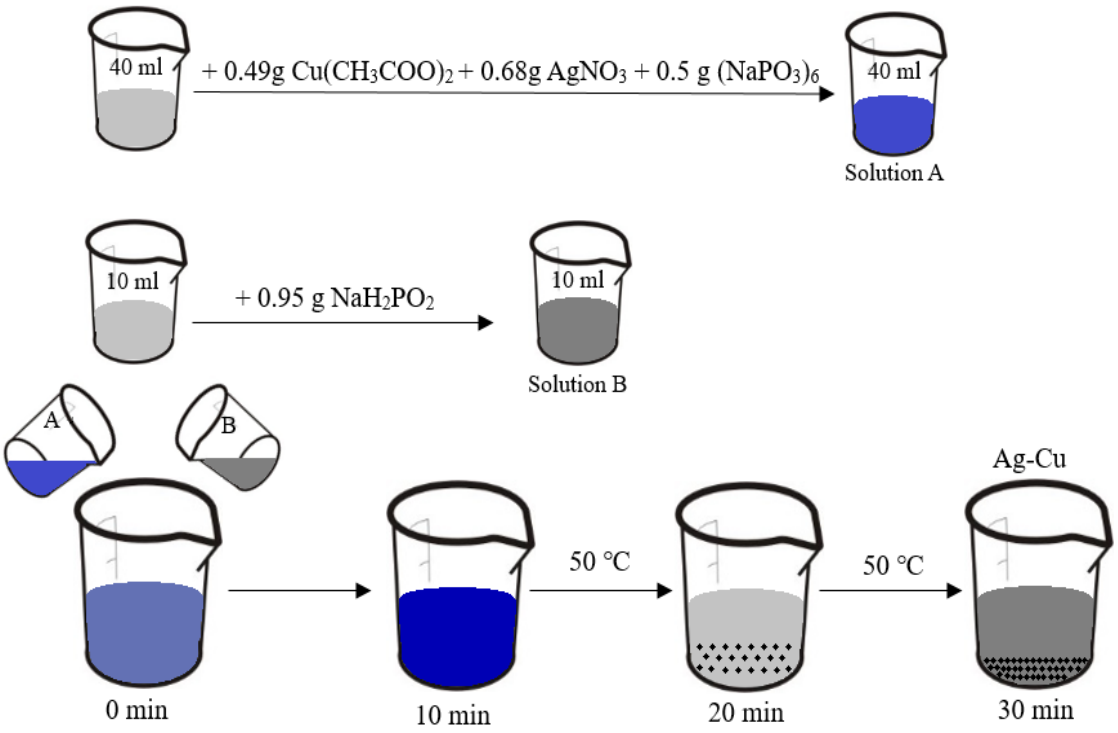

Figure 1. The experimental procedure of synthesizing Ag-Cu bimetallic nanomaterials

2.3 Characterization

The products were characterized by X-ray powder diffraction (XRD) with a D/Max-IIIA X-ray diffractometer. The analytical conditions were Cu Kα radiation (λ = 1.54178 Å), 40 kV tube voltage , 30 mA tube current and 2˚/ min scan speed. The diffraction angle of the scanning is range of 30˚ ~ 80˚ (2θ). The UV-vis absorption spectra of the samples were measured by a Shimadzu U-2550 UV-Vis spectrophotometer. The morphology of the samples were observed by a Hitachi S 4800 field emission scanning electron microscopy (FESEM) and analyzed by energy dispersive X-ray spectroscopy (EDS). The electrochemical performance of Ag-Cu bimetallic nanomaterial was investigated by an electrochemical workstation (Shanghai Chenhua, CHI760E).

3. RESULTS AND DISCUSSION

In the preparation system, $Cu(CH_3COO)_2 \cdot H_2O$ and $AgNO_3$ were used as precursors and sodium hypophosphite was used as the reducing agent. Ag^+ and Cu^{2+} were reduced to Ag-Cu bimetallic nanomaterials in aqueous solution of sodium hexametaphosphate.

According to the periodic table of chemical elements, standard electrode potential of Ag^+ is greater than Cu^{2+}. Therefore, in this system, Ag^+ was reduced to Ag first. Then Cu^{2+} was reduced to Cu and grew on Ag to form Ag-Cu bimetallic nanomaterial.

In this experimental system, sodium hypophosphite acted as a reducing agent. As this reaction system was an open system, it was in contact with O_2 and was partially oxidized. According to the experimental result, when the amount of the reducing agent was 3 to 4 times to the theoretical value, Ag^+ and Cu^{2+} could be reduced completely. Besides, nitric acid was added to adjust the pH during the reaction.

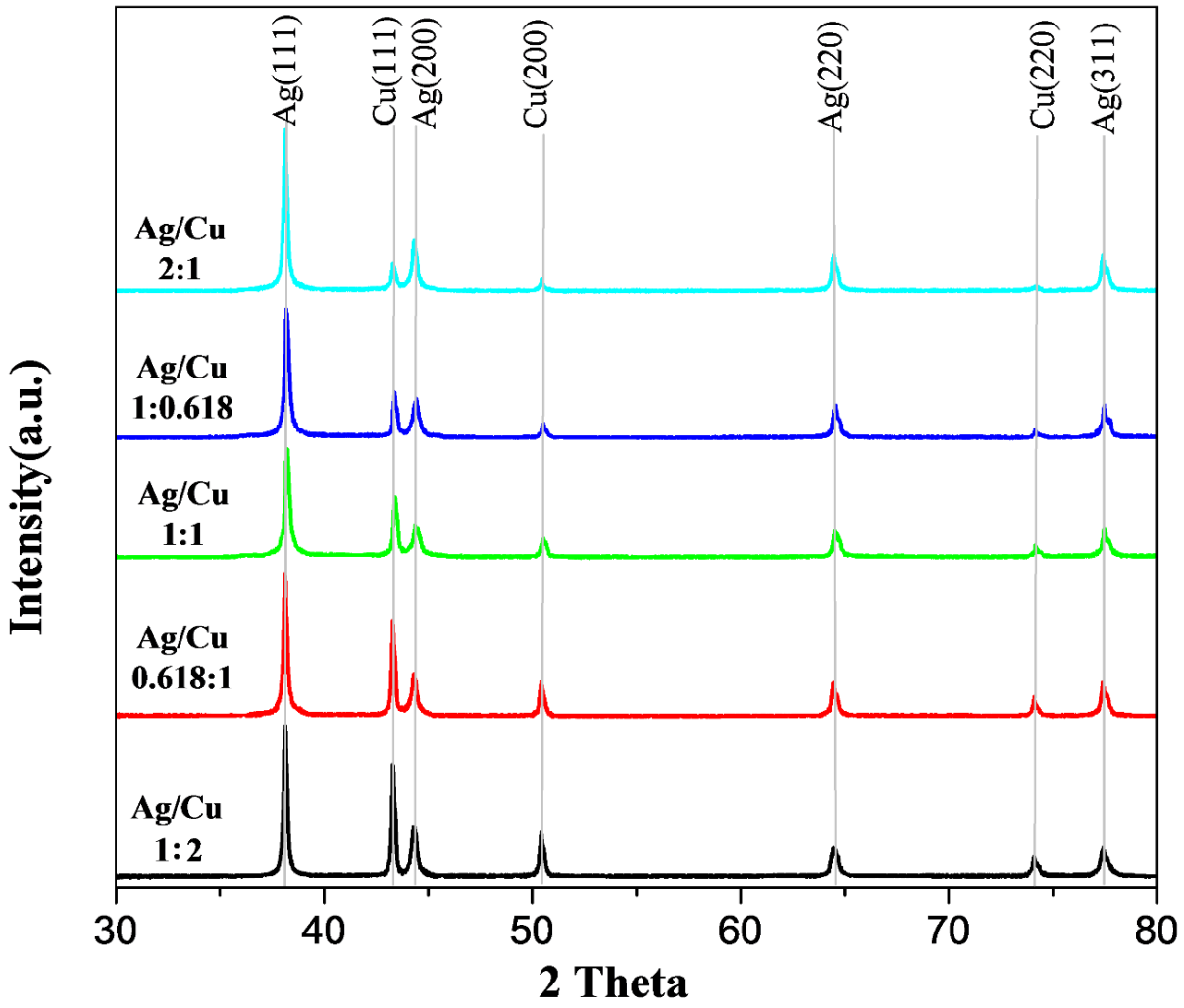

Figure 2. The XRD pattern of different proportions of the sample synthesized at 50 ℃ for 30 min

XRD analysis was performed to determine the component and crystal structure of the products. Figure 2 is the XRD pattern of different proportions of Ag-Cu bimetallic nanomaterial. In the XRD pattern, peaks at 2θ of 38, 44, 64 and 77 correspond to (111), (200), (220), (311) planes of cubic structure Ag (JCPDS card No. 04-0783). While the diffraction peaks observed at 2θ of 43, 50 and 74

correspond to (111), (200) and (220) planes of cubic structure Cu (JCPDS card No. 04-0836). The sharpness of the peaks shown that the products were well-crystalline [23]. No other characteristic peaks were observed, indicating the high purity of the Ag-Cu bimetallic material. As is shown in Fig. 2, when Ag-Cu molar ratio increases, the copper peak becomes gradually weak while the change of silver peak is not obvious.

Figure 3a is a typical FESEM image of Ag-Cu bimetallic materials with the Ag: Cu mole ratio of 1: 0.618. It can be found that the as-prepared Ag-Cu bimetallic nanomaterial is tiny spherical with the diameter range of 60-150 nm. Fig. 3b is the EDS images of the Ag-Cu bimetallic crystallites. The blue one (Fig. 3c) represents copper nanomaterials and the red one (Fig. 3d) represents silver nanomaterials. It can be seen that the main elements of the product are Ag and Cu, while the blue area almost overlap with the red area. This indicates that Ag and Cu are not mechanical mixing but the combination at the atom scale and lattice level [24]. Such structure is expected to be an antioxidant structure [25], because of the existing of surfactant in the preparing process.

Figure 4 is the ultraviolet-visible absorption spectrum of Ag-Cu bimetal nanomaterials with different mole ratio of Ag and Cu. There are obvious absorption peaks between 350-450 nm. The absorption peaks shift to the short-wave direction with the increasing of Ag-Cu ratio. It is obvious that the absorption peak is affected by its morphology and crystallinity [26].

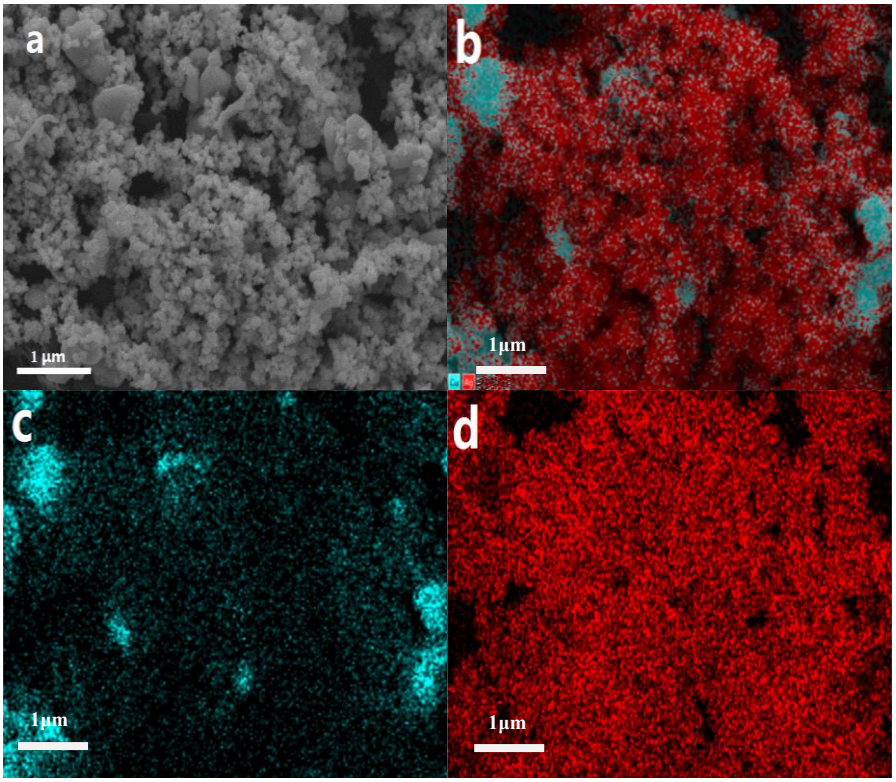

Figure 3. FESEM-EDS images of the as-prepared Cu-Ag nanoparticles: (a) FESEM image of the as-prepared product; (b) EDS image of the products; (c) EDS image of Cu (blue); (d) EDS image of Ag (red)

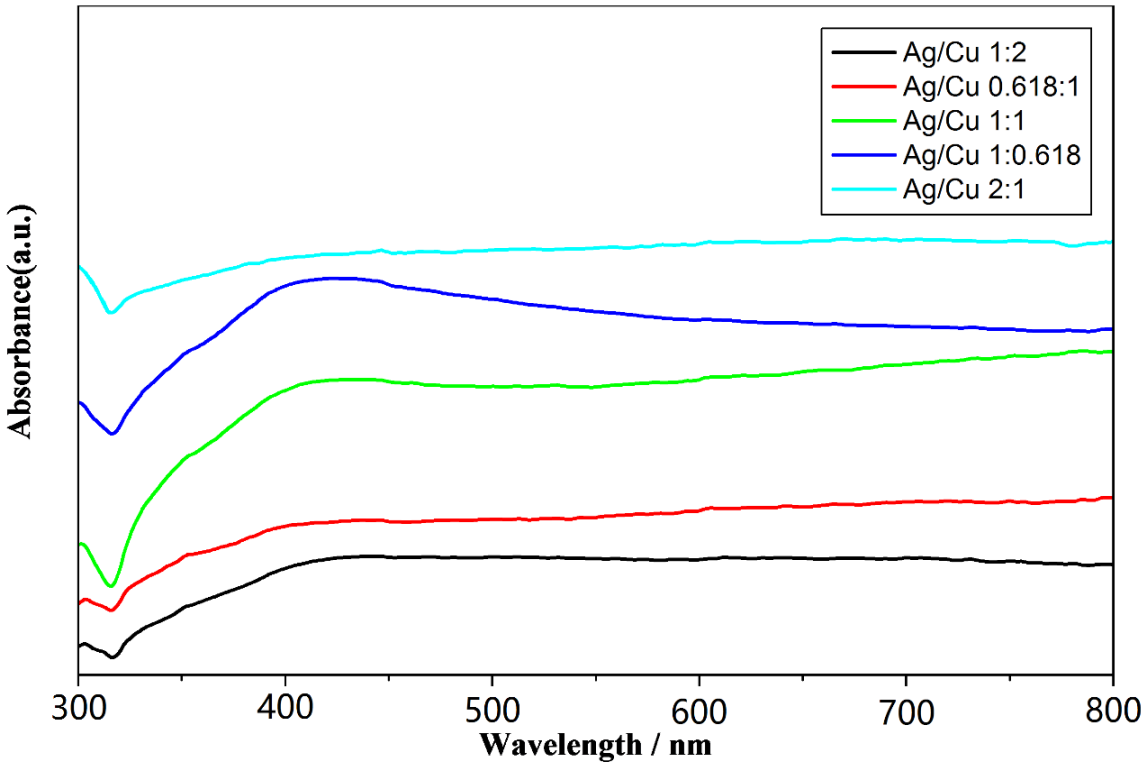

Figure 4. The UV-Vis spectrum of different proportions of Cu-Ag bimetallic nanomaterials.

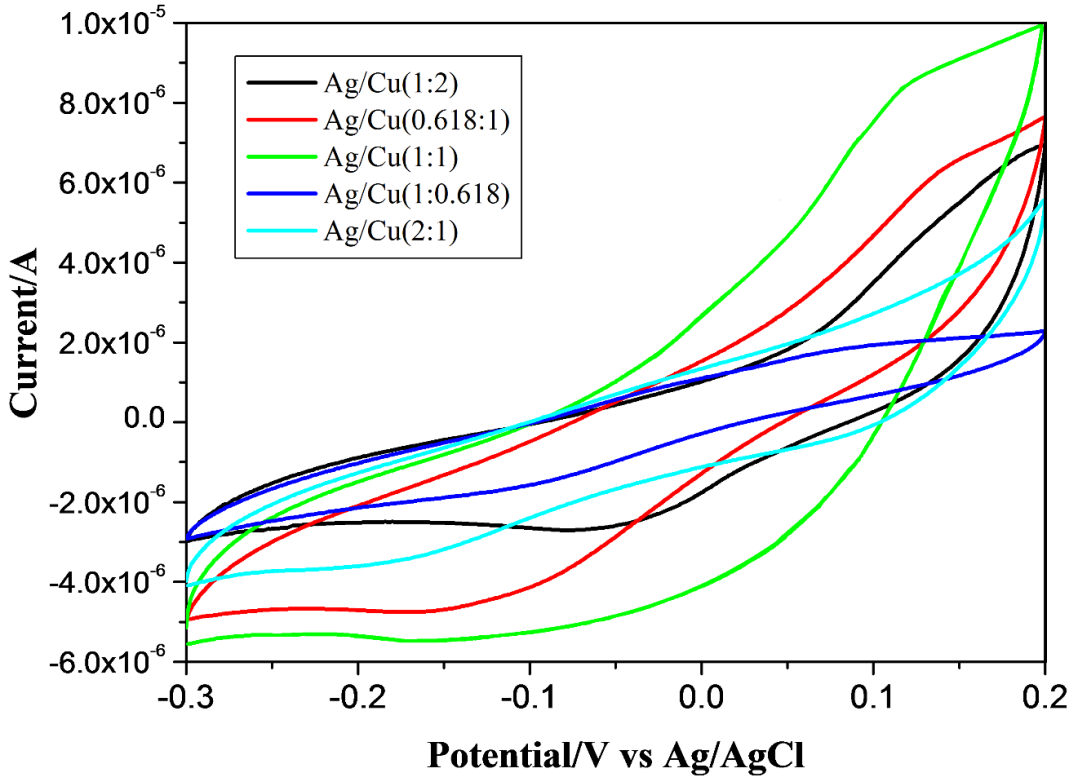

Figure 5. The Cyclic voltammograms (CV) curves on different proportions of Cu-Ag bimetallic nanomaterials in 1 mol·L^{-1} Na_2SO_4 solution at 50 ℃ with the scan rate of 0.1 V s^{-1}.

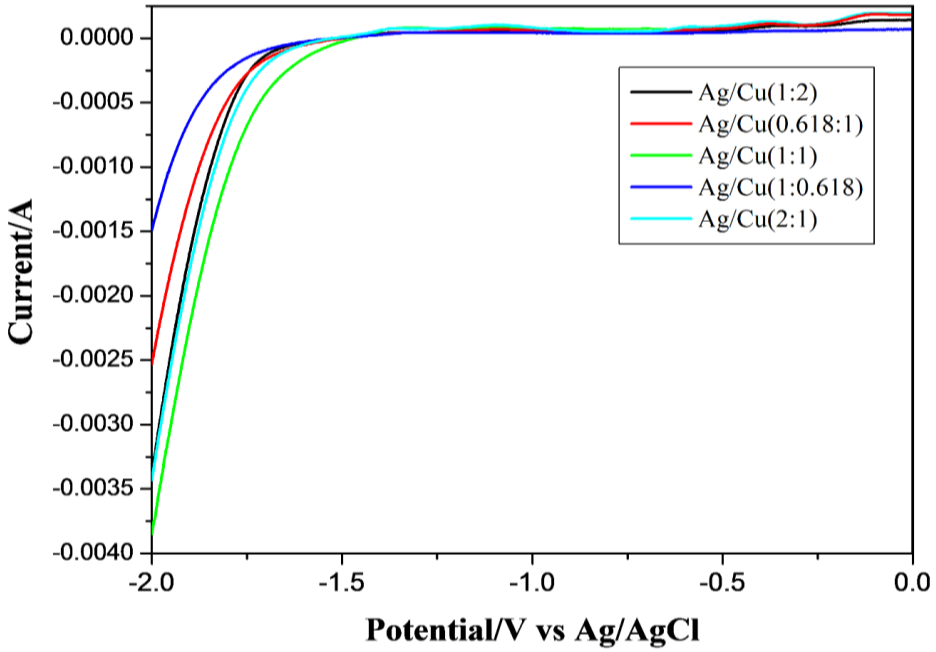

Figure 6. The Linear sweep voltammetry (LSV) curves on different proportions of Cu-Ag bimetallic nanomaterials in 1 mol·L^{-1} Na_2SO_4 solution at 50 ℃with the scan rate of 2 V s^{-1}.

To explore the electrochemical property of the products, the as-prepared Ag-Cu bimetal materials were used as the working electrode. Figure 5 is the cyclic voltammetric curves of the Ag-Cu bimetallic nanomaterials in1mol·L^{-1} Na_2SO_4 electrolyte, with the scan range from -0.3 V to +0.2 V and the scan rate of 0.1 V/s. The samples were prepared at 50 ℃ for 30 min, with the proportion of Ag with Cu is 1:0.618, 1:1, 0.618:1, 1:2 and 2:1, respectively. Obviously, when the ratio of Ag/Cu is 1:0.618, the curve shows more redox peaks and broaden electrochemical window. That is, it shows a better electrochemical activity, which is similar to the literature [27, 28].

Figure 6 presents the linear sweep voltammetry (LSV) curves of the electrochemical hydrogen evolution reaction (HER) of Ag-Cu bimetal catalytic in different mole ratio of Ag and Cu. It can be found that the more positive the potential, the higher the current density. Such trend is in keeping with the previous report [29]. When the reaction time is 30 min, the reaction temperature is 50 ℃ and the ratio of Ag/Cu is 1:0.618, the starting potential is the highest.

4. CONCLUSION

In this paper, Ag-Cu bimetallic nanomaterial with good morphology, excellent optical and electrochemical properties have been successfully prepared in mild and simple aqueous solutions by using sodium hypophosphite as a reducing agent. When the reaction temperature is 50 ℃ and reaction time is 30 min, Ag-Cu nanomaterial has good morphology. The surfactant sodium hexametaphosphate play an important role on the structure of the products. When the molar ratio of Ag/Cu is 1: 0.618, the reaction temperature is 50 ℃ and the reaction time is 30 min, the silver-copper bimetallic nanomaterial exhibits UV-Vis absorption peaks between 350-450 nm. In additions, it shows better electrochemical

activities. This convenient methodology might be used for both fundamental research and future manufacture of other bimetallic nanomaterial electrical devices.

ACKNOWLEDGEMENTS
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