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Recent Advances in Hydrogen Evolution Reaction Using First-Row Transition Metal Complexes as Catalyst

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ABSTRACT

The precise use of an electrocatalyst for the HER reaction mainly depends on synthesis cost, durability and over potential. Recently there is promising research for electrocatalyst synthesis using first row transition metals. Working towards this herein we present, synthesis, physio-chemical characterization and hydrogen evolution activity of amino guanidium metal naphthoate complexes. The obtained electrocatalysts were characterized by element analysis, IR spectra, UV-Visible spectroscopy, TG-DTA, and powder-XRD. The thermal behavior of these compounds has been studied by simultaneous TG-DTA techniques. The isomorphic nature of the metal complexes is evident from powder-XRD data.
Key Words: HER, electrocatalyst, cyclic voltammetry, aminoguanidine

1. INTRODUCTION

Hydrogen gas is a perfect, clean and pollution free fuel for the future generation. Production of hydrogen in recent era is mostly attained from burning of fossil fuels. But the main draw back in this method is evolution of large amount of greenhouse gases. The hydrogen production is also possible by means of electro, photo electrocatalytic, and water splitting process but it requires more efficient catalyst (1, 2) . Noble metals like platinum, iridium, and ruthenium exhibit a good catalytic activity but it is too expensive (3,4). Many metal oxide semiconductors like titanium oxide, nickel oxide and zinc oxide were extensively used as catalyst for both HER and OER (5-10). The high band gap energy and formation of free radicals in presence of UV light are considered as main disadvantage of these metal oxides (11,12). We found from literature that the conversion of dative bond to sigma bond between metal and nitrogen atom will increase the metal complex stability and thereby increases hydrogen evolution (13,14). Hence, it is extremely needed to synthesis a simple, low-cost metal complexes as catalyst to increase the evolution of hydrogen. The present work focused on synthesis of new transition metal complexes as electrocatalyst for hydrogen evolution.

2. MATERIALS AND METHODS

Chemicals and reagents were purchased commercially from Aldrich in pure grade. Solvents were purified and used according to a standard procedure. Thermal conductivity was determined in ELIII CHNS analyzers. The decomposition temperature for complexes was observed in the melting point Fisher-John apparatus. Infrared spectra which range from 4000-400 cm^{-1} were noted in the FT-IR-8000 Shimadzu spectrometer. Uv- visible spectral range at 180-400 nm were recorded in Varian-Cary 5000 analyzer. Thermogravimetric analysis was recorded in EXSTAR/63000. The powder diffraction pattern (metal complex) was verified in Siemens D-500. Metrohm Autolab M204 was used to analyze cyclic voltammetry. In which a three-electrode system is used and glassy carbon as a working electrode, Ag/Ag^{+} electrode as the reference electrode. Tetrabutylammonium hexafluorophosphate was used as a supporting electrolyte. The resulting solution was sparged with nitrogen for 10 minutes under a nitrogen atmosphere at a scan rate of -2.0 to +1.0V till constant current was obtained and then acid was added till the current get saturated which establish variation in the scan- rate-independent (15,16).

2.1 Synthesis of electrocatalyst

1-naphthoic acid with aminoguanidine bicarbonate was added to 20 ml of distilled water in 1:1 ratio. The resulting mixture was refluxed for 3 hours. The solid product thus obtained was drained off, flushed with methanol and kept for recrystallization. The above-prepared ligand was dissolved in 20 ml of water and gradually mixed to a of copper nitrate solution (0.24 g). The resulting mixture was evaporated in a water bath till the solution reduces to a partial amount of its original volume at a boiling temperature. After one day solid polycrystalline was found they were filtered, washed, and evaporated at room temperature Figure 1.
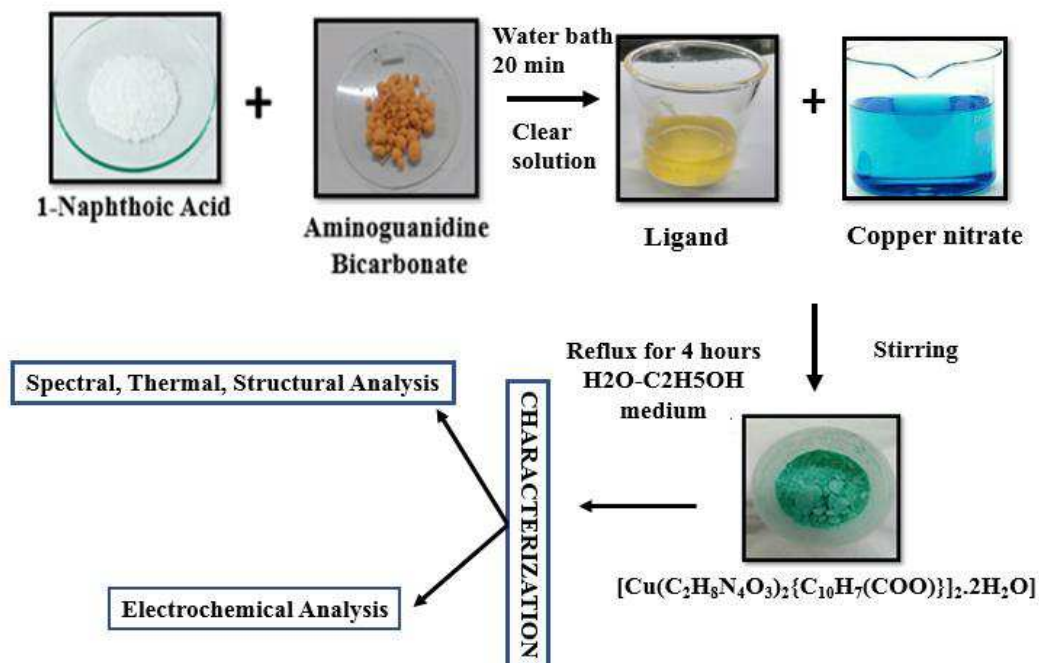

Figure 1. A pathway for electrocatalyst synthesis

3. **RESULTS AND DISCUSSION**

3.1 Spectral, thermal and structural characterization of electrocatalyst

The newly synthesized electrocatalyst was characterized by CHN analysis in Table I and were presented in Figure 2a. The broad peak in the range of 3677-3082 cm^{-1} is assigned for O-H stretching frequencies of naphthoate complexes. The N-H stretching frequency occurs at 3250 cm^{-1}. N-N stretching frequencies were found in the region of 1046-1108 cm^{-1}. Symmetric and asymmetric stretching frequencies of COO^{-} ion occur in the region 1348-1428 cm^{-1}. The vibration frequency for M-O bond appears in the range 461-443 cm^{-1} which confirms the linkage of metal with ligand.
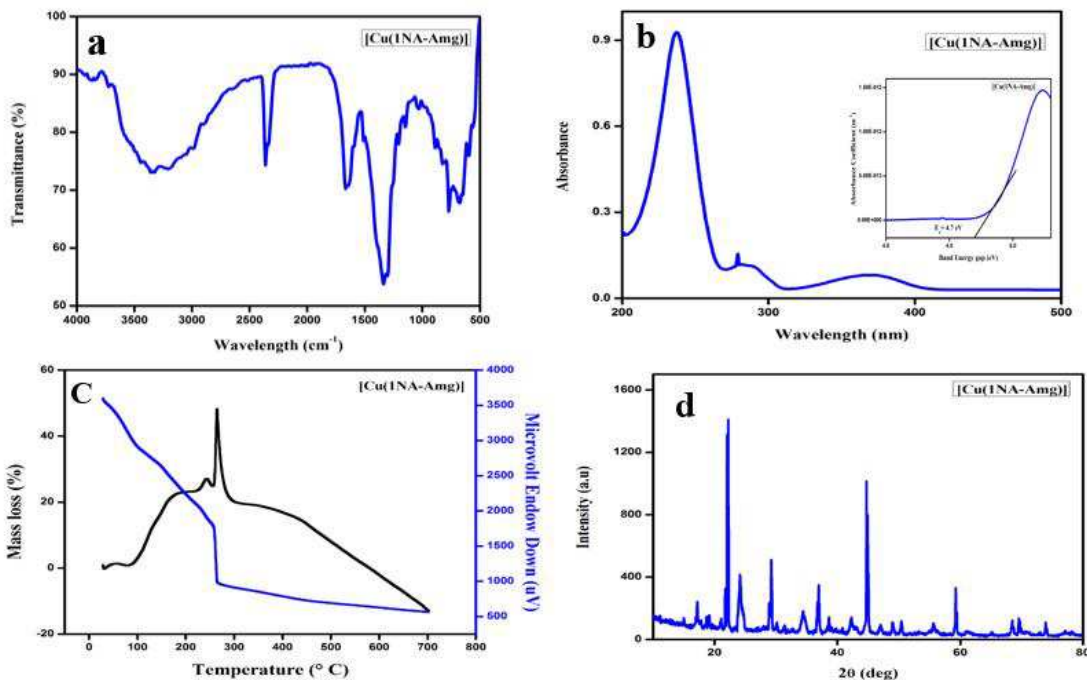

Figure 2. a) FT-IR, b) UV-Spectra, c) TG-DTA and d) XRD of [Cu(1NA-Amg)]

The electronic spectra of [Cu(1NA-Amg)] was shown in Figure 2b. The electronic spectra Cu (II) complex shows band at 220nm and 370 nm which is tentatively assigned to $^2B_{1g} \rightarrow {}^2E_g$, $^2B_{2g} \rightarrow {}^2A_{tg}$ transitions respectively. Tetragonally elongated octahedral geometry for the copper complex is evident from UV spectra. In addition, Tauc plot was drawn from UV spectra, in order to determine the bandgap energy for the maximum absorption peak and it was found to be 4.7eV. TG-DTA thermogram for the catalyst, is shown in Figure 2c, where mass loss starts from elimination of water molecule with endothermic peak. The dehydrated sample on further heating gives unstable compound after the removal of aminoguanidine moiety and was shown by exothermic peak. Finally, a stable copper oxide was formed as end product around 620^0 C.

The powder XRD pattern of electrocatalyst was shown in Figure 2d. The sharp and line broadening in the diffraction pattern confirms that the synthesized electrocatalyst have well defined crystalline structure with nano behavior in nature.

3.2 Electrochemical Characterization

CV experiments have been performed for the synthesized electrocatalyst in the range of −0. 5 to +2.0 V vs RHE, and the voltammograms thus obtained is given in figure 3a. In the CV curve during the 5th cycle one current maxima is observed at 0.74V vs RHE which can be easily distinguished from anodic part of the curve Table II. Variations in both position and with intensity of the peaks may to due incomplete reversibility. The same fact was also supported by difference in curve shape at different cycles. The area of the anodic peak was more which implies the nano-crystalline behaviour of electrocatalyst. It can be seen the electrocatalyst has more H_2 ion adsorption and as well as desorption current at 0.21mM. Hence CV curves confirms that the synthesized electrocatalyst has higher cathodic current density at 0.74 V vs RHE, hence Cu-AMG has act good electrocatalyst for hydrogen evolution.

Figure 3b shows Tafel plot of the electrocatalyst with slope 99 mV dec^{-1} implies that hydrogen evolution reaction will follow Volmer-Heyrosky mechanism. The slope was appreciably less than reported one (17) which implies that hydrogen evolution will be higher with the use of the electrocatalyst. The effect of the Cu-AMG electrocatalyst towards hydrogen evolution was measured in terms of TOF (Turn over frequency) which was found to be 27.4S^{-1}.
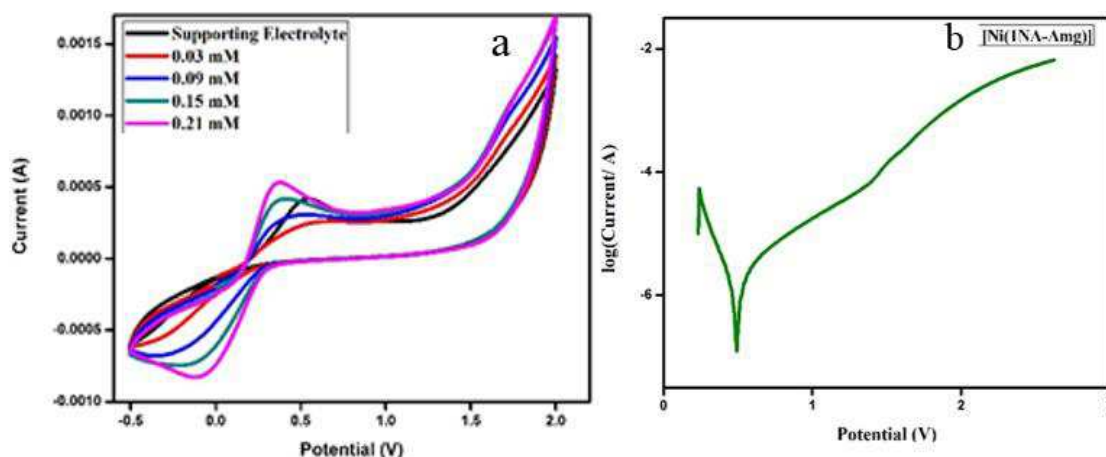

Figure 3. Cyclic voltammogram and Tafel plot of [Cu(1NA-Amg]

TABLE I. Analytical and Elemental data

Molecular Formula of the synthesized compounds	Colour	M.pt/ °C	Analytical data (%)					
			Carbon Fd. (calcd.)	Hydrogen Fd. (calcd.)	Nitrogen Fd. (calcd.)	Oxygen Fd. (calcd.)	Hydrazine Fd. (calcd.)	Metal Fd. (calcd.)
[Cu(C₂H₈N₄O₃)₂{C₁₀H₇(COO)}₂. H₂O]	Blue		50.38 (49.41)	7.75 (7.10)	19.58 (18.00)	11.18 (11.00)	11.3 (11.1)	11.3 (11.0)

TABLE II. Current densities found from CV curves recorded at potential range of -0.5 to 2.0 V vs RHE

Cycles	Current Density at Obtained Range
1st	0.68
2nd	1.02
3rd	1.06
4th	0.74
5th	0.74

4. CONCLUSION

A new, novel six coordinated, distorted octahedral copper complexes was synthesized with 1-naphthoic acid and aminoguanidine as mixed ligand. Several characterizations like structural, spectral and thermal studies were performed and confirms the bridging nature and stability of the complex. This copper complex exhibits an amazing electrochemical performance with Tafel slope value 99 mV dec^{-1} and 27.4S^{-1} TOF value. Hence this complex will be an excellent electrocatalyst for HER.

Acknowledgement

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