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Green coupling of 3,5-diamino-1*H*-1,2,4-triazole into the azo compound

**Mingzhen Xie, Jiaxu Gong, Jie Zhou, Jiaheng Wang, Yulong Cao,
Tianlong Zhou and Yatang Dai**

Experimental reaction process

3,5-Diamino-1,2,4-1*H*-triazole **1** is provided by Aladdin. Using an electrochemical workstation model chi760e from Shanghai Chen Hua Instrument. tests were performed on C, Cu, Ni and Pt electrodes. The constant voltage electrolytic cell is carried out in a glass cell that is indivisible at room temperature (25 °C). A magnetic stirrer is used to stir the solution during electrolysis. The one-pot preparation of 3,3'-diamino-5,5'-azo-1*H*-1,2,4-triazole **2** is carried out at 1 V voltage, and the reaction stops every molar amino triazole reaching 2 F mol^{-1}. The final color changes from colorless to deep red. Adjust PH to neutral with sulfuric acid, stir at 100 °C for 30 min and filter while hot (because of 3,3'-diamino-5,5'-azo-1,2,4-triazole **2** is insoluble in methanol, chloroform, toluene, DMSO, DMF, and is only slightly soluble in water at high temperature, impurities are removed by heating filtration), and dry the filtered substances in a vacuum oven for 12 h to obtain deep red powder. Materials are characterized by a range of physical characterization methods (infrared, carbon spectroscopy, thermal analysis).

Figure S1 The picture shows the color change under the reaction device and the final product **2**

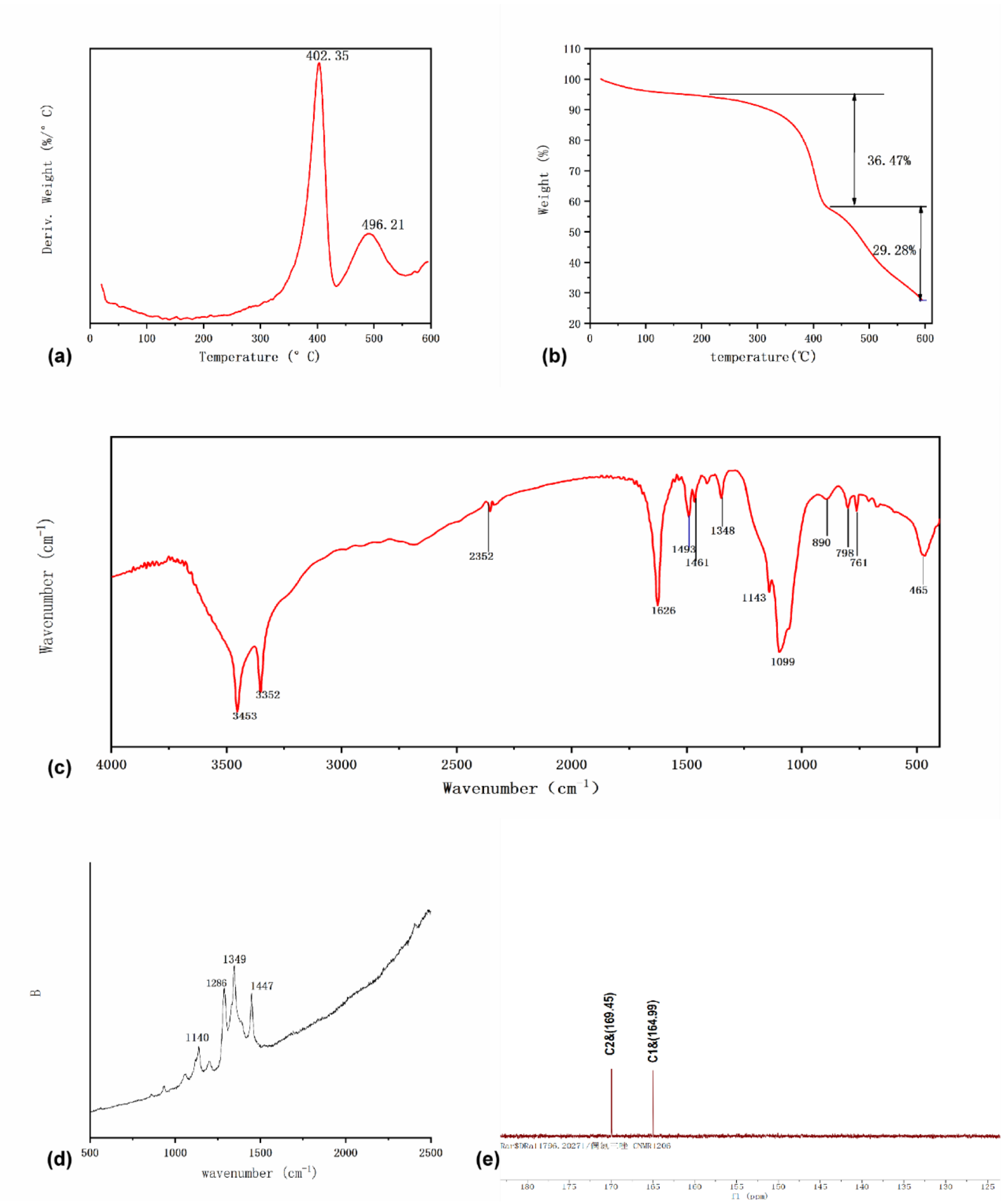

Figure S2 (*a*) Differential thermal analysis plot for 3,3'-diamino-5,5'-1*H*-1,2,4-triazole **2**; (*b*) Thermogravimetric analysis of 3,3'-diamino-5,5'-1*H*-1,2,4-triazole **2**; (*c*) Infrared analysis spectra of **2**; (*d*) Raman analysis spectra for **2**; (*e*) ^{13}C NMR spectrum of **2**.

Ni is the electrode to achieve the coupling of 3,5-diamino-1*H*-1,2,4-triazole **1** under 1 M sodium hydroxide electrolyte. In the later stage of electrolysis, black substances were observed to be attached to both the anode and cathode electrode sheets, and the current value gradually increased during the electrolysis process and suddenly dropped to the normal value, considering that the nickel electrode itself generated a new substance at a potential of 1 V, resulting in a change in current value. Consider the effect of $Ni(OH)_2$ first. Under the condition of carbon cloth as the working electrode voltage of 1.0 V and 1 M sodium hydroxide, 3,5-diamino-1*H*-1,2,4-triazole **1** was coupled with carbon cloth as the working electrode, and the electrolyte was 1M sodium hydroxide and 1 M nickel chloride to form Ni(OH)$_2$, and it was found that the current value increased by 2/3 times, and a large amount of black matter was deposited after a period of reaction, and no azo products were detected. Secondly, considering the influence of NiOOH, the nickel electrode was electrolyzed at 1.5 V voltage (1 M NaOH, 50 ml aqueous solution) for 1h to obtain NiOOH electrode, and electrolyzed to Q = 2 F mol^{-1} at 1.0 V voltage (without placing sodium hydroxide electrolyte) to obtain 1 mg 3,3'-diamino-5,5'-azo-1*H*-1,2,4-triazole **2**. Figure S3, *a* is the CV diagram of the prepared NiOOH electrode, and it can be seen that the oxidation potential of nickel hydroxyoxide is 0.75 V. The peak of NiOOH can be observed on XPS.

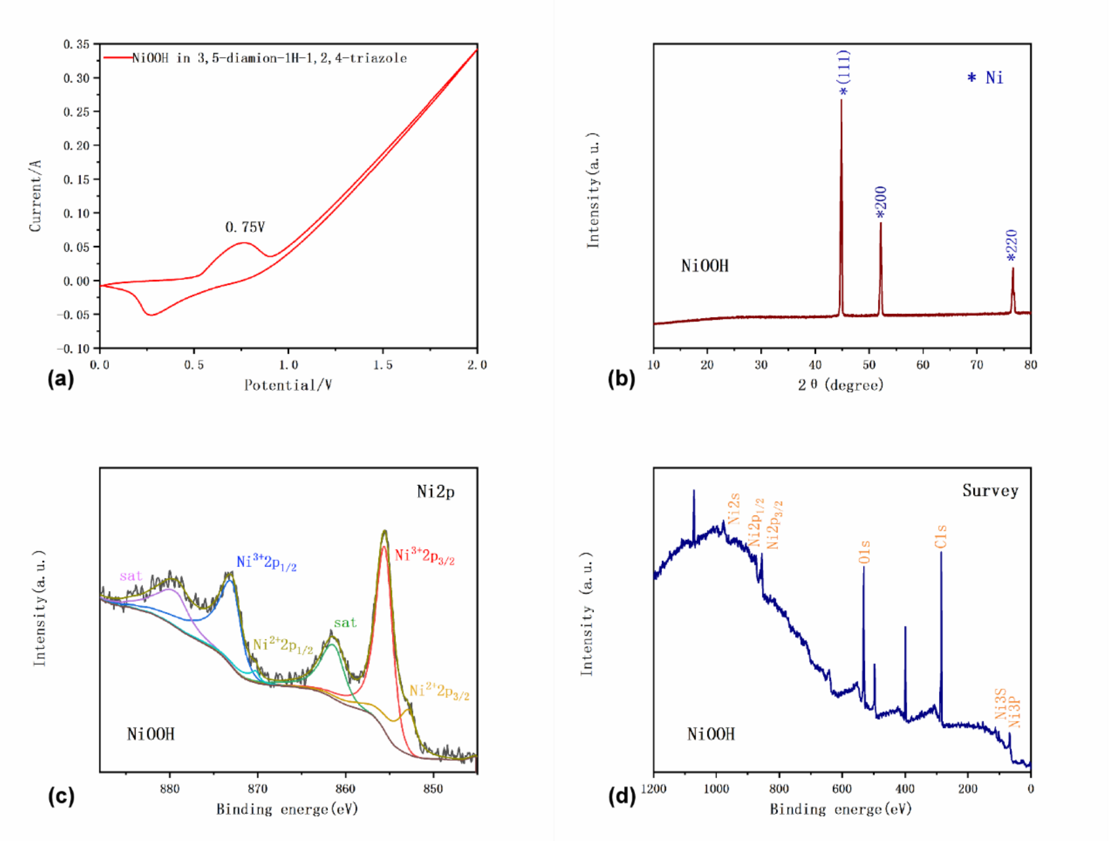

Figure S3 (*a*) The Cyclic Voltammogram (CV) curve of NiOOH in 0.1 M 3,5-diamino-1*H*-1,2,4-triazole **1** solution; (*b*) The XRD pattern of the as-prepared NiOOH;
(*c*) The XPS spectra of the Ni 2p; (*d*) The XPS survey spectrum of NiOOH

Electrolysis of sodium chloride produces the active substance sodium hypochlorite, realizing the coupling of 3,5-diamino-1*H*-1,2,4-triazole **1**. Sodium chloride (4 M) and 3,5-diamino-1*H*-1,2,4-triazole **1** were placed in aqueous solution (50 ml) at the same time, and the peak of the original sodium chloride could be seen to be masked, indicating that 3,5-diamino-1*H*-1,2,4-triazole **1** and chlorine inhibited each other. Using a two-step method, 4 M sodium chloride aqueous solution (50 ml) is electrolyzed to Q =2 F mol^{-1} at 1.4 V voltage to obtain sodium hypochlorite containing 0.14 mmol (iodine method), and then 0.42 mmol of 3,5-diaminotriazole is added at a ratio of 1:3, and its oxidation potential can be seen in Figure S4, *b* as 1.2 V, and finally the coupling product is obtained with a yield of 16.67%.

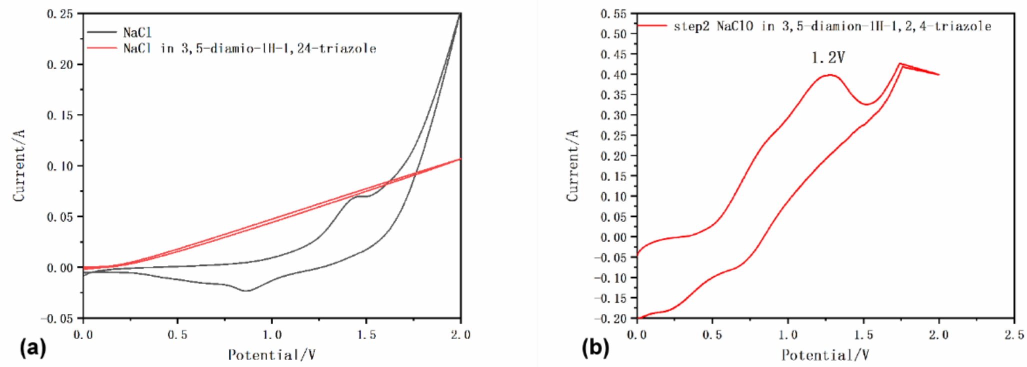

Figure S4 (*a*) The Cyclic Voltammogram (CV) curve of NaClO in 0.1M 3,5-diamino-1*H*-1,2,4-triazole **1** and NaClO; (*b*) The Cyclic Voltammogram (CV) curve of NaClO in 0.1 M 3,5-diamino-1*H*-1,2,4-triazole **1**