

Supramolecularly Modified Graphene for Ultrafast Responsive and Highly Stable Humidity Sensor

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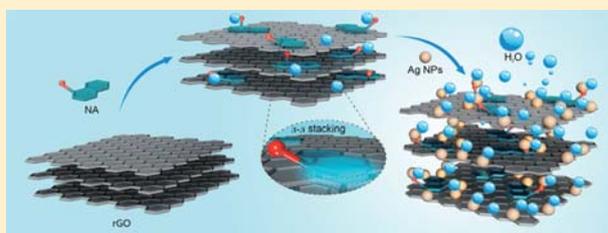
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Supporting Information

ABSTRACT: We report the fabrication and detailed characterization of an ultrafast responsive, excellently stable and reproducible humidity sensor based on a supramolecularly modified graphene composite. The fabricated humidity sensors exhibited a response and recovery time of less than 1 s, which is the lowest among the values found in the literature. In addition, various sensing performances of the fabricated humidity sensors were studied in detail, and the corresponding kinetic model and mechanism have also been deduced and described.



INTRODUCTION

Recently, humidity sensors (HSs) have attracted considerable attention because of their wide practical and potential industrial applications in the areas of production, process control, environmental monitoring, storage, and so on.^{1,2} An ideal HS should be cost-effective and possess high sensitivity, quick response time, broad operational range, and excellent durability and reproducibility.³ Recently, the performance of HSs, in terms of sensitivity and reproducibility, have been improved to a certain extent.^{4–6} However, it is still a challenge to fabricate efficient HSs with ultrafast response and high stability toward relative humidity (RH).⁷

Graphene oxide (GO) is a novel carbon material which possesses excellent properties and is therefore used in a variety of applications, for example, analysis and detection, biomedicine, polymer modifications, electronics, and optoelectronics,^{8,9} to name but a few. Because of the very particular and interesting properties of GO, such as a two-dimensional (2D) platform structure with numerous oxygen functional groups on the basal plane and its edges, such as hydroxyl, epoxy groups, and carboxylic acid groups, which are highly hydrophilic and reactive groups, GO-based materials are considered to be good candidates for fabricating efficient HSs.^{10–21}

These intrinsic properties make GO-based materials a promising candidate for fabricating efficient humidity nano-sensors.^{17–21} A survey of the literature revealed that covalently bonding with functional molecules was usually chosen as a major approach to obtain functionalized GO materials for efficient sensor applications.²² However, it is known that during

chemical modifications, the original perfect atomic lattices of pristine GO can be affected by chemical bonds which seriously affect the intrinsic electrical properties of graphene.²³ Therefore, to avoid such drawbacks, supramolecular assembly based on the noncovalent interactions is an alternative way which does not show any chemical effect on the intact structure of GO because of the noncovalent interaction.^{24,25} Importantly, to the best of our knowledge, such an approach of modifying GO using small-molecule supramolecular modification (SM) and its application in humidity sensors has never been reported in the literature.

This work reports the successful fabrication and characterization of an ultrafast responsive and highly stable humidity sensor based on supramolecularly modified graphene with naphthalene-1-sulfonic acid sodium salt (NA) and silver nanoparticles (Ag). Interestingly, the fabricated HS based on Ag-NA-rGO (where rGO indicates reduced graphene oxide) composite exhibited extremely excellent sensing characteristics, including ultrafast response and recovery time (≤ 1 s) for measuring RH between 11% and 95% in air at room temperature (25 °C) with the test frequency at 100 Hz, which have reached the record limit of the operating instrument. Furthermore, the fabricated HS exhibited quite high stability and reproducibility. The ultrafast response of the fabricated HS can be attributed to the introduction of a

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