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Moisture-triggered actuator and detector with high-performance: interface engineering of graphene oxide/ethyl cellulose

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ABSTRACT **Actuators that can directly convert other forms of environmental energy into mechanical work offer great application prospects in intriguing energy applications and smart devices. But to-date, low cohesion strength of the interface and humidity responsive actuators primarily limit their applications. Herein, by experimentally optimizing interface of bimorph structure, we build graphene oxide/ethyl cellulose bidirectional bending actuators — a case of bimorphs with fast and reversible shape changes in response to environmental humidity gradients. Meanwhile, we employ the actuator as the engine to drive piezoelectric detector. In this case, graphene oxide and ethyl cellulose are combined with chemical bonds, successfully building a bimorph with binary synergy strengthening and toughening. The excellent hygroscopicity of graphene oxide accompanied with huge volume expansion triggers giant moisture responsiveness greater than 90 degrees. Moreover, the open circuit voltage of piezoelectric detector holds a peak value around 0.1 V and exhibits excellent reversibility. We anticipate that humidity-responsive actuator and detector hold promise for the application and expansion of smart devices in varieties of multifunctional nanosystems.**

Keywords: actuator, humidity responsiveness, interface optimization, graphene oxide, detector

INTRODUCTION

Smart materials and structures with controllable intelligent response to external stimulus have become a major technological trend, which offers great application prospects in intriguing nano-system applications [1–3]. In this regard, smart actuators that reversibly change shape, size, or mechanical properties in response to magnetic, electric, thermal, moist, and optical stimuli have attracted considerable interest because of their potential applications in advanced artificial actuating and shape-memory structures and devices [4–6]. However, as an experimental fact, previous actuators, especially equipped with inorganic materials, are rarely in response to environmental humidity gradients [7]. In many ways, environment moisture state is an important factor that must be considered. Thus, catering for practical applications, there is an urgent need but it is still a significant challenge to develop a smart actuator with humidity responsiveness. Moreover, present researches on smart actuators mainly focused on bimorph structure consisting of two layers with the isotropic volume change factor [5,8]. However, low cohesion strength of contact interface is stills great challenge for bimorphs, which limit the application prospects to intriguing nanodevices.

Graphene oxide, contains a large-scale oxygen functional groups, showcases several exceptional functions (unique mechanical, thermal, hydrophilic, and optical properties) that can address emerging energy needs, in particular for the ever-growing market of portable and wearable smart actuation systems and energy conversion devices [9,10]. Graphene/polymer composites have also been used over a wide range of applications [11–13]. Recent observation has seen that graphene-based smart actuators have sprung up over the past decade. The smart actuators based on graphene fibers display deformation once exposed to moisture [7]. A self-controlled photoreduction of GO paper has been applied to prepare GO/RGO bilayer structures [14]. A bilayer multi-walled carbon nanotubes-graphite oxide paper curled depending on

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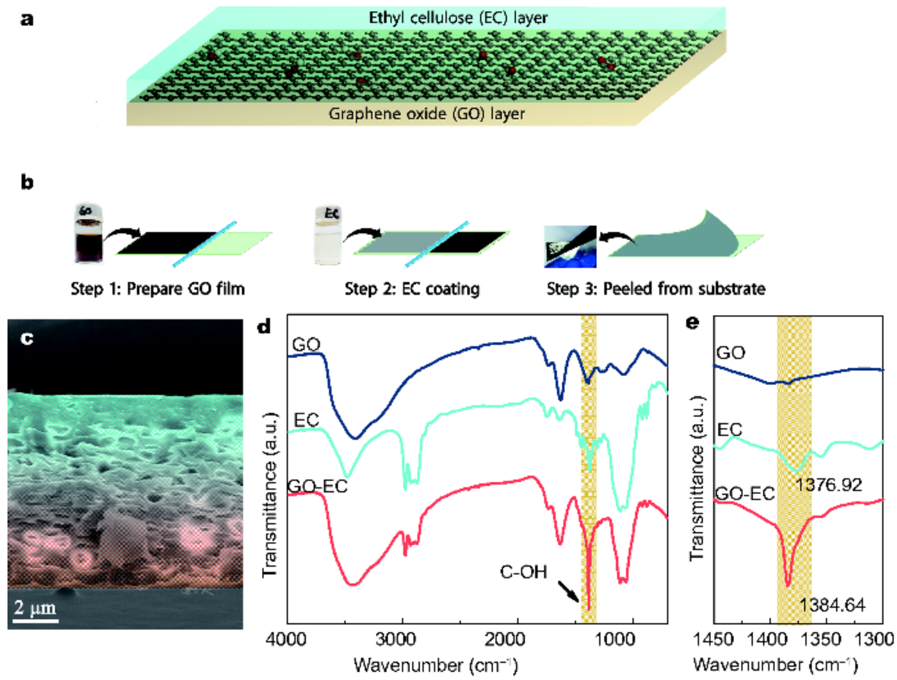

Figure 1 Preparation processes and characterizations of GO/EC actuator. (a) Bimorph structure of GO/EC. (b) Schematic illustration of the fabrication process of GO/EC actuator. (c) Cross-sectional SEM image of the GO/EC bimorph. (d) FT-IR spectra of GO, EC and GO-EC. (e) detail in FT-IR spectra of GO, EC and GO-EC.

humidity and/or temperature [15]. A humidity-driven graphene actuator was prepared by unilateral UV irradiation of GO papers [16]. Large area graphene was used as an ultrasensitive photothermal actuator that realizes a new prototype robotic motions under infrared-light stimuli [17]. A small graphene oxide sheet/polyvinylidene fluoride bilayer actuator exhibited large and rapid responses to multiple stimuli [18]. Single phase nematic GO liquid crystals with hydration-responsive was observed with folding and unfolding phenomena [19]. The rise of smart actuation systems triggered the fast increasing research upsurge in unique applications associated with its actuating performance.

Herein, by experimentally optimizing the interface of bimorph structure, graphene oxide/ethyl cellulose (GO/EC) bidirectional bending actuators are built (Fig. 1a), representing a first experimental case of bimorphs with fast and reversible shape changes in response to environmental humidity gradients. Meanwhile, we employ the actuator as the engine to drive piezoelectric detector. In this case, GO and EC combined with chemical bonds, successfully building a bimorph with binary synergy strengthening and toughening. The excellent hygroscopicity of graphene oxide accompanied with huge volume expansion triggers giant moisture responsiveness greater than 90 degrees. Moreover, the open circuit voltage of piezoelectric detector holds a peak value around 0.1 V. We anticipate that humidity-responsive actuator and detector hold promise for the application and expansion of smart devices in varieties of multifunctional nanosystems.

EXPERIMENTAL SECTION

Materials

Ethylcellulose (EC, medium viscosity, 18–22 mPa s) was purchased from Aladdin Industrial Co. (Shanghai, China). Sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), potassium permanganate ($KMnO_4$), anhydrous alcohol (EtOH), glass slide (25.4 mm×76.2 mm) and graphite powder (mesh: 300) were purchased from Sinopharm Group. Deionized (DI) water was used in all experimental processes.

Synthesis of GO

GO was prepared from natural graphite flakes by an improved Hummers method [20]. In detail, 2 g graphite powder and 100 mL concentrated H_2SO_4 were mixed in a

500 mL beaker with magnetic stirring in an ice bath. Then 12 g $KMnO_4$ was slowly added. The mixture was stirred for 2 h at 0°C and another 24 h at 35°C. After cautiously adding, dropwise, 200 mL H_2O and 20 mL 30% H_2O_2 at 95°C, the color of the solution changed from black to purple and finally became bright yellow. The final product was washed with HCl (5%) and deionized water in turn and separated by centrifugal until the supernatant was close to neutral. The collected product was dispersed in deionized water followed by an ultrasonic treatment. Finally, the concentration of GO solution was quantified as 10 mg mL^{-1}.

Fabrication of GO film

First, GO solution (10 mL) was sealed in a glass bottle with ultrasonic treatment. After 60 min, a homogenized, gray-black suspension was prepared. Then, the as-obtained suspension was uniformly coated on a glass slide substrate and heated on a flat heater at 45°C. Approximately 10 min later, dried GO film was obtained.

Fabrication of GO/EC flexible film

The EC solution was prepared as follow: EC powder (20 g) and EtOH (200 mL) were sealed in a glass bottle with magnetic stirring at room temperature. After 24 h, a homogenized, translucent gelatin was obtained. After that, 0.5 mL as-prepared gelatin was coated onto GO film and then dried at room temperature for 10 min. Finally, the dry GO/EC flexible film was peeled from the substrate very easily, getting a freestanding flexible film.

Assembly of piezoelectric detector

The piezoelectric detector is composed of two parts: piezoelectric layer and actuator layer. Actuator layer is as-prepared GO/EC flexible film. Piezoelectric layer is a flexible component comprising a 28 μm thick piezoelectric PVDF polymer film with screen-printed Ag-ink electrodes. Testing wires were connected to the top and bottom silver electrodes with two crimped contacts. The end of the testing wires was fixed on a glass slide with a silver paste and a thin layer of 3M7413D tape.

Characterization

The field-emission scanning electron microscopy (FE-SEM) images were taken on a JEOL JSM-6700F SEM. Mechanical effect of humidity sensing properties were measured by home-made setups. Dynamic water vapor sorption analysis was measured by DVS, SMS Intrinsic. Open circuit potential (OCP) was performed on a Zahner IM6 electrochemical workstation. FT-IR spectra were carried out by Nicolet 8700 infrared spectrometer (Thermo Scientific Instrument Co. U.S.A). Experimental demonstrations of the actuator were captured by using a digital camera.

RESULTS AND DISCUSSION

The GO/EC bimorph actuator was fabricated by a simple two-step coating process (Fig. 1b). Fig. 1c clearly shows the cross-sectional laminated structure of the GO/EC actuator, which was combined together tightly without delamination. As well-known, EC is a derivative of cellulose in which some of the hydroxyl groups on the repeating glucose units are converted into ethyl ether groups. GO, a hexagonal carbon network with both sp^2- and sp^3- hybridized carbons, possesses a multitude of oxygen-containing functional groups (–OH, –COOH, etc.) on its surface, which further improve the interfacial interactions with the EC by numerous H-bonding networks [21]. FT-IR spectra of GO, EC, and GO-EC are shown in Fig. 1d, e. Compared with the pure GO and EC, GO-EC exhibited a significantly enhanced peak at 1,384 cm^{-1}, which is ascribed to the O–H deformation vibrations of tertiary C–OH [22]. The intensity of the absorption peak is related to the probability of molecular transition. Also, the peak has shifted slightly to higher wavenumbers due to the inductive effect [23,24]. Moreover, high-resolution synchrotron radiation photoelectron spectroscopy (HR-SRPES) of the C 1s components (Fig. S2) revealed that four oxygen-related peaks corresponding to C–OH, C–O–C, C=O, and O–C=O groups in GO/EC composite slightly shifted toward lower binding energy from GO (285.7, 286.95, 288.55, and 289.45 eV) to GO/EC (285.4, 286.75, 288.2, and 289.05 eV), indicative of cooperation between GO and EC [25]. Besides, the relative areas of all peaks are changed in degree, in particular, the increase of the C–OH groups, suggesting that more C–OH groups are generated [26]. These results mentioned above indicate that more C–OH bonds were formed between GO and EC, making the bimorph tightly bonded.

It is well-known that GO is extremely sensitive to changes in ambient humidity [27]. Fig. 2a schematically shows the humidity-triggered bending actuation mechanism. The adsorption and desorption process of water molecules in GO layers could cause the fast and reversible expansion/contraction of GO films. The humidity-driven bending properties in Fig. 2c are measured by a home-made setup in Fig. 2b. First, we demarcate the relative humidity levels at different heights from the water surface with a humidity meter. Then, the bending angles at dif-

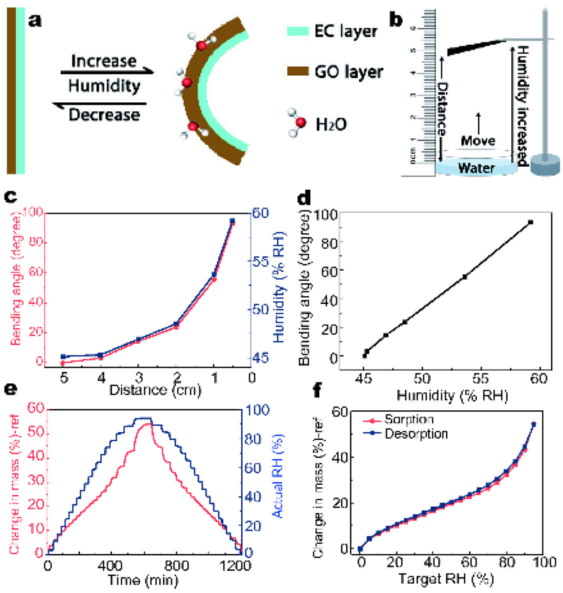

Figure 2 Demonstration and evaluation of the bimorph as a practical humidity actuator. (a) The mechanism of humidity-responsive actuator. (b) A home-made setup to measure the bending angle of the humidity actuator. (c) Bending angle and humidity as a function of the distance between the water and actuator. (d) Bending angle as a function of humidity. (e) Relative humidity and weight change *versus* time of GO. (f) Dynamic water vapor sorption isotherm analysis for GO.

ferent heights are measured by a goniometer. From these two parameters, we acquire the relative relations of bending angles *vs.* relative humidity, as shown in Fig. 2d. The relationship between bending angles and relative humidity is linear. Movie S1 (Supplementary Information 2) shows that the actuator bent when it moved close to the water surface and restituted when it moved away from the moisture. To further understand the mechanism of the humidity-triggered bending actuation, dynamic water vapor sorption isotherm analysis for GO was carried out. As shown in Fig. 2e and f, the mass of GO change with moisture content, which indicates that water vapor adsorption and desorption was a dynamic as well as a reversible process.

Benefited from this unique humidity-triggered bending actuation, a practical hygro-sensitive piezoelectric detector became possible to be achieved. A schematic demonstration of the structure for the detector is shown in Fig. 3a. The structure of the detector is composed of such parts: actuator bilayer, top electrode, piezoelectric layer and bottom electrode. Fig. 3b is a digital photograph of the detector. With periodical alternation of the moisture, the piezoelectric detector brings a remarkable periodic voltage output. Fig. 3d and e show the transient voltage responses of the detector driven by moisture gradient. In

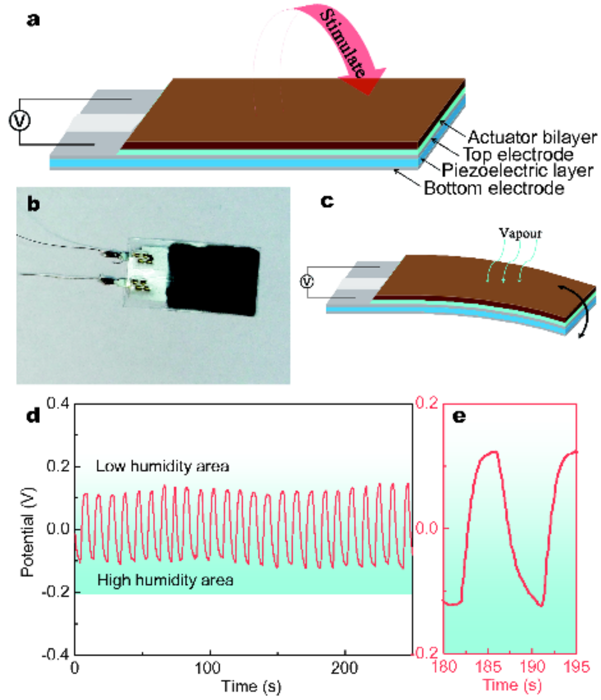

Figure 3 Demonstration of the humidity-responsive actuator as a practical piezoelectric detector. (a) Schematic demonstration of the structure for the detector. (b) Photograph of the detector. (c) A moisture-triggered detector. (d, e) Transient responses of the detector driven by moisture.

this model, the results show that the material has a sensitive response and excellent cyclic performance. Moreover, the as-established device can be readily built on anywhere that needs the sensor to respond quickly to changes in ambient humidity. In this regard, the humidity-triggered actuator and hygro-sensitive piezoelectric detector indicate a promising direction for the development of advanced multi-stimulus triggered actuators and detectors in the fields of soft-bodied robots, microfluidic handling system, and high-performance transducers.

CONCLUSIONS

In conclusion, a humidity-triggered actuator and hygro-sensitive piezoelectric detector based on graphene oxide/ethyl cellulose bimorph are presented here. In order to achieve high cohesion strength of the interface and sensitive response to humidity, interface optimization strategy and GO with abundant hydroxy were developed, which possess fast and reversible shape changes in response to environmental humidity gradients. In this case, graphene oxide and ethyl cellulose are combined with chemical bonds, successfully building a bimorph with binary synergy strengthening and toughening. Excellent hygroscopicity of graphene oxide accompanied with huge volume expansion triggers giant moisture responsiveness greater than 90 degrees. Meanwhile, we employ the actuator as the engine to drive piezoelectric detector. Moreover, the open circuit voltage of piezoelectric detector holds a peak value around 0.1 V and exhibits excellent reversibility. We anticipate that the humidity-responsive actuator and detector hold promise for the application and expansion of smart devices in varieties of multifunctional nanosystems.

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Author contributions Wu C conceived the idea, co-wrote the paper, supervised the entire project and is responsible for the infrastructure and project direction. Yang B experimentally realized the study, analyzed the data and co-wrote the paper. Bi W, Zhong C and Huang M experimentally realized the study, Ni Y and He L supervised the whole experimental procedure and co-wrote the paper. All authors discussed the results and commented on and revised the manuscript.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

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湿度驱动的高性能致动器与传感器: 界面工程调控氧化石墨烯与乙基纤维素

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摘要 致动器可以将外界环境中的能量直接转换成机械能, 在能源应用和智能设备上有着广阔的应用前景. 但迄今为止, 界面接触强度较低以及湿度响应是制约驱动器发展的瓶颈问题, 限制了其实际应用. 本文从实验上构建了优化双层膜结构驱动器界面接触的模型, 所构建的氧化石墨烯与乙基纤维素双层膜致动器对于环境湿度的变化具有快速可逆的响应性, 同时可以驱动压电探测器. 此结构模型中, 氧化石墨烯与乙基纤维素之间通过化学键结合, 成功地构建了机械强度和韧性协同增强的双层膜驱动器. 由于氧化石墨烯的优异吸湿特性, 同时伴随着明显的体积膨胀, 引起双层膜驱动器对于湿度变化超过90度弯曲的响应. 同时, 构建的压电传感器具有优异可逆性的0.1 V开路电压. 我们期望湿度响应驱动器和传感器有望在各种多功能纳米系统中得到应用并能服务于智能设备领域.

