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A Zn_2GeO_4–ethylenediamine hybrid nanoribbon membrane as a recyclable adsorbent for the highly efficient removal of heavy metals from contaminated water†

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Zn_2GeO_4–ethylenediamine (ZGO–EDA) hybrid nanoribbons have been synthesized on a large-scale and directly assembled to membranes, which exhibit an excellent recyclability, high selectivity, and good thermal stability for highly efficient removal of heavy metal ions, *i.e.*, Pb^{2+}, Cd^{2+}, Co^{2+}, and Cu^{2+}, from contaminated water.

Toxic heavy metal ions, such as Pb^{2+}, Cd^{2+}, Co^{2+}, and Cu^{2+}, often originate in large quantities from nuclear, metallurgical, tannery, mining, and battery plants. Unlike some organic pollutants, these toxic heavy metal ions are non-biodegradable and can exist for a long time and thus will cause serious environmental and public health problems.[1] So, it is necessary to remove these metal ions from industrial effluents for their subsequent safe disposal. The adsorption-based process is one of the most promising strategies; however, most of the adsorbents usually operate by a modified process using functionalized thiol,[2] amino,[3] hydroxyl,[4] carboxylic[5] or sulfur groups,[6] and have some problems, such as the lack of enough active surface sites, difficulties of separation and regeneration of absorbents from water. Therefore, searching and designing advanced adsorbent materials for target ions have been actively conducted.

One dimensional (1D) inorganic–organic hybrid materials have attracted considerable attention because they exhibit not only the advantages of combining both inorganic and organic components, but also more comprehensive functions. So far, a variety of binary compounds based inorganic–organic hybrid nanomaterials have been reported, and studies performed have been focused on their preparation and physical properties.[7,8] However, few reports are available on ternary compound–organic hybrids and their applications, because of the considerable difficulties in their synthetic process.

Herein, a novel inorganic–organic hybrid material, *i.e.*, Zn_2GeO_4–ethylenediamine (ZGO–EDA) nanoribbons, has been synthesized on a large scale for the first time using a facile solvothermal route. Importantly, a membrane made of this new hybrid material, as a recyclable, highly selective, and good thermal stable adsorbent, can highly efficiently remove heavy metal ions, *i.e.*, Pb^{2+}, Cd^{2+}, Co^{2+}, and Cu^{2+}, from contaminated water.

ZGO–EDA hybrid nanoribbons have been synthesized on a large-scale using a solvothermal method (see ESI† for the detailed synthetic procedure). Field-emission scanning electron microscopy (FE-SEM) images, Fig. 1a and b, show that the products consist of a large quantity of fascinating, twisted, very long nanoribbons, typically, with a length up to hundreds of micrometres (Fig. S1, ESI†). The X-ray diffraction (XRD)

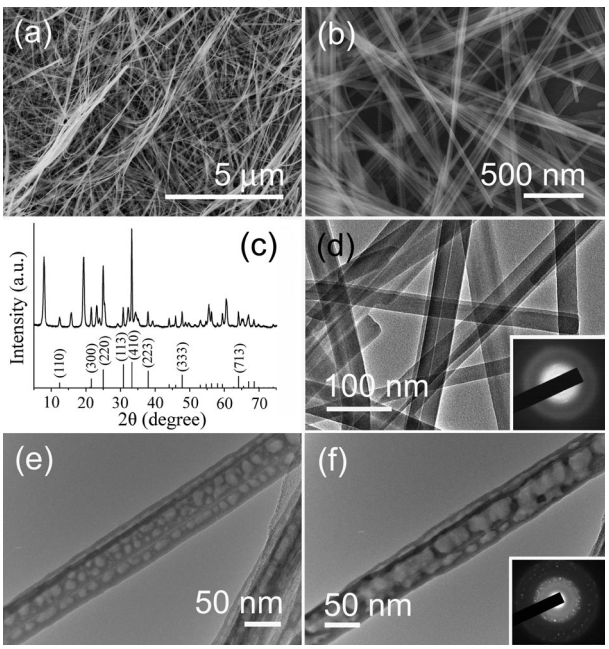

Fig. 1 (a–d) Low-, high-magnification SEM images, XRD pattern, and TEM image of the as-synthesized ZGO–EDA nanoribbons, respectively. (e, f) TEM images showing the nanoribbons by *in situ* electron beam irradiation inside the TEM for 10 s and 20 s, respectively.

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pattern of as-synthesized nanoribbons is shown in Fig. 1c (top). Referring to the pattern (Fig. 1c, bottom) of a standard ZGO powder, most of the peaks can be readily indexed to the rhombohedral phase of ZGO with lattice constants of $a = b = 14.231$ Å, $c = 9.53$ Å. Interestingly, the other peaks display a series of typical diffraction peaks (starting from a low angle) at $2\theta = 7.90°$, $15.82°$, $23.14°$ and $32.22°$, with d-spacing of 11.182 Å, 5.597 Å, 3.840 Å and 2.776 Å, respectively, thus showing a decrease by degrees among these spacings, corresponding to (001), (002), (003) and (004) planes of the EDA molecules,[8b] suggesting that chemical bonds form between the EDA molecules and ZGO. Consequently, the product is ZGO–EDA inorganic–organic hybrid nanoribbons. A transmission electron microscopy (TEM) image, Fig. 1d, indicated that the nanoribbons have a uniform width (50–60 nm) along their entire lengths. Due to their organic constituent within this hybrid, these ribbons exhibit extreme sensitivity to the electron beam irradiation, the product undergoes amorphization very quickly during the TEM investigation, as suggested by the electron diffraction (ED) pattern (bottom-right inset), which is a frequently observed phenomenon for inorganic–organic hybrids.[7b,8c,9] Interestingly, on extending the period of irradiation, these ribbons became porous and polycrystalline ZGO material, Fig. 1e (10 s) and Fig. 1f (20 s), which originated from the recrystallization of many ZGO particles within these ribbons under *in situ* irradiation (Fig. S2, ESI†).

Infrared (IR) (Fig. 2a), energy dispersive X-ray (EDX) (Fig. S3, ESI†), and X-ray photoelectron spectroscopy (XPS) (Fig. S4, ESI†) spectra further confirmed the hybrid components of this synthesized material. As shown in Fig. 2a, the interaction between EDA molecules and inorganic components was demonstrated by the absorption peaks at 3336, 845 and 803 cm^{-1}, assigned to the stretching and out-of-plane bending vibration of $-NH_2$, which show a red shift of 19, 72 and 34 cm^{-1}, respectively, compared to the absorption peaks of pure EDA, which showed molecular stretching at 3355 cm^{-1} and bending at 917 and 837 cm^{-1}. Thermogravimetric (TG) analysis, which was performed under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}, Fig. 2b, revealed that ~1.6% weight loss occurred before 200 °C, which can be attributed to the loss of water and free EDA molecules, and a large weight loss (~6.4%) occurred at 438 °C, due to the evaporation or decomposition of the EDA within these hybrid nanoribbons. Herein, the weight loss occurred at the temperatures above the boiling point (117 °C) of the EDA, indicating that an intimate interaction existed between the EDA and inorganic Zn_2GeO_4 frameworks and the removal of the EDA from the hybrid material is more difficult. After being annealed at 500 °C for 3 h, the EDA molecules are completely lost from the as-synthesized hybrid, and then the material is made up of pure ZGO (Fig. S5†), suggesting that the as-synthesized ZGO–EDA hybrid nanoribbons possess a high thermal stability.

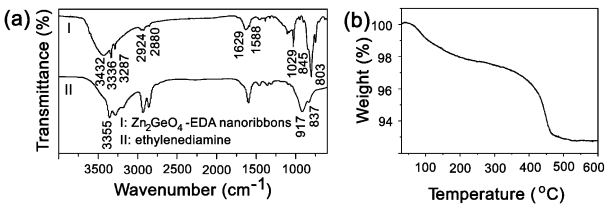

Fig. 2 (a, b) IR spectra and TG curve of the as-synthesized ZGO–EDA hybrid nanoribbons, respectively.

Recent studies suggested that II–VI compound based hybrids have been synthesized by incorporating segments (*e.g.*, slab, chain) of a compound and organic spacers *via* coordinate or covalent bonds.[7,10] It is also known that alkylamines can mediate the crystal growth and control the 1D morphology of the inorganic–organic hybrids through H bonding.[8b,11] So, we presume that the EDA molecules can intercalate into the ZGO frameworks to form the hybrid nanoribbons; in this process, the ZGO quantum dots are produced first and then are connected by the EDA molecules through (N–H···O–Ge–Zn) H bonding, which is confirmed by a broad peak at 3432 cm^{-1} in the IR spectrum, Fig. 2a. This is why the as-synthesized hybrid has good thermal stability, and the removal of the EDA from the hybrid is more difficult, Fig. 2b.

Paper-like membranes made of the ZGO-EDA hybrid nanoribbons have been constructed according to a modified process available in the literature,[12] and show good thermal stability, high selectivity, and excellent recyclability as an adsorbent for the removal of heavy metallic ions from contaminated water (even when the water has a mixture of heavy metallic ions and sodium ions, Table S1, ESI†). White floccules made of a large amount of the as-synthesized product dispersed in ethanol can be directly assembled to a free-standing membrane, top left inset of Fig. 3a. (With the support of nonwoven, the ZGO–EDA hybrid nanoribbon membranes possess improved mechanical properties, see ESI† for details). To examine the performances of as-prepared membranes as adsorbents for removing heavy metal ions from water, a solution containing Pb^{2+}, Cd^{2+}, Co^{2+} and Cu^{2+}, respectively, was prepared as an imitator. As described in Fig. 3a, the adsorption capacity of the membrane increases gradually with increase in the initial concentration of salt aqueous solutions, following an order of $Pb^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+}$ (Fig. S6, ESI†).[13] Among four heavy metal ions, the membrane exhibited high adsorption capacity for Pb^{2+}, namely, ranging from 37.1 to 53.7 mg g^{-1} with the initial concentration increasing from 2.5 to 5.0 and 10 mM. As the membrane shows good adsorption capacity for Pb^{2+}, we further discovered that an extension of the adsorption time leads to an increase in the adsorption amount of Pb^{2+}, *i.e.*, from 27.5 to 58.7 mg g^{-1}, 46.6 to 71.3 mg g^{-1}, 51.2 to 74.6 mg g^{-1} within 1 h with the initial concentrations of Pb^{2+} being 2.5 mM, 5.0 mM, and 10 mM, respectively, Fig. 3b. Clearly, the adsorption equilibrium is achieved in as fast as 1 h, and further extending the adsorption time cannot result in any obvious change in the adsorption amount. The desorption performances of the ZGO–EDA hybrid nanoribbon membranes were also examined by using disodium EDTA as an efficient eluent. During this process, the membranes were first immersed in a solution with 5 mM of Pb^{2+} for 2 h, and then eluted by 10 mM of disodium EDTA. Excitingly, the desorption efficiency of the adsorbed Pb^{2+} on the membranes can reach as high as 91.5% within 20 min, and 94.2% within 90 min, Fig. 3c, indicating that the high desorption efficiency can be obtained in a very short time. In addition, the membrane was also confirmed to have a good recyclability for

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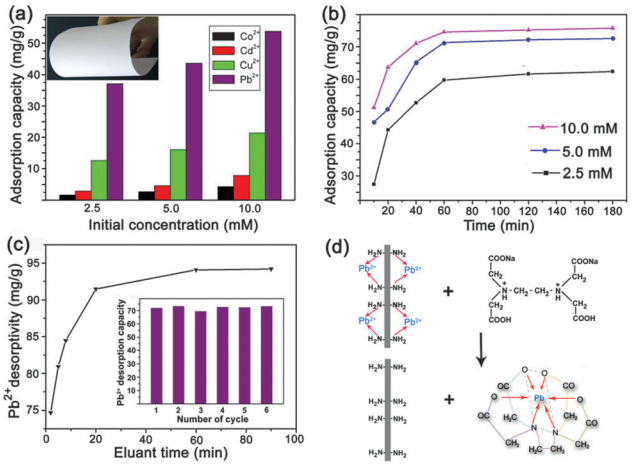

Fig. 3 (a) The adsorption capacity of the membrane to four different metal ions with concentrations of 2.5 mM, 5.0 mM, and 10.0 mM, respectively, and adsorption time of 2 h. A top-left inset showing a photograph of the as-prepared paper-like ZGO-EDA hybrid nanoribbon membrane. (b) Effects of the adsorption time on the adsorption capacity of Pb^{2+} on the ZGO-EDA membrane with the initial concentrations of 2.5 mM, 5.0 mM, and 10 mM, respectively. (c) The desorption of Pb^{2+} from the as-adsorbed ZGO-EDA hybrid nanoribbon membranes using 10 mM of disodium EDTA as an eluent. A bottom-right inset showing six cycles of reuse of the ZGO-EDA nanoribbon membrane. (d) A possible desorption mechanism of Pb^{2+} from the membrane in disodium EDTA solution.

the removal of Pb^{2+} from contaminated water, and after six cycles of reuse of the membrane, the adsorption capacity for Pb^{2+} did not exhibit any conspicuous decrease, bottom-right inset of Fig. 3c. Accordingly, the novel hybrid recyclable membranes with high removal efficiency and fast desorption equilibrium would be more practical in decontamination of polluted water. Finally, a possible desorption mechanism (Fig. 3d) shows that a lot of $-NH_2$ groups in EDA molecules within the hybrid nanoribbons have an intimate contact with metal ions, *e.g.*, Pb^{2+}, in solutions; however, when the membranes were eluted by the disodium EDTA solution, stronger coordination ligands in the disodium EDTA would have a stronger bonding with Pb^{2+}, making Pb^{2+} easily desorb from the membranes. Thus, with a rapid release of Pb^{2+}, the membrane quickly restores to its original state and can be reused as a recyclable adsorbent.

In summary, ternary ultralong Zn_2GeO_4–ethylenediamine inorganic–organic hybrid nanoribbons were firstly synthesized on a large-scale by a one-step mild solvothermal route and can be directly assembled to a novel membrane. The as-fabricated membrane as an absorbent possesses excellent recyclability, high selectivity, and good thermal stability, and can highly efficiently remove heavy metal ions, *i.e.*, Pb^{2+}, Cd^{2+}, Co^{2+}, and Cu^{2+}, from contaminated water. The fascinating membranes may open up a new avenue toward heavy metals removal and meet the growing demands for environmental purification from industrial effluents for subsequent safe disposal.

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