

## COMMUNICATION

## From macropore to mesopore: diatomite reassembled into a multifunctional composite†

Cite this: *RSC Adv.*, 2014, 4, 23690

Hong-Wen Gao,\* Gang Xu and Yue Wang

Received 5th February 2014

Accepted 7th May 2014

DOI: 10.1039/c4ra01002g

www.rsc.org/advances

A 'dissolving first and then reassembling' way was presented for preparing a multifunctional composite with diatomite and an antistatic agent SN. The composite binding of SN@SiO<sub>2</sub> with a sulfonic dye formed the color antistatic agent. Also, it captured nonylphenol from wastewater with a partition coefficient of  $5.37 \times 10^4$  L kg<sup>-1</sup>, and the waste sludge produced was calcined to form mesoporous sieves.

About 20 countries own diatomaceous earth mines worldwide. Diatomite reserves are more than two billion tons, where approximately 1% is mined annually.<sup>1</sup> It is a fine-grained, low-density biogenic sediment, which consists of amorphous silica (SiO<sub>2</sub>·nH<sub>2</sub>O) derived from opalescent frustules of diatoms.<sup>2</sup> Owing to the advantages of a highly porous structure, low density, good stability and low price, diatomite has a wide range of applications, including aids for beer filters,<sup>3</sup> fabrication of porous ceramics,<sup>4</sup> decolorization in food production and wastewater cleanup.<sup>5–8</sup> Waste diatomite accounts to more than 4.7 million tons annually only in the Taiwan area,<sup>9</sup> either abandoned for polluting the environment or disposed cheaply as a building filler. Its recycling utilization is an urgent task so as to avoid resource wasting and environment pollution. Aivalioti *et al.* modified diatomite by heat treatment to increase the effective void ratio for raising the adsorption capacity to aromatic compounds.<sup>10</sup> The surface modification of diatomite with ferric oxide improved the removal rate of arsenic.<sup>11</sup> Chaisena *et al.* presented the modification with sulphuric acid by the hydrothermal method to successfully prepare sodium zeolite, which can be used as a catalyst, an ion exchanger, a sorbent and a water softener.<sup>12</sup>

However, conventional surface modification usually exhibits some serious defects, such as inapparent improvement of adsorption capacity, easy separation of active groups, difficult

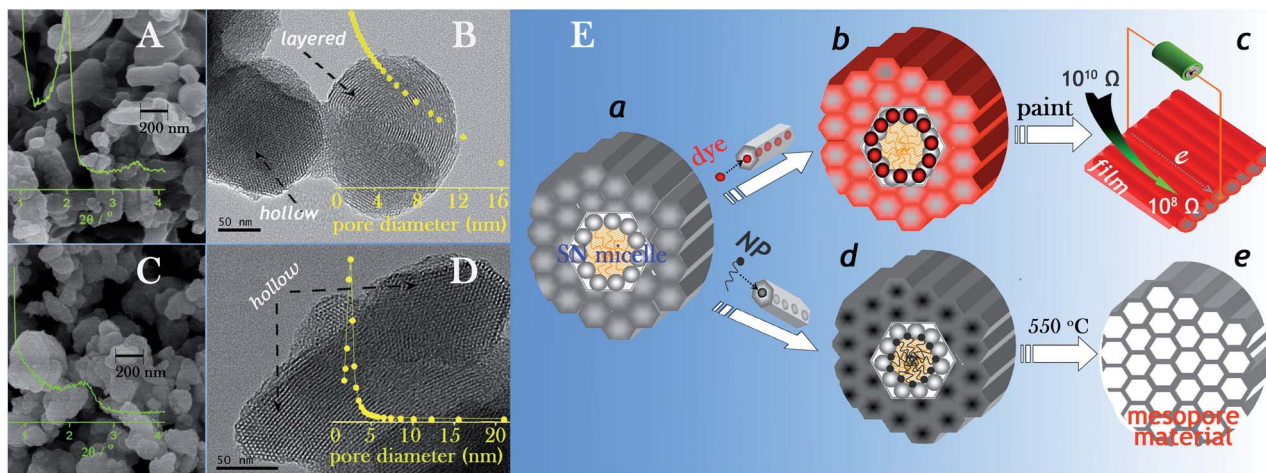
reuse as well as causing secondary pollution.<sup>13</sup> In order to overcome these disadvantages, it is necessary to design a simple process to prepare a cost-effective diatomite composite with affluent raw materials. This work presented a 'dissolving first and then reassembling' way, and turning a diatomite into a multifunctional composite was attempted.

From the infrared (IR) spectra of the composite (Fig. S1A, ESI†), the Si–O absorption peak changed from 1151 to 1058 cm<sup>-1</sup>, may be attributed to the interaction of octadecyl dimethyl hydroxyethyl quaternary ammonium nitrate known as antistatic agent SN (chemically structured in Fig. S1A, ESI†) with a negatively charged SiO<sub>2</sub> layer. The peaks at 3342, 2922, 2853 and 1383 cm<sup>-1</sup> indicated that SN is successfully embedded. From thermal gravimetric analysis (TGA), the loss of weight between 200 and 500 °C indicated that approximately 50% SN was hybridized in the SN@SiO<sub>2</sub> composite (Fig. S1B, ESI†), which accorded with the reaction rate of SN. From the SEM images (Fig. 1A), the composite particles in sizes of 100 to 500 nm are irregular and are stacked up as layers, faintly observed (Fig. 1B and S2, ESI†). From small-angle XRD, the interlayer space is calculated to be 4.4 nm ( $2\theta^{001} = 2.0^\circ$ ) (Fig. 1A), which is twice as long as one SN. It may be attributed to the fact that a part of SN formed layer micelles,<sup>14</sup> and SiO<sub>2</sub> grew on surface of the layer.

In addition, many hollow hexagonal prisms were found in the SN@SiO<sub>2</sub> composite (Fig. 1B and S3, ESI†), and all macropores (>50 nm) disappeared from diatomite (Fig. 1B and S4, ESI†). However, no peak appeared in the pore distribution curve (Fig. 1B). Also, the specific surface area of the SN@SiO<sub>2</sub> composite was measured to be 33 m<sup>2</sup> g<sup>-1</sup>, where nanopores occupy only 16 m<sup>2</sup> g<sup>-1</sup> (Fig. S5, ESI†). It may be attributed to the fact that a part of SN formed micellar rods<sup>14</sup> at the beginning of composite preparation. SiO<sub>2</sub> grew around the SN micellar rods to form the prism framework. In other words, SN was filling into the SiO<sub>2</sub> prism cavity so that N<sub>2</sub> cannot enter, as illustrated in Fig. 1E(a). As a result, many SN@SiO<sub>2</sub> prisms were stacked into the layer sheet, and the sheets built further into a composite particle.

State Key Laboratory of Pollution Control and Resource Reuse, College of Environmental Science and Engineering, Tongji University, Shanghai 200092, China. E-mail: hwgao@tongji.edu.cn; Fax: +86-21-65988598; Tel: +86-21-65988598

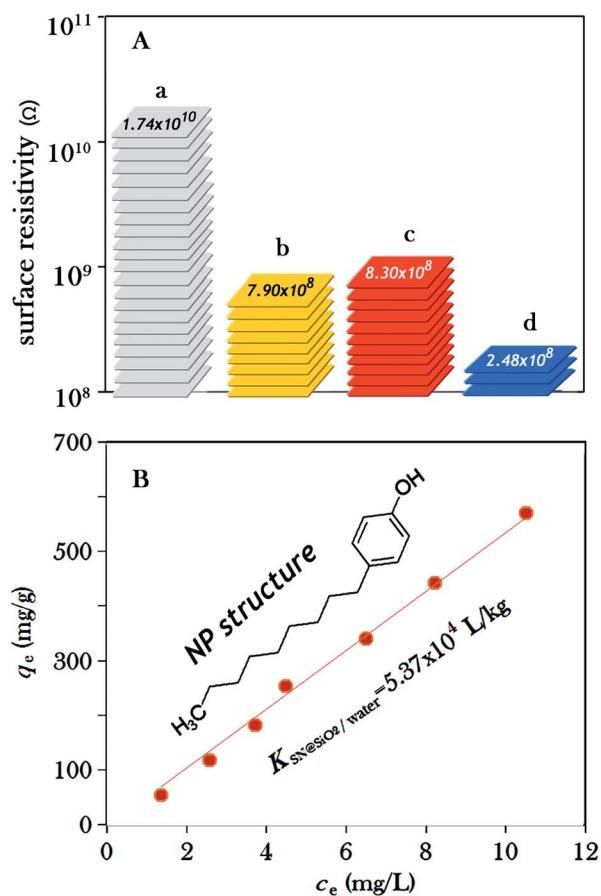
† Electronic supplementary information (ESI) available: Experimental details and Fig. S1–S8. See DOI: 10.1039/c4ra01002g



**Fig. 1** SEM (A and C) and TEM (B and D) images, small-angle XRD (curves in A and C) and pore size distribution (curves in B and D) of the materials. (A and B) SN@SiO<sub>2</sub> composite, (C and D) NP-SN@SiO<sub>2</sub> waste calcined. (E) cartoon illustration for 3D structure of the materials/products, (a) SN@SiO<sub>2</sub> composite, (b) composite adsorbing dye, (c) dye-SN@SiO<sub>2</sub> used for preparing the antistatic paint, (d) composite adsorbing NP and (e) NP-SN@SiO<sub>2</sub> waste calcined.

Owing to enough SN<sup>+</sup> embedded, the SN@SiO<sub>2</sub> composite carries plenty of positive charges, confirmed by the ζ-potential of +44 mV at pH 6.8. It will adsorb sulfonic dye *via* opposite charge attraction.<sup>15</sup> The SN@SiO<sub>2</sub> composite was mixed in aqueous solutions of three lightfast dyes, respectively, direct fastlight flavine 5GL, direct fast red F3B and direct fast turquoise blue GL. The dye-SN@SiO<sub>2</sub> products were rapidly formed. The direct fast red F3B-SN@SiO<sub>2</sub> composite was immersed into water for 24 h. The results indicated less than 0.1% SN, and almost no dye stripped from the composite. As an example, the interaction of direct fast red F3B with the SN@SiO<sub>2</sub> composite obeyed the Langmuir isotherm model (Fig. S6, ESI†). The saturation binding amounts of direct fast red F3B was calculated to be 637 mg g<sup>-1</sup> of the composite, and its mole ratio to the SN embedding to be 1 : 3. Two of five sulfonic groups of direct fast red F3B cause the steric effect (chemically structured in Fig. S6, ESI†); thus, one dye molecule may bind with at most three SN<sup>+</sup>. According to the same method, the carboxyl dyes *i.e.* eosin Y and alizarin yellow R were adsorbed, and their capacities were less than 300 mg g<sup>-1</sup> on the composite, less than those of sulfonic dyes. As a result, the dye molecule entered the SiO<sub>2</sub> prism cavity and bound to the SN's quaternary amine group located on the inside wall of prism, as illustrated in Fig. 1E(b).

It is well known that, the electrostatic charges embedded in the plastic and polymer fiber products often cause nuisance to people's life and even cause fire or explosion accidents in factories and mines. To overcome this problem, various antistatic agents were applied to dissipate the static.<sup>16–18</sup> As an excellent antistatic agent, SN is most frequently added into the silk, wool and nylon products. Epoxy paint (EP) was used to prepare antistatic paint by mixing with only 3% of the dye-SN@SiO<sub>2</sub> composite and coated on the plastic plates. The surface resistivity of the EP-only film (gray) was measured to be  $1.74 \times 10^{10} \Omega$  (Fig. 2A), being 21, 20 and 70 times higher than those of the EP-direct fastlight flavine 5GL-SN@SiO<sub>2</sub> film



**Fig. 2** Surface resistivity of the EP-dye-SN@SiO<sub>2</sub> composite films (A) and plots  $q_e$  vs.  $c_e$  of NP solutions treated with 50 mg L<sup>-1</sup> of the SN@SiO<sub>2</sub> composite (B). (a) EP only, (b) EP-direct fastlight flavine 5GL-SN@SiO<sub>2</sub>, (c) EP-direct fast red F3B-SN@SiO<sub>2</sub>, and (d) EP-direct fast turquoise blue GL-SN@SiO<sub>2</sub>.

( $7.90 \times 10^8 \Omega$ , yellow), EP-direct fast red F3B-SN@SiO<sub>2</sub> film ( $8.30 \times 10^8 \Omega$ , red) and EP-direct fast turquoise blue GL-SN@SiO<sub>2</sub> film ( $2.48 \times 10^8 \Omega$ , blue). It may be attributed to compactly filling SN into the SiO<sub>2</sub> prism to form a weak electrical conductor (Fig. 1E(c)). The surface resistivity of the EP-dye-SN@SiO<sub>2</sub> films is less than the strict limit, *i.e.*  $1.0 \times 10^9 \Omega$  standardized by the U.S. Department of Defense (Documentation no. DOD-HDBK-263) and China National Standard Bureau (no. SJ/T 11294 – 2003). Therefore, the dye-SN@SiO<sub>2</sub> products may be used as colored antistatic agents for adding into polymer paints *e.g.* EP and polyurethane.

SN contains a long alkyl chain (Fig. S1A, ESI<sup>†</sup>) so that it is able to capture hydrophobic organic compounds *e.g.* endocrine-disrupting chemicals (EDCs). Nonylphenol (NP) is one typical kind of EDC, jokingly called the “sperm killer”.<sup>19</sup> It is usually emitted from chemical wastewater. The EPA's standard indicated that NP should be lower than  $6.6 \mu\text{g L}^{-1}$  in freshwater. Wastewater containing 4 to 40 mg L<sup>-1</sup> NP was treated with the wet SN@SiO<sub>2</sub> composite prepared above, and the result is shown in Fig. 2B. Without doubt, the adsorption of NP accorded with the partition law. Its partition coefficient ( $K_{\text{SN@SiO}_2/\text{water}}$ ) was calculated to be  $5.37 \times 10^4 \text{ L kg}^{-1}$ , which is 4 times higher than that of *n*-octanol/water ( $K_{n\text{-octanol/water}} = 1.32 \times 10^4 \text{ L kg}^{-1}$ ).<sup>20</sup> Being different from the above dyes, the hydrophobic NP with a long alkyl chain (chemically structure in Fig. 2B) may enter the SiO<sub>2</sub> prism center to interact hydrophobically with the alkyl chain of SN, as illustrated in Fig. 1E(d). Only 50 mg L<sup>-1</sup> of the SN@SiO<sub>2</sub> composite extracted over 70% NP from its aqueous solution (Fig. S7, ESI<sup>†</sup>). It is superior to the carbon-base materials in terms of adsorption speed, capacity and selectivity.<sup>21</sup> It demonstrates that such adsorption is not dependent on the specific surface area of material but rather on the SN-NP hydrophobic interaction.<sup>22</sup> The SN@SiO<sub>2</sub> composite exhibits a potential applied to the treatment of phenolic wastewater.

The spent material, *i.e.* NP-SN@SiO<sub>2</sub> waste, was calcined at 550 °C. The IR absorption peaks of both SN and NP disappeared, and the Si–O peak shifted to 1081 cm<sup>-1</sup> (Fig. S1A, ESI<sup>†</sup>). Undoubtedly, calcination destroyed the SN and NP structures, and their decomposition products escaped from the composite waste. The hexagonal mesopores were exposed (Fig. 1D and S8, ESI<sup>†</sup>), leaving only the silica skeleton as a honeycomb illustrated in Fig. 1E(e). The interlayer disappeared from the small-angle XRD pattern (Fig. 1C). Such a morphology is similar to that of self-assembled materials prepared by the strict design and complicated synthesis.<sup>23–25</sup> N<sub>2</sub> adsorption and desorption isotherm curves (Fig. S5B, ESI<sup>†</sup>) showed a typical type IV isotherm with a small H1 hysteresis loop for the calcined product, implying its complex 2D pore structure. From the pore size distribution curve (Fig. 1D), majority of the pores appeared at 2.5 nm and mean at 3.7 nm, calculated by the BJH method. The specific surface area of the mesoporous silica increased significantly up to 1066 m<sup>2</sup> g<sup>-1</sup>, which is 30 times more than that of the SN@SiO<sub>2</sub> composite. Such a mesoporous sieve is valuable in gas adsorption, as catalysts, in heat insulation and in other fields.<sup>26–30</sup>

This work suggested a simple preparation process of the multifunctional diatomite composite from alkali dissolution

and acid neutralization to SN coprecipitation. Such in-depth functionalization is essentially different from conventional surface modification.<sup>11,12,31,32</sup> The performance of the SN@SiO<sub>2</sub> composite significantly increases, *e.g.* the active group SN firmly embedded, high adsorption capacity and rapid adsorption equilibrium to sulfuric dye and NP. It can bind with sulfonic dyes to prepare excellent colored antistatic agents, and can be used as outstanding sorbents for the remediation of water contaminated by organic pollutants. Furthermore, preparing a potentially valuable mesoporous sieve realized the resource-oriented utilization of the diatomite waste, and possible secondary pollution is avoided. In brief, the ‘dissolving first and then reassembling’ way will make waste profitable.

The authors acknowledge the financial support from The Foundation of State Key Laboratory of Pollution Control and Resource Reuse (Tongji University), China (Grant no. PCRRK11003).

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