

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/nanoenergy

RAPID COMMUNICATION

Facile structural tuning and compositing of (iron oxide-graphene anode towards enhanced supacapacitive performance



nano enero

Q.X. Low^a, G.W. Ho^{a,b,*}

^aEngineering Science Programme, National University of Singapore, Singapore ^bDepartment of Electrical and Computer Engineering, National University of Singapore, 4 Engineering Drive 3, 117576 Singapore, Singapore

Received 26 November 2013; received in revised form 8 January 2014; accepted 21 January 2014 Available online 31 January 2014

Abstract

Hydrothermal has been demonstrated to effectively tune the various morphologies of nanostructured Fe_2O_3 materials from 0D nanoparticles, 1D nanorods to self-assembled nanorods which form 3D ovoid architecture. Subsequently, compositing and reduction of graphene oxide (GO) were carried out simultaneously via facile base reduction. The as-synthesized nanocomposite was fabricated into an electrode material of hybrid supercapacitor and characterized by cyclic voltammetry (CV), and galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The synergistic effects of highly uniform 1D Fe_2O_3 nanorods of low internal resistance, enhanced ion diffusion as well reduced graphene sheets incorporation lead to superior electrochemical performances. The nanocomposite exhibits pseudocapacitive properties of high specific capacitance $\sim 504 \text{ F g}^{-1}$ at 2 mA/cm². Although many metal oxide and reduced GO hybrid systems have been investigated as electrode materials, this study demonstrates simple and effective tuning of Fe_2O_3 nanostructures morphologies to significantly impact the pseudocapacitive performances.

© 2014 Elsevier Ltd. All rights reserved.

Introduction

Hybrid capacitor utilizes both Faradaic and non-Faradaic processes to store charges hence exploit the advantages of electrochemical double-layer (EDL) capacitors and pseudocapacitors characteristics to achieve enhance energy and

*Corresponding author. Tel.: +65 65168121.

power densities. To fabricate an effective composite supercapacitor, carbon-based materials are commonly integrated with either conducting polymer or metal oxide materials. The carbon-based materials provide capacitive double-layer charge and high surface area matrix to increase contact between the deposited pseudocapacitive materials and electrolyte. On the other hand, the conducting polymer or metal oxide materials aim to improve the pseudocapacitance through Faradaic reactions. However, metal oxide is

2211-2855/\$ - see front matter @ 2014 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.nanoen.2014.01.002

E-mail address: elehgw@nus.edu.sg (G.W. Ho).

commonly used over conducting polymer for pseudocapacitive properties since there is a lack of efficient, n-doped conducting polymer. Furthermore, the charge-discharge cycle instability of conducting polymer hampers its development as pseudocapacitive material. There have been many studies on transition metal oxides as electrode material in pseudocapacitors. One of the most promising electrode materials is hydrous ruthenium dioxide (RuO₂), which exhibits pseudocapacitance as high as 720 F g⁻ However, its toxic nature and high cost limit its commercial applications [1]. Other transition metal oxides such as manganese oxide (MnO₂), nickel oxide (NiO) and cobalt oxide (Co_3O_4) have also been intensively investigated as potential materials for electrochemical capacitors [2-7]. Even though these classes of metal oxides have been wellestablished for its electrochemical energy storage applications, there is still a high demand to explore alternative electrode materials that is cost-effective, non-toxic and yet exhibit superior capacitive behavior.

Iron oxide is one of the most studied transition metal oxides for various technological applications [8]. Two commonly examined iron oxide phases are hematite, α -Fe₂O₃ and magnetite, Fe₃O₄. Hematite has its Fe ions in a trivalent state (ferric Fe), where each of its oxygen atoms is bonded to two Fe ions, and therefore, only two out of three available oxygen octahedrons are occupied. This arrangement makes the structure neutral with no charge excess or deficit, making it a chemically stable compound. It has n-type conductivity (E_g =2.1 eV) with highly chemical and thermodynamical stable structure [9] hence allow it to be a promising pseudocapacitor electrode material with respect to both its high specific capacitance and cost effectiveness [10-12].

Synthesis of functional iron oxide nanostructures in different dimensional and morphologies has always fascinated researchers because of their versatile range of scientific and technological applications. Though many aqueous chemical methods are widely known to synthesize iron oxides nanomaterials, tailoring morphologies in nano dimension still remains a challenging task. Here, we demonstrated a facile synthetic route towards tunable Fe₂O₃ nanostructures from OD nanoparticles, 1D nanorods to 3D self-assembled nanorods composited with rGO and investigated their morphology dependent electrochemical properties. An added advantage of this method is its non-templated synthesis avenue towards large scale and economical production. Although many metal oxide and rGO hybrid systems have been investigated as electrode materials, this study demonstrates simple and effective tuning of Fe₂O₃ nanostructures morphologies as one of the predominant factors to significantly enhance pseudocapacitive performances.

Material and methods

In a typical procedure, 0.32 g of H_3BO_3 was added to 10 ml of DI water followed by 2.3 ml of the 2.0 M aqueous FeCl₃ and 1.75 ml of the 4 M aqueous NaOH solution. The molar ratio of FeCl₃/H₃BO₃/NaOH was 2:3:4. The mixture was stirred and transferred to a teflon-lined autoclave and heated at 90 °C for 12 h. The resultant nanorods (NR)

product was washed and dried overnight to form powder. To obtain Fe₂O₃ nanoparticles (NP) and assembled nanorods (ANR) which forms ovoid architecture, the molar ratio of FeCl₃/H₃BO₃/NaOH was tuned to 2:3:6 and 2:1:6 respectively. The growth temperature was set at 120 °C for 12 h. Finally, reduction and compositing of GO were carried out simultaneously. 10 ml of 2 mg/ml GO solution (produced by modified Hummers method) was added to 10 ml of methanol and DI water for photo and base reduction methods respectively. Then, 20 mg of the as prepared Fe_2O_3 sample was added to the solution. The photo reduction was carried out by a 300 W Xe lamp (Excelitas, PE300BFM) illumination for 3 h under constant stirring. The base reduction method was carried out by addition of 1 ml NaOH (4 M) solution under 1 h reflux at 90 °C. Finally, the nanocomposite was washed and dried for further characterizations.

Scanning electron microscopy (SEM) characterization was carried out using a JEOL FEG JSM 6700F field-emission operating at 15 kV. X-ray photoelectron spectroscopy (XPS), VG ESCALAB 220I-XL system equipped with an Mg K α x-ray source was employed chemical composition studies. X-ray diffraction (XRD) was carried out on a Philips X-ray diffractometer with Cu K α radiation (λ =1.541 Å). The crystalline structures were analyzed using transmission electron microscopy (TEM, Phillips FEG CM300) operated at 200 kV.

A three-electrode system, a Pt foil and a Ag/AgCl were used as the counter and reference electrodes, respectively. The working electrode consists of the nanocomposite slurry coated on a stainless steel mesh. All 3 electrodes were immersed in an aqueous 1 M Na₂SO₄ electrolyte to evaluate the capacitive performances of the electrode materials. Cyclic Voltammetry (CV), Galvanostatic Charge Discharge (GCD) and Electrochemical Impedance Spectroscopy (EIS) measurements were conducted using the Versastat 4000 Potentiostat/Galvanostat (Metek) to test the capacitance and internal resistance of the electrochemical cell. In CV test, scan rates of 0.02, 0.05 and 0.1 V/s were carried out within a fixed potential window of -1.0 to 0 V for all the CV measurements. In GCD measurement, charge and discharge of the electrochemical cell were conducted at a constant current. Multiple loops of chronopotentiometry measurements using both forward and reverse current in each loop were conducted. The specific capacitance was calculated from galvanostatic discharge according to the formula:

$$C = \frac{I}{(\Delta V / \Delta t)m} \tag{1}$$

where *I* is the discharge current (A), $\Delta V/\Delta t$ is the best fit slope of the discharge curve after the IR drop, Δt is the discharge time (s) and *m* is mass of the electroactive material (g). In potentiostatic EIS mode, a DC voltage superimposed by a sinusoidal AC excitation signal was applied to the electrochemical cell. During testing, the frequency of the input signal was varied and the AC response was measured to calculate the impedance *Z* of the system. The data, in the form of Nyquist plot was plotted, where $Z_{\rm im}$ and $Z_{\rm re}$ refer to the imaginary and the real parts of the complex impedance. The EIS measurements were recorded under AC voltage amplitude of 5 mV, frequency range of 100 kHz to 0.01 Hz at 0 V reference.

Results and discussion

Based on the various hydrothermal reaction parameters, morphology evolution of Fe₂O₃ nanostructures base reduced composite are demonstrated. From the SEM images in Figure 1a and b, Fe₂O₃ nanoparticles (NP-rGO) with a size distribution of 20-60 nm are observed. Figure 1c and d shows 1D Fe₂O₃ nanorods (NR-rGO) of highly uniform in structure with average diameters of ~10 nm and lengths of 50 nm. Next, the nanorods were self-assembled (ANR-rGO) into 3D architecture ovoid of average dimension ~0.3-0.5 μ m (Figure 1e). Higher magnification image (Figure 1f) reveals that the 3D ovoid is composed of similar dimension nanorods. The nanorods have agglomerated to reduce the overall surface energy, leading to self-assembling of nanorods into compact ovoid nanoarchitecture.

Two steps phase transformations from $Fe(OH)_3$ to β -FeOOH and subsequently to α -Fe₂O₃ take place as follows:

$$Fe^{3+} + 3OH^{-} \rightarrow Fe(OH)_{3}$$
⁽²⁾

 $Fe(OH)_3 \rightarrow \beta - FeOOH + H_2O$

$$2\beta - FeOOH \rightarrow \alpha - Fe_2O_{3+} + H_2O \tag{4}$$

The growth of the nanostructures involves the use of additive H₃BO₃ which plays an important role to uniform structure and dimension formation. As such, H₃BO₃ is a weak acid which reacts with NaOH to form sodium borate (i.e. borax) buffer solution. The buffer solution tunes the release of hydroxyl ions, and control the mild formation of amorphous Fe(OH)₃ gel derived from co-precipitation. As reported, iron oxyhydroxides (FeOOH) can crystallize to form either goethite (α -FeOOH), lepidocrocite (γ -FeOOH), or akaganeite (β -FeOOH). However in this case, Cl⁻ rich ambient favors the formation of β -FeOOH phase [13]. The β -FeOOH nanostructures of uniform size is formed which then undergoes 12 h hydrothermal to transform to Fe₂O₃ nanostructures.

As mentioned, compositing and reduction of GO were carried out simultaneously via two methods; photo and base reduction as schematically depicted in Figure 2. The photo reduction of GO under UV irradiation causes the π - π * excitation of electrons in sp² domains on the GO surface. This then generates electron hole pairs that break the C-O-C



(3)

Figure 1 SEM images of low and high magnifications of based reduced (a and b) NP-rGO (c and d) NR-rGO (e and f) ANR-rGO composites.



Figure 2 Schematic of different GO reduction methods, base reduction and photo reduction which are used to form the nanocomposites. Insets show the digital photos of GO, photo reduced and base reduced GO solutions.



Figure 3 XPS spectra of C1s (a) GO (b) photo reduced GO and (c) based reduced GO. (d) Fe 2p spectrum of the Fe_2O_3 -rGO nanocomposites.

bonds and releases O2, effectively reduces the oxygen functional groups [14]. With the presence of methanol, an effective hole scavenger, the mean lifetime of electrons can be increased, thus promoting the reduction of GO to rGO and compositing of iron oxide nanostructures [15]. On the other hand, the base reduction method involves heating of the GO suspension and the iron oxide nanostructures under strong alkaline condition. It has been demonstrated that oxygen functionalities can be successfully removed due to alkaline reduction, where increase in pH promotes higher degree of reduction [16]. This is attributed to repulsive interaction between the deprotonated oxygen debris and the covalently functionalized GO under basic conditions which then promote the separation of oxygen functionalities from the GO [17]. The color changes of the GO solutions from light brown to dark brown and black are apparent for the photoreduced and base reduced GO respectively (see digital pictures in Figure 2 insets). The color change is due to the restoration of a sp² π -conjugated network in the



Figure 4 XRD spectra of NP-rGO, NR-rGO and ANR-rGO based reduced nanocomposites.

reduced GO. In both cases, the composites are observed to be well-dispersed in solution without forming any sediment. It is postulated that the carboxyl groups have been converted to carboxylate COO^- group to form water soluble rGO sheets where the negatively charged groups keep the Fe₂O₃-rGO composite from agglomerating [16].

Chemical analysis by XPS was carried out to verify the effectiveness of reduction and compositing of Fe₂O₃ nanostructures. Figure 3a shows the C 1s XPS spectrum of the GO sample. The deconvoluted peak at a binding energy of 285 eV is attributed to C-C and C=C bonds. The deconvoluted peak centered in the binding energy ranges of 286.8-287.0 eV is attributed to the C-O (C-O-C and C-OH), which is mainly due to epoxy and hydroxyl groups present on the GO surface. The peak intensities of the C-O as compared to the C-C and C=C bonds are significantly higher in the GO sample. Figure 3b shows the C 1s spectrum of the Fe_2O_3 rGO nanocomposite formed via photo reduction method, it can be observed that after photo reduction, the peak intensities of oxygenated groups decreased with respect to the C-C and C=C peaks. This suggests that photo irradiation causes the decomposition of C-O-C epoxy bond hence resulted in the overall decrease of C-O peak. Figure 3c shows the C 1s of the Fe₂O₃-rGO nanocomposite formed via base reduction route. The peak intensities of the oxygenated groups decrease more significantly as compared to the photoreduced GO. The XPS results correlate to the extent of color change (Figure 1 insets digital photographs) which demonstrates the effectiveness of base reduction method. Aside from being more effective, the other advantage of employing the base reduction method is the ability to tune the degree of GO reduction simply by adjusting the pH. Henceforth, base reduction method was adopted for simultaneous reduction of GO and compositing with Fe₂O₃ nanostructures. Figure 3d shows the Fe 2p spectrum where



Figure 5 TEM images of low and high magnification of based reduced Fe₂O₃ (a-c) nanoparticles and (d-f) nanorods.

two peaks at 724.6 and 711.2 eV, corresponds to the Fe $2p_{1/2}$ and Fe $2p_{3/2}$ spin-orbit of Fe₂O₃. Moreover, a satellite peak is observed at 718.9 eV, which is one of the distinct features of Fe₂O₃ phase [11]. This proves the successful compositing of rGO by facile base reduction method without affecting the chemical composition of Fe₂O₃ nanostructures.

Structural studies using XRD were carried out on the base reduced Fe₂O₃-rGO nanocomposites. The XRD diffraction peaks of Figure 4 can be readily indexed to a pure rhombohedral hexagonal phase of hematite α -Fe₂O₃. (JCPDS: 33-0664, space group: *R*-3*c*, *a*₀=5.0356 Å, *c*₀=13.7489 Å). No other peaks are observed which suggests absence of impurities in the as-synthesized samples. TEM was employed to further investigate the structure of the Fe₂O₃ nanoparticles (Figure 5a-c) and nanorods (Figure 5d-f). It can be observed the nanoparticles have size distribution of 20-60 nm. Highresolution TEM image (Figure 5c) shows well-resolved lattice fringes of ca. 0.37 nm attributed to (012) planes of rhombohedral hexagonal Fe₂O₃ crystals. TEM images of nanorods show monodispersed and uniform diameters of 5-15 nm and average length of 50 nm. High-resolution image of Figure 5f shows lattice fringes having an interplanar distance of 0.25 nm which agrees well with the (110) plane of rhombohedral hexagonal Fe_2O_3 . The obtained crystal planes are consistent with the obtained XRD diffraction spectra.

CV was carried out on the base reduced nanocomposites over various scan rates from 20, 50 and 100 mV s⁻¹. GCD was tested with the current density from 2, 4 and 6 mA/cm². The working voltage windows were between 0 and -1.0 V for aqueous electrolyte. The CV measurements of the NP-rGO nanocomposite (Figure 6a) present similar quasi-rectangular CV curves for a wide scan range of 20-100 mV s⁻¹. The current increased with the scan rate as expected, while the CV curves lost the rectangular shape when the applied scan rates were higher. This is due to the kinetics of electron transportation in the electrode materials and the limited ion adsorption-desorption at electrode and electrolyte interface. The GCD curves of the NP-rGO nanocomposite, with Na₂SO₄ electrolyte, are



Figure 6 Electrochemical properties of electrode materials measured using a three-electrode system CV and GCD of (a and b) NP-rGO (c and d) NR-rGO and (e and f) ANR-rGO based reduced nanocomposite.

shown in Figure 6b at different current densities. The linear shapes with nearly symmetric charge and discharge curves reveal a fast and reversible Faradic reaction between alkali cations (Na⁺) and the Fe_2O_3 nanocomposite. The specific capacitance of the composite materials is calculated from the galvanostatic discharge curve at a current density of 2 mA/cm². The NP-rGO nanocomposite yields specific capacitance of 138 F g^{-1} . The capacitive results of the NR-rGO nanocomposite are shown in Figure 6c. Two redox peaks are identified at a low scan rate at potential of around -0.7 and -0.3 V, showing the presence of pseudocapacitive characteristics. The current attained for the NR-rGO nanocomposite is higher than the NP-rGO nanocomposite and it increased with the scan rate, indicating enhanced electrochemical charge storage capabilities. The CV curves with increasing scan rates exhibit a gradual deviation from the rectangular shape owing to both EDL capacitance and pseudocapacitance characteristics. Figure 6d shows GCD curves of the NR-rGO nanocomposite at different current densities. The voltage drop due to the ESR at the beginning of charge/discharge was found to be small, suggesting a low internal resistance of the electrode. The NR-rGO nanocomposite displays a much higher specific capacitance of 504 F g^{-1} , which is 2.6 times higher than the NP-rGO. Finally, the capacitive behaviors of the ANR-rGO, a 3D nanoarchitecture which is composed of assembled 1D NRs is investigated (Figure 6e). Two redox peaks were identified at a low scan rate at around -0.8 and -0.2 V. The ANR-rGO nanocomposite seems to exhibit moderately high specific current, hence resulted in relatively lower overall capacitance of \sim 193 F g $^$ as compared to the NR-rGO nanocomposite. Similarly, the ANRrGO nanocomposite exhibits both EDL capacitance and pseudocapacitance with a low internal resistance from the small drop in potential at the initial stage of discharging (Figure 6f). The NR-rGO nanocomposite shows highest pseudocapacitive performance manifested by its small dimension (diameter \sim 10 nm) which promotes higher redox activity due to increase electrolyte cations interaction at the electrode surface. In addition, the 1D nanorods as compared to nanoparticles and 3D selfassembled nanorods have better dispersivity hence forming favorable path for penetration and transportation of electrolyte ions. Notably, simple tailoring of Fe₂O₃ nanostructures morphologies from 0D nanoparticles to 1D nanorods and 3D ovoids has shown to improve the pseudocapacitive performances.

EIS measurements were performed at room temperature on the base reduced nanocomposites to obtain information on charge-transfer resistance. The resulting Nyquist plots are shown in Figure 7 where the obtained curves are rather similar in shape, an arc in the high frequency region and inclined line in the low frequency region. The arc is usually attributed to the interparticle resistance and charge transfer impedance while the inclined line is ascribed to the Warburg impedance, which is a result of the frequency dependence of ion diffusion/transport in the electrolyte to the electrode surface [18]. A distinct difference that is observed between the samples is the phase angle of the inclined line at Warburg region. In the low frequency range, NP-rGO nanocomposite shows a relatively lower phase angle, indicating a higher ion diffusion resistance. On the other hand, the phase angle increases with ANR-rGO and NR-rGO nanocomposites supercapacitors due to reduced charge-transfer and ion diffusion resistance. The higher intercalation and deintercalation of Na⁺ ions may have



Figure 7 EIS measurements of various based reduced nanocomposites with inset showing the high-frequency region of the Nyquist plot.

possibly lead to higher capacitance in the case of NR-rGO nanocomposite sample. It is also noted that amongst the nanocomposites samples, the ANR-rGO shows a more distinct semi-circle, implying a higher charge transfer resistance developed at the electrode/electrolyte interface. Hence, the EIS spectra corroborate with the specific capacitances that were measured, where NR-rGO nanocomposite has the highest capacitance with the lowest charge-transfer resistance.

Conclusions

In this work, we have demonstrated a facile synthetic route to tune iron oxide nanocomposite morphology from monodispersed 0D nanoparticles and 1D nanorods to hierarchical 1D nanorods. The electrochemical performance has been characterized via CV, GCCD and EIS which show that the different nanocomposite morphologies affect their capacitive properties. As such, the synergistic effects of highly uniform nano dimension 1D rods with low charge transfer resistance and reduced graphene oxide composite lead to high energy density. The low cost, abundancy, and environmental friendliness of iron oxides may render their nanocomposites as a promising candidate for energy storage applications.

Acknowledgments

This work is supported by R-263-000-653/654-731/112.

References

- [1] J.P. Zheng, P.J. Cygan, T.R. Jow, J. Electrochem. Soc. 142 (1995) 2699.
- [2] Z.-S. Wu, W. Ren, D.-W. Wang, F. Li, B. Liu, H.-M. Cheng, ACS Nano 4 (2010) 5835.
- [3] J. Yan, Z. Fan, T. Wei, Z. Qie, S. Wang, M. Zhang, Mater. Sci. Eng. B 151 (2008) 174.
- [4] S. Vijayakumar, S. Nagamuthu, G. Muralodharan, ACS Appl. Mater. Interfaces 5 (2013) 2188.

- [5] Q. Lu, M.W. Lattanzi, Y. Chen, X. Kou, W. Li, X. Fan, Karl M. Unruh, J.G. Chen, J.Q. Xiao, Angew. Chem. Int. Ed. 50 (2011) 6847.
- [6] J. Yan, T. Wei, W. Qian, B. Shao, Q. Zhao, L. Zhang, Z. Fan, Electrochim. Acta 55 (2010) 6812.
- [7] J.P. Cheng, X. Chen, J.-S. Wu, F. Liu, X.B. Zhang, P.D. Vinayak, CrystEngComm 14 (2012) 6702.
- [8] M. Mohapatra, S. Anand, Int. J. Eng., Sci. Technol. 2 (2010) 127.
- [9] R.M. Cornell, U. Schwertmann, The Iron Oxides: Structure, Properties, Reactions, Occurrences and Uses, Wiley-Vch, 2003,http://dx.doi.org/10.1002/3527602097. Online ISBN: 9783527602094; Print ISBN: 9783527302741.
- [10] M. Zhu, Y. Wang, D. Meng, X. Qin, G. Diao, J. Phys. Chem. C 116 (2012) 16276.
- [11] D. Wang, Y. Li, Q. Wang, T. Wang, J. Solid State Electrochem. 16 (2012) 2095.
- [12] K.K. Lee, S. Deng, H.M. Fan, M. Mhaisalkar S., H.R. Tan, E.S. Tok, K.P. Loh, W.S. Chin, C.H. Sow, Nanoscale 4 (2012) 2958.
- [13] W. Zhu, X. Cui, X. Liu, Y. Zhang, J. Huang, X. Piao, Q. Zhang, Nanoscale Res. Lett. 8 (2013) 2.
- [14] Y. Matsumoto, M. Koinuma, S.Y. Kim, Y. Watanabe, T. Taniguchi, K. Hatakeyama, H. Tateishi, S. Ida, ACS Appl. Mater. Interfaces 2 (2010) 3461.
- [15] K. Dai, T. Peng, D. Ke, B. Wei, Nanotechnology 20 (2009) 125603.
- [16] H. Wang, H.-W. Tian, X.-W. Wang, L. Qiao, S.-M. Wang, X.-L. Wang, W.-T Zheng, Y.-C. Liu, Chem. Res. Chin. Univ. 27 (2011) 857.

- [17] J.P. Rourke, P.A. Pandey, J.J. Moore, M. Bates, I.A. Kinloch, R.J. Young, N.R. Wilson, Angew. Chem. 50 (2011) 3173.
- [18] W. Shi, J. Zhu, D.H. Sim, Y.Y. Tay, Z. Lu, X. Zhang, Y. Sharma, M. Srinivasan, H. Zhang, H.H. Hng, Q.Y. Yan, J. Mater. Chem. 21 (2011) 3422.



Qian Xian Low received his B.S. (honors) degree of Engineering Science Programme at National University of Singapore in 2013. His research interests are synthesis of novel nanomaterials for energy applications.



Ghim Wei Ho received her Ph.D. (2006) in Electrical Engineering (Nanoscience) from University of Cambridge. She is currently an Assistant Professor at National University of Singapore. Her current research thrusts focus on the development of nanostructured materials for sustainable environmental and energy applications.