Gas Sensing of SnO₂ Nanocrystals Revisited: Developing Ultra-Sensitive Sensors for Detecting the H₂S Leakage of Biogas

Lin Mei, Yuejiao Chen & Jianmin Ma

Key Laboratory for Micro-Nano Optoelectronic Devices of Ministry of Education, State Key Laboratory for Chemo/Biosensing and Chemometrics, Hunan University, Changsha 410082, P. R. China.

As a typical mode of energy from waste, biogas technology is of great interest to researchers. To detect the trace H₂S released from biogas, we herein demonstrate a high-performance sensor based on highly H₂S-sensitive SnO₂ nanocrystals, which have been selectively prepared by solvothermal methods using benzimidazole as a mineralization agent. The sensitivity of as-obtained SnO₂ sensor towards 5 ppm H₂S can reach up to 357. Such a technique based on SnO₂ nanocrystals opens up a promising avenue for future practical applications in real-time monitoring a trace of H₂S from the leakage of biogas.

Nowadays, energy and environmental problems have become two of the greatest challenges, which strongly influence the social manner and quality of people all over the world. As a renewable energy source, biogas technology, which converts wastes into energy, has attracted great attention in many countries, and been well developed. Biogas mainly contains methane (CH₄), together with a trace of other toxic gases, in which H₂S is identified as the main toxic component. Due to the high toxicity of H₂S, it is extremely detrimental for human being to be exposed to H₂S if the leaking of biogas happens. At present, 4 ppm is the maximum value of H₂S, allowed by the fuel gas specifications for pipeline transportation. Although there are physical and chemical absorption as well as biological treatments of H₂S for biogas purification, it is still difficult to completely remove H₂S gas from biogas with low-cost methods. To prevent potential risks of biogas leakage, it is necessary to realize real-time monitoring a trace amount of H₂S gas (<5 ppm) released from biogas during production and transportation processes.

Gas sensors are of great interest due to their capability for a real-time analysis of gaseous chemicals in a wide range of applications. Accordingly, different gas sensors have been readily applied in the biogas process. However, there is no report on detecting H₂S from biogas during its production and transportation processes. To detect a trace amount of H₂S gas, it is a prerequisite that high-performance sensing material towards H₂S gas should be available. It is well recognized that the sensing material is the core of gas sensors. Typically, tin oxide (SnO₂) is a well-known gas-sensing material, which has been intensively studied with various shapes and morphologies for its detection towards various gases. Meanwhile, numerous efforts have been exerted on the synthesis strategies of favorable SnO₂ structures to detect H₂S gas. Especially, Lee and his co-workers developed a synthetic route to obtain the CuO-functionalized SnO₂ nanowires with a response as high as 419 towards 20 ppm H₂S. Unfortunately, the sensor requires a temperature as high as 400°C to achieve a satisfied function. Therefore, it is necessary to develop highly H₂S sensitive sensors based on novel materials with higher selectivity, lower-detection limit, and low-power consumption for monitoring the H₂S gas from the leakage of biogas.

Herein, we report a solvothermal method for the preparation of high-performance SnO₂ nanocrystals with benzimidazole as a mineralization agent. The sensor with SnO₂ nanocrystals as the sensing material shows an ultrahigh sensitivity towards trace H₂S gas, and a high selectivity to H₂S in CH₄. Moreover, structural characterizations and sensing mechanism analysis were undertaken to study the correlation between the sensor performance and the materials structure. It is expected that these as-prepared SnO₂ nanocrystals are promising for a real-time monitoring of trace H₂S during biogas production and transportation processes.
Results

In this work, different shapes and morphologies of SnO$_2$ nanocrystals could be easily obtained under solvothermal conditions with benzimidazole as a mineralization agent. The amount of benzimidazole plays crucial roles in determining the growth of SnO$_2$ nanocrystals. When the amount of benzimidazole is 0.1, 0.3 and 0.6 g respectively, while other conditions kept the same, different SnO$_2$ samples can be prepared accordingly SnO$_2$ nanocrystals, denoted as SNC1; longer SnO$_2$ nanocrystals, denoted as SNC2; SnO$_2$ larger nanocrystals, denoted as SNC3). The phase of as-prepared SnO$_2$ nanocrystals (SNC1, SNC2 and SNC3) was confirmed as pure tetragonal phase of SnO$_2$ (JCPDS Card 41-1445) by X-ray diffraction (XRD) measurements, as shown in Figure 1.

Transmission electron microscopy (TEM) was employed to further examine the representative morphologies and structures of as-prepared SnO$_2$ nanocrystals. TEM image in Figure 2a shows that SNC1 exists as homogeneous nanocrystals. In the high-resolution
TEM (HR-TEM) image (Figure 2b), it clearly shows that the size of SNC1 nanocrystals is about 3.4 ± 0.8 nm. The SNC2 has an average edge length of 7.4 ± 0.5 nm and width of 4.8 nm as shown in Figure 2d. Meanwhile, the SNC3 sample shows an average diameter of 5.2 ± 0.8 nm (Figure 2e and f). TEM gives us a direct proof that the present method is very effective for controlling the size and morphology of SnO$_2$ nanocrystals. To support our given data, the size distribution for three SnO$_2$ samples is also given in Figure 3. Similarly, the dynamic light scanning (DLS) characterization gave larger diameters compared to the one from TEM images, which is probably due to the existence of hydrated layers around the particle surfaces and the aggregation of SnO$_2$ nanocrystals. Furthermore, we also found that only homogeneous SnO$_2$ samples were obtained without the use of benzimidazole. No obvious difference has been observed when the ratios of water and ethanol were changed (Figure S1). Electron energy loss spectroscopy (EELS) was further used to characterize SCN1 (Figure S2). No other elements (C, N) originated from benzimidazole were detected on SCN1, which further proved the high purity of our samples. Here, the roles of benzimidazole should be included: directing the growth of inorganic nanocrystals; aggregation effect or assembly due to its rich interactions (hydrogen bond, π-π stacking, and van der Waals interaction). Under these interactions, different shapes and morphologies of SnO$_2$ nanocrystals could be obtained by adjusting the amount of benzimidazole used.

Nitrogen isotherm adsorption-desorption curves together with the pore size distributions of these as-synthesized SnO$_2$ nanocrystals are given in Figure 4. In Figure 4a, SNC1 shows a typical type-IV isotherm with H2-type hysteresis loop. Base on the Barrett-Joyner-Halenda (BJH) equation, the main pore size (Figure 4b) for SNC1 is determined as 3.8 nm, which further confirms a uniform pore size distribution. The BET specific surface area ($S_{BET}$) for SNC1 is 223.6 m$^2$.g$^{-1}$. The higher $S_{BET}$ of the adsorption-desorption curve shows that SNC1 has the larger inter particle distance and homogenized sizes. SNC2 and SNC3 exhibit a type IV isotherm with H2-type hysteresis loops shown in Figure 4a. The high $S_{BET}$ of SNC2 (181.2 m$^2$.g$^{-1}$) shows the large interparticle distance as revealed in Figure 2d. The smaller hysteresis loop and the $S_{BET}$ of SNC3 (109.7 m$^2$.g$^{-1}$) is probably a result of the severe aggregation in the sample. These results further indicate that it is effective to tailor the aggregated structure of SnO$_2$ nanocrystals with high $S_{BET}$ by simply changing the amount of benzimidazole.

High $S_{BET}$ metal oxides have been demonstrated to be promising for gas sensing. Especially, a sensitive gas sensor with high selectivity for trace H$_2$S is extremely important to detect the biogas. In this study, a comparison of the sensor response of SnO$_2$ nanocrystals to 25 ppm of various gases at operating temperature of 125°C is shown in Figure 5 and S8. Notably, all the sensor response stowards different gases are all less than 2 orders of magnitude as compared to the signal from H$_2$S. From the plot, it is clear that SCN1 shows not
only enhanced sensitivity towards H2S but also a very high selectivity. The variation of sensitivity of SNC1 under different operating temperature towards 25 ppm of H2S is shown in the Table (the inset of Figure 5). It is clear that SNC1 has an obvious response to H2S gas between 45°C and 200°C, and excellent selectivity towards H2S gas. The excellent selectivity of SNC1 facilitates the application for detecting H2S.

Figure 6 shows the response and recovery of SNC1 sensors upon exposure to 5 ppm H2S at 45, 125, 160 and 275°C, respectively. It is obvious that the sensor shows switch-like characteristics after an H2S exposure, and the response intensity is extremely high. At operating temperatures of 45°C and 125°C, the response times are about 120 and 224 s, respectively, while the recovery time is both several hours. Raising the operating temperature can immediately shorten both the recovery and response time. At 160°C, the response of the sensor is the most sensitive one (S = 320). Detecting H2S with a trace level (<5 ppm) at such a low temperature is very useful for real-time monitoring H2S gas released from biogas during production and transportation processes. The results are also excellent in comparison with previous results for tin oxide or modified tin oxide as gas sensor for H2S detection, as shown in Table 1.

The typical response-recovery curves of the sensors made from the as-synthesized SNC1 and commercial SnO2 (c-SnO2) exposed to different concentrations of H2S ranging from 0.5 ppm to 30 ppm were shown in Figure 7a. Figure 7b displays the sensor response of different SnO2 nanocrystals towards various concentrations of H2S. The SNC1 sensor shows a much larger response magnitude to each concentration of H2S, compared with other SnO2 sensors. It is obvious that the sensor based on SNC1 is able to detect a wide range of H2S concentrations, with detection limit in the ppb level while the response towards 0.5 ppm of H2S is still as high as 20.4, indicating its excellent sensitivity and stability. However, the response for SNC3, c-SnO2 and SNCb (Figure S9) are extremely slow, probably due to their aggregated characteristics and lower S BET (The characterization of c-SnO2 is shown in Figure S6 and S7). When H2S concentration is in range of 0.5–30 ppm, the logarithm of the sensor response shows a

| Table 1 | Comparison of gas-sensing characteristics of SnO2-based gas sensor |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| Materials       | H2S Concentration (ppm) | Response S = Rg/Ro | Work Temperature (°C) | Ref. |
| SnO2 nanofibers | 4               | 23              | 300              | 28             |
| SnO2 nanocrystals | 20              | 27              | 150              | 32             |
| SnO2 thin films | 80              | 96              | 100              | 33             |
| SnO2 submicrotubes | 0.5          | 11.7             | 160              | 34             |
| Ag-SnO2 nanopowders | 50            | 55              | 332              | 35             |
| CuO doped SnO2 nanowires | 20           | 419             | 400              | 36             |
| Fe/SnO2 composite | 67.9          | 50              | 250              | 37             |
good linearity against the logarithm of the gas concentrations shown in Figure S10, which is in agreement with the theory of the power laws for semiconductor sensors. 

Figure 8a shows the sensor response of SNC1 at different working temperatures to 5 ppm H₂S. The sensor response increases and reaches its maximum at about 160 °C and then decreases rapidly with the increase of temperatures. Figure 8b displays the sensor response of SNC1 at different working temperatures to 100 ppm CH₄. The sensor response is similar from 45 °C to 350 °C, and reaches its maximum of 3.0 at about 200 °C. Figure 8c and d show a continuous measurement of 5 ppm H₂S and 100 ppm CH₄. The result indicates that the SNC1 sensor have good repeatability.

An alternate experiment is also carried out to detect the composite gases between biogas (5 ppm of H₂S gas and 95 ppm of CH₄) and 100 ppm pure CH₄ at 160 °C (Figure 9). Firstly, a low signal was observed at 3.1 after exposed to 100 ppm of CH₄. Then, the response increased sharply to 335 after encountering a composite biogas with 5% H₂S. Similarly, we can also test the repeatability of our sensor performance by switching the working environment between pure CH₄ and a composite biogas. It is clear that no obvious deterioration
of the response can be observed during this experiment although there indeed exists a slight drop after extended cycles. It can be concluded that SNC1 nanoparticles-based H$_2$S sensor is promising for biogas composition monitoring.

**Discussion**

The change in the electrical resistance of a semiconductor is closely related to the chemical properties of the surface oxygen. Oxygen is adsorbed on SnO$_2$ nanocrystal surface in different forms depending on the temperature, from physisorption (molecular form) to chemisorption (dissociative form) as temperature increase$^{33,42}$. These oxygen adsorbates (O$_2$,$^\bullet$, O$^-$ and O$^{2-}$) on the surface of n-type SnO$_2$ induce an electron depletion layer, resulting in the decrease in carrier concentration and the increase in the surface potential barrier$^{42–46}$. Upon exposures to reducing gases like H$_2$S, the surface oxygen is consumed due to the chemical reaction.

$$O_2(gas)\rightarrow O_2(phys)\rightarrow O_2^-(chem)\rightarrow 2O^-(chem)\rightarrow 2O^{2-}(chem)$$

Then the electrons donate back to the surface of semiconductor, leading to the decrease in electrical resistance. Therefore, the concentration of surface oxygen depends on the concentration of the reducing gas as the same operating temperature. The chemical adsorption of oxygen and its reaction with reducing gases underlie the sensing mechanism of SnO$_2$ nanocrystals$^{32}$. It can be expressed by Eq.(1),

$$S = \frac{R_d}{R_g} \propto P_{H_2S}^m$$

Where $P_{H_2S}$ is the concentration of H$_2$S gas in air, the power law exponent $m$ takes the value of 1, 0.5 or 0.25 respectively depending on the species of chemisorbed (ionosorbed) oxygen (O$_2^-$, O$^-$ and O$^{2-}$—correspondingly) and thus on the temperature. Comparing the value of $m$ obtained from experiment results ($m = 0.8$) with that from theoretical analysis, that is 0.5 < $m$ < 1

This relation indicates that at 160°C the oxygen chemical desorption on SnO$_2$ nanocrystals surfaces might be dominated by O$_2^-$ and O$^-$ simultaneously, which is in accordance to the TPD, FTIR and EPR studies conducted on SnO$_2$ surfaces$^{47,48}$, indicating that the molecular form (O$_2^-$) dominates below 150°C, and above this temperature the ionic species dominate, predominately as O$^-$ below 400°C and O$^{2-}$ above 400°C, which is then directly incorporated into the lattice above 600°C.

The proportions of O$_2^-$ and O$^-$ involved here can be calculated through the reaction Eqs.(2,3):

$$H_2S(ads) + xO_2^- + 2yO^- \rightarrow SO_2(gas) + H_2(gas) + (x + 2y)e^-$$

$$x + y = 1$$

Where $x$ and $y$ are the proportions of O$_2^-$ and O$^-$ respectively. And we obtain:

$$S = \frac{R_d}{R_g} \propto P_{H_2S}^{1+y}$$

Inserting the value of $m$ into Eq. (4) leads to: $x = 0.75$, $y = 0.25$. Therefore, oxygen might be ionosorbed on SnO$_2$ surfaces as O$_2^-$ and O$^-$ with the proportion ratio of 3:1 at 160°C, which needs to be demonstrated by further spectroscopy study. The above discussion suggests that the power law exponent is characteristic of the surface reaction. It determines the dominating species of oxygen adsorbates and the proportion.

The height of energy barrier to electron transport between neighboring grains in the SnO$_2$ is an important factor, which determines sensitivity of the material$^{47}$. The temperature dependence of the conductivity of a semiconductor can be approximated by the Arrhenius equation$^{40}$.

![Figure 9](image.png)

**Figure 9** | A repeatedly alternate experiment to detect the composite gases between biogas (5 ppm of H$_2$S gas and 95 ppm of CH$_4$) and CH$_4$ at 160°C.

![Figure 10](image.png)

**Figure 10** | Schematic illustration of chemical reactions on SnO$_2$ nanocrystals surface underlying H$_2$S sensor mechanism.
Where $\sigma_0$ is a factor that includes the bulk in trigranular conduc-
tance, $k$ the Boltzmann’s constant, $T$ the absolute temperature, and $eV_i$ the potential energy barrier at the interface between two neigh-
boring particles.

$$eV_i = \frac{e^2N_i^2}{2\varepsilon\varepsilon_0N_d}$$

Where $N_i$ is the surface density of adsorbed oxygen ions ($O_{2^-}$ or $O^-$), $\varepsilon\varepsilon_0$ is the permittivity of the semiconductor, and $N_d$ is the volumetric density of the electron donors. Clearly, the energy barrier is a func-
tion of temperature and atmosphere (oxygen partial pressure), each of these parameters influences the energy barrier, conductivity, and thus the sensitivity. Further, $eV_i$ depends on the particle size, espe-
cially when the particle size is reduced to nanometer or in the order of

In summary, we have successfully obtained a high-performance
SnO$_2$ sensor for detecting trace H$_2$S from the biogas. By means of a
control over the size and morphology of SnO$_2$ nanocrystals, the sensor
performance can be accordingly tuned due to the difference in the $S_{\text{BET}}$ of the sensor materials. The mechanism of gas sensing towards H$_2$S has been discussed in detail. The sensor built on the as-
prepared SNC1 shows promising sensing properties towards a real

Methods

Hydrothermal synthesis of SnO$_2$ nanocrystals. In a typical synthesis, 0.35 g of
SnCl$_4$·5H$_2$O and 0.1 g of benzentimazole were first dissolved into mixed solution
with 20 ml of distilled H$_2$O and 20 ml of ethanol, and then transferred into a
30 ml. Teflon-lined stainless-steel autoclave at 180 °C for 2 h. Finally, the
obtained white sample was rinsed with deionized water and ethanol for several
times, and dried in ambient conditions. In order to investigate the effect of
benzentimazole on the morphology of final products, a series of controlled
experiments were also conducted, and the amount of benzentimazole is 0.3 and
0.6 g, respectively.

Characterization. The morphology and structural characteristics were observed
using X-ray diffraction (XRD), Rigaku D/max 2500 diffractometer), high-resolution
transmission electron microscopy (HRTEM, JEOL 1010) equipped with and electron
energy loss spectroscopy (EELS), and nitrogen adsorption–desorption isotherms
(ASAP 2020 nitrogen adsorption apparatus). The Brunauer–Emmett–Teller (BET)
specific surface areas ($S_{\text{BET}}$) were calculated using the BET equation. Desorption
isotherm was used to determine the pore size distribution using the Barrett–Joyner–
Halender (BjH) method. Particle size range was estimated using a dynamic light
scattering (DLS) device (Malvern Zetasizer Nano ZS90).

Sensor measurements. The fabrication and testing principles of the gas sensor
are similar to that described in our previous reports. Firstly, the SnO$_2$ samples were
mixed with terpinene to form a paste and then coated onto the outside surface of
an alumina tube with diameter of 1 mm and a length of 5 mm. A platinum coil through
the tube was employed as a heater to control the operating temperature. To improve
their stability and repeatability, the gas sensors were aged at 300 °C
for 48 h. After the aging process, the sensors were stored in a dry nitrogen
atmosphere.

When air and ppm-level target gas were flowed through the sensor element, the
sensor’s response ($R$) was defined as the ratio of the sensor resistance in air ($R_{\text{air}}$)
and in the gas-air mixture ($R_{\text{gas}}$) recorded, respectively. The sensor response ($S$) for oxidizing
gas (NO or NO$_2$) is defined as the ratio of $R_{\text{NO}}/R_{\text{air}}$, while the response for reducing gas
(H$_2$S, H$_2$, CO or CH$_4$) is defined as the ratio of $R_{\text{gas}}/R_{\text{air}}$.

1. Hightower, M. & Pierce, S. A. The energy challenge. Nature 452, 285–286 (2008).
2. Jacobson, M. Z. Review of solutions to global warming, air pollution, and energy
security. Energy Environ. Sci. 2, 148–173 (2009).
3. Mei, L. et al. Hierarchicalc.mushroom-likeCoNi$_2$S$_4$ arrays: a novel electrode
material for supercapacitors. Nano Energy 3, 36–45 (2014).
4. Cantrell, K. B. et al. Livestock waste-to-bioenergy generation opportunities.
Bioreour. Technol. 99, 7941–7953 (2008).
5. Belmabkhout, Y. Simultaneous adsorption of H$_2$S and CO on triamine-grafted
pore-expanded mesoporous MCM-41 silica. Energy Fuels 25, 1310–1315 (2011).
6. Nakamura, S. & Yoda, M. Removal of hydrogen sulfide from an anaerobic biogenic
using a bio-scrubber. Water Sci. Technol. 36, 349–356 (1997).
7. Ma, J. M. et al. Poiseuochemicalpreparation of WO$_3$ nanotubes through precursor
H$_2$WO$_4$, and their gas-sensing performances. J. Phys. Chem. C 115, 18157–18163
(2011).
8. Lai, X. Y. et al. General synthesis and gas-sensing properties of multiple-shell
metal oxide hollow microspheres. Angew. Chem. Int. Ed. 52, 2799–2793 (2013).
9. Cui, S. M. et al. Fast and selective room-temperature NH$_3$ sensors using silver
nanocrystals-functionalized carbon nanotubes. ACS Appl. Mater. Interfaces 4,
4998–4994 (2012).
37. Ma, J. M. et al. Sb$_2$S$_3$ with various nanostructures: controllable synthesis, formation mechanism, and electrochemical performance toward lithium storage. Chem. Eur. J. 16, 13210–13217 (2010).

38. Ma, J. M. et al. One-dimensional Sb$_2$Se$_3$ nanostructures: solvothermal synthesis, growth mechanism, optical and electrochemical properties. CrystEngComm 13, 2369–2374 (2011).

39. Kong, X. H. & Wang, T. H. High sensitivity of CuO modified SnO$_2$ nanoribbon S$_2$ at room temperature. Sens. Actuators B: Chem. 105, 449–453 (2005).

40. Xue, X. Y. et al. Synthesis and H$_2$S Sensing Properties of CuO-SnO$_2$ Core/Shell PN-Junction Nanorods. Sens. Actuators B: Chem. 112, 12157–12160 (2008).

41. Kim, T. K. et al. Nanoporous metal oxides with tunable and nanocrystalline frameworks via conversion of metal–organic frameworks. J. Am. Chem. Soc. 135, 8940–8946 (2013).

42. Xue, X. Y. et al. One-step synthesis and gas-sensing characteristics of uniformly loaded Pt@SnO$_2$ nanorods. J. Phys. Chem. C 114, 3964–3972 (2010).

43. Yan, Q. et al. Fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. Appl. Phys. Lett. 84, 3654–3656 (2004).

44. Paulose, M. et al. Unprecedented ultra-high hydrogen gas sensitivity in undoped titania nanotubes. Nanotechnology 17, 398–402 (2006).

45. Chang, S. C. Oxygen chemisorption on tin oxide: correlation between electrical conductivity and EPR measurements. J. Vac. Sci. Technol. 19, 366–369 (1980).

46. Barsan, N. & Weimar, U. Conduction model of metal oxide gas sensors. J. Electroceram. 7, 143–167 (2001).

47. Zhang, G. & Liu, M. L. Effect of particle size and dopant on properties of SnO$_2$-based gas sensors. Sens. Actuators B: Chem. 69, 144–152 (2000).

48. Lantto, V. et al. A study of the temperature dependence of the barrier energy in porous tin dioxide. Sens. Actuators 14, 149–163 (1988).

49. Yin, X. M. et al. SnO$_2$ monolayer porous hollow spheres as a gas sensor. Nanotechnology 20, 455503 (2009).

50. Mei, L. et al. Ultrasmall active ethanol sensor based on 3D aloe-like SnO$_2$. Sens. Actuators B: Chem. 166–167, 7–11 (2012).

51. Ma, J. M. et al. α-Fe$_2$O$_3$ nanochains: ammonium acetate-based ionothermal synthesis and ultrasensitive sensors for low-ppm-level H$_2$S gas. Nanoscale 5, 895–898 (2013).

52. Deng, J. W. et al. Porous α-Fe$_2$O$_3$ nanosphere-based H$_2$S sensor with fast response, high selectivity and enhanced sensitivity. J. Mater. Chem. A 1, 12400–12403 (2013).

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 51302079) and the Young Teachers’ Growth Plan of Hunan University (Grant No. 2012-118).

Author contributions

J.M.M. proposed and designed the experiments. L.M. carried out the synthetic experiments and conducted the characterization. L.M. performed the HRTEM, SEM characterization and structural analysis. Y.J.C. and L.M. prepared the gas sensors. L.M. and J.M.M. wrote the manuscript. All the authors participated in discussions of the research.

Additional information

Supplementary information accompanies this paper at http://www.nature.com/scientificreports

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Mei, L., Chen, Y.J. & Ma, J.M. Gas Sensing of SnO$_2$ Nanocrystals Revisited: Developing Ultra-Sensitive Sensors for Detecting the H$_2$S Leakage of Biogas. Sci. Rep. 4, 6028; DOI:10.1038/srep06028 (2014).

This work is licensed under a Creative Commons Attribution-NonCommercial-ShareAlike 4.0 International License. The images or other third party material in this article are included in the article’s Creative Commons license, unless indicated otherwise in the credit line; if the material is not included under the Creative Commons license, users will need to obtain permission from the license holder in order to reproduce the material. To view a copy of this license, visit http://creativecommons.org/licenses/by-nc-sa/4.0/