



OPEN

SUBJECT AREAS:

SYNTHESIS AND
PROCESSING

NANOWIRES

A facile strategy to decorate Cu_9S_5 nanocrystals on polyaniline nanowires and their synergetic catalytic properties

Xiao-feng Lu, Xiu-jie Bian, Zhi-cheng Li, Dan-ming Chao & Ce Wang

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012 PR China.

Received
4 September 2013Accepted
1 October 2013Published
16 October 2013Correspondence and
requests for materials
should be addressed to
X.-F.L. (xflu@jlu.edu.cn)
or C.W. (cwang@jlu.
edu.cn)

Here, we demonstrated a novel method to decorate Cu_9S_5 nanocrystals on polyaniline (PANI) nanowires using the dopant of mercaptoacetic acid (MAA) in the PANI matrix as the sulfur source under a hydrothermal reaction. TEM images showed that Cu_9S_5 nanocrystals with a size in the range of 5–20 nm were uniformly formed on the surface of PANI nanowires. Significantly, the as-prepared PANI/ Cu_9S_5 composite nanowires have been proven to be novel peroxidase mimics toward the oxidation of the peroxidase substrate 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H_2O_2 . Due to the synergetic effects between polyaniline nanowires and Cu_9S_5 nanocrystals, the obtained PANI/ Cu_9S_5 composite nanowires exhibit superior catalytic activity over the independent components. This work not only presents a simple and versatile method to decorate semiconductor nanocrystals on the surface of conducting polymer nanostructures, but also provides fundamental guidelines for further investigations into the synergetic effect between conducting polymers and other materials.

Over the past few decades, artificial enzyme mimics have generated great interest because of their improved properties relative to natural enzymes, such as easy and low costs of preparation, purification and storage, greater resistance to extremes of acidity, temperature and inhibitors^{1–3}. Indeed, many enzyme mimics such as hemin, hematin, hemoglobin, cyclodextrin, porphyrin etc. have been developed and applied in the fields of clinical diagnosis, environmental science and biotechnology^{4–12}. At present, the synthesis and application of nanomaterials in the field of catalysis has become an active field of scientific research because of their large surface area, high catalytic activity and good selectivity, and some nanomaterials have been found to possess enzyme mimetic activity¹³. For example, Fe_3O_4 magnetic nanoparticles were first reported to process intrinsic peroxidase-like activity, which could be used to detect H_2O_2 and thrombin^{14–16}. The nanomaterials as artificial enzyme mimics take the advantages of low cost, easy preparation, high activity and good stability. In the past few years, various kinds of nanomaterials have been explored as enzymatic mimics, including metal oxide nanoparticles (NPs) and nanowires (such as Fe_3O_4 NPs, Co_3O_4 NPs, CuO NPs, CeO_2 NPs, V_2O_5 nanowires)^{14,17–20}, metal-based nanomaterials (such as Au NPs, bimetallic alloy NPs, bimetallic hybrid nanorods)^{21–24}, carbon nanomaterials (such as graphene oxide, carbon nanotubes, carbon nanodots)^{25–27}, chalcogenide nanomaterials (such as FeS , FeSe , CuS , CdS NPs)^{28–31}, multiferroic nanomaterials (such as BiFeO_3 NPs, CoFe_2O_4 NPs)^{32,33}, and even coordination polymer NPs³⁴ or carboxyl functionalized mesoporous polymer³⁵.

During the process of catalytic reactions, the interfaces play an important role, which could result in a better activity and selectivity³⁶. Recently, Yang and co-workers designed multiple metal-metal oxide interfaces to study the catalysis of sequential reactions³⁷. It was found that two different kinds of metal-metal oxide interfaces could catalyze two distinct sequential reactions. Therefore, the fabrication of composite nanomaterials with well-defined composition and interfaces has been extensively studied to enhance or extend the functionality of each component. A variety of graphene or carbon nanotube based nanomaterials have been explored with peroxidase-like catalytic activity^{38–41}. Typically, the Au NPs/graphene composite nanosheets process an enhanced catalytic activity in comparison to the independent Au-NPs and graphene, which could be due to the synergetic effect at their interfaces⁴¹. However, such synergetic effect has few been observed in other systems except the carbon based nanomaterials. In this study, we have shown for the first time that conducting polyaniline (PANI)/ Cu_9S_5 composite nanowires showed a superior catalytic activity as artificial enzyme mimics compared to the independent polyaniline and Cu_9S_5 nanocomponents due to their synergetic effect.

PANI is one kind of conducting polymers that has been extensively studied in the past few decades. Compared to other intrinsic conducting polymers, the doping level of PANI can be simply controlled by a reversible acid/



base doping/dedoping process⁴². In recent years, PANI nanomaterials have attracted much attention because of their unique physical and chemical properties such as large surface area and high conductivity. Especially, one-dimensional PANI nanostructures such as nanofibers, nanorods and nanowires have become a focus subject in the field of conducting polymer nanotechnology because they possess the advantages of both excellent conductivity and low-dimensional systems⁴³. On the other hand, nanocomposites with PANI and inorganic nanomaterials showed improved electrical, thermal and optical properties due to the combined effect of the two components⁴⁴. For the PANI based nanocomposites, the interactions between PANI and the inorganic nanomaterials are very vital to produce cooperatively enhanced performances. In the past few years, a series of PANI/sulfide nanocomposites have been fabricated for optic, optoelectronic and photoelectrochemical applications^{45–47}. However, it is still a great challenge to prepare low dimensional PANI nanocomposites with strong interactions between PANI and another inorganic nanocomponent to generate synergetic effect, which achieve an enhanced performance of the nanocomposites.

Herein, we have developed a novel method to fabricate PANI/Cu₉S₅ composite nanowires using the dopant of mercaptoacetic acid (MAA) in the PANI matrix as the sulfur source under a hydrothermal reaction. During the process of the reaction, the Cu₉S₅ nanocrystals could be in-situ formed on the surface of PANI nanowires with strong interactions because the sulfur source of MAA was interacted with PANI nanowires through ionic bonds. Furthermore, it was found that the as-prepared PANI/Cu₉S₅ composite nanowires exhibited an enhanced catalytic activity toward the oxidation of 3,3',5,5'-tetramethylbenzidine (TMB) in the presence of H₂O₂ over the independent PANI and Cu₉S₅ nanocomponents due to the synergetic effect between them.

Results

In this study, PANI/Cu₉S₅ composite nanowires were prepared by mixing MAA doped PANI nanowires and CuCl₂·2H₂O under a

hydrothermal reaction. The synthetic strategy mainly involves three steps: (1) PANI nanowires doped with HCl was synthesized through a rapid-mixing method. (2) After treated by NH₃·H₂O, the dedoped PANI nanowires were again doped with MAA to form MAA doped PANI nanowires. (3) Mixing MAA doped PANI nanowires with copper ions under a hydrothermal condition to form PANI/Cu₉S₅ composite nanowires. During the reaction, the Cu₉S₅ nanocrystals were in-situ formed on the surface of PANI nanowires (Figure 1a). Figure 1b shows the TEM image of HCl doped PANI nanowires. It can be seen that the diameter of the PANI nanowires is in the range of 50–100 nm with a relatively smooth surface. After dedoping with NH₃·H₂O and again doping with MAA, the size of nanowires did not change much, but showed a little aggregation (Figure S1 and 1c). After hydrothermal reaction, it can be clearly seen that Cu₉S₅ nanocrystals with a size in the range of 5–20 nm were uniformly formed on the surface of PANI nanowires (Figure 1d). A high resolution TEM (HRTEM) image exhibits that the as-prepared Cu₉S₅ nanocrystals showed a good crystallinity, with the lattice spacing of 0.20 nm which could be corresponding to the {0120} facet of Cu₉S₅⁴⁸ (Figure 1e). A control experiment was also performed to synthesize pristine Cu₉S₅ nanocrystals, which exhibit a particle or rod shape with a size of about 20–80 nm (Figure S2). This result indicates that the presence of PANI nanowires make for the Cu₉S₅ nanocrystals with a smaller size, which should be due to the strong interactions between the dopant of MAA and PANI nanowires during the hydrothermal reaction.

The formation of Cu₉S₅ nanocrystals on the surface of PANI nanowires were characterized by XRD measurement. Figure 2a shows the XRD patterns of the as-prepared PANI/Cu₉S₅ composite nanowires and Cu₉S₅ nanocrystals alone. From Figure 2a (red line), the diffraction peaks at $2\theta = 27.8^\circ, 29.5^\circ, 32.2^\circ, 37.6^\circ, 42.0^\circ, 46.3^\circ, 48.8^\circ, 54.7^\circ$ are indexed to the (0015), (107), (1010), (0114), (0117), (0120), (119), (1115) planes of Cu₉S₅, which is in good agreement with the Rhomb-centered structure (JCPDS 47-1748). Moreover, most of the strong diffraction peaks including (0015), (1010),

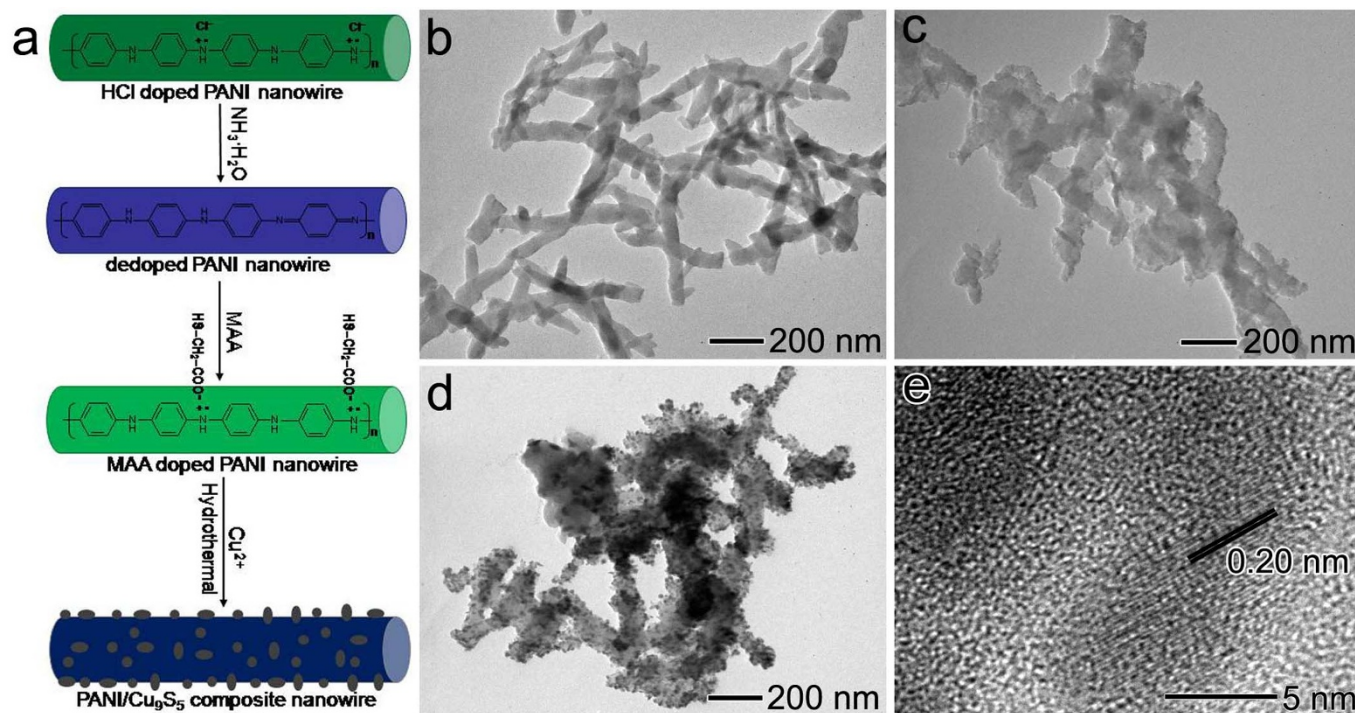


Figure 1 | Fabrication and morphology of the PANI/Cu₉S₅ composite nanowires. (a) Schematic illustration of the fabrication process to synthesize PANI/Cu₉S₅ composite nanowires. TEM images of the as-prepared (b) HCl doped PANI nanowires, (c) MAA doped PANI nanowires and (d) PANI/Cu₉S₅ composite nanowires. (e) HRTEM image of the as-prepared PANI/Cu₉S₅ composite nanowires.

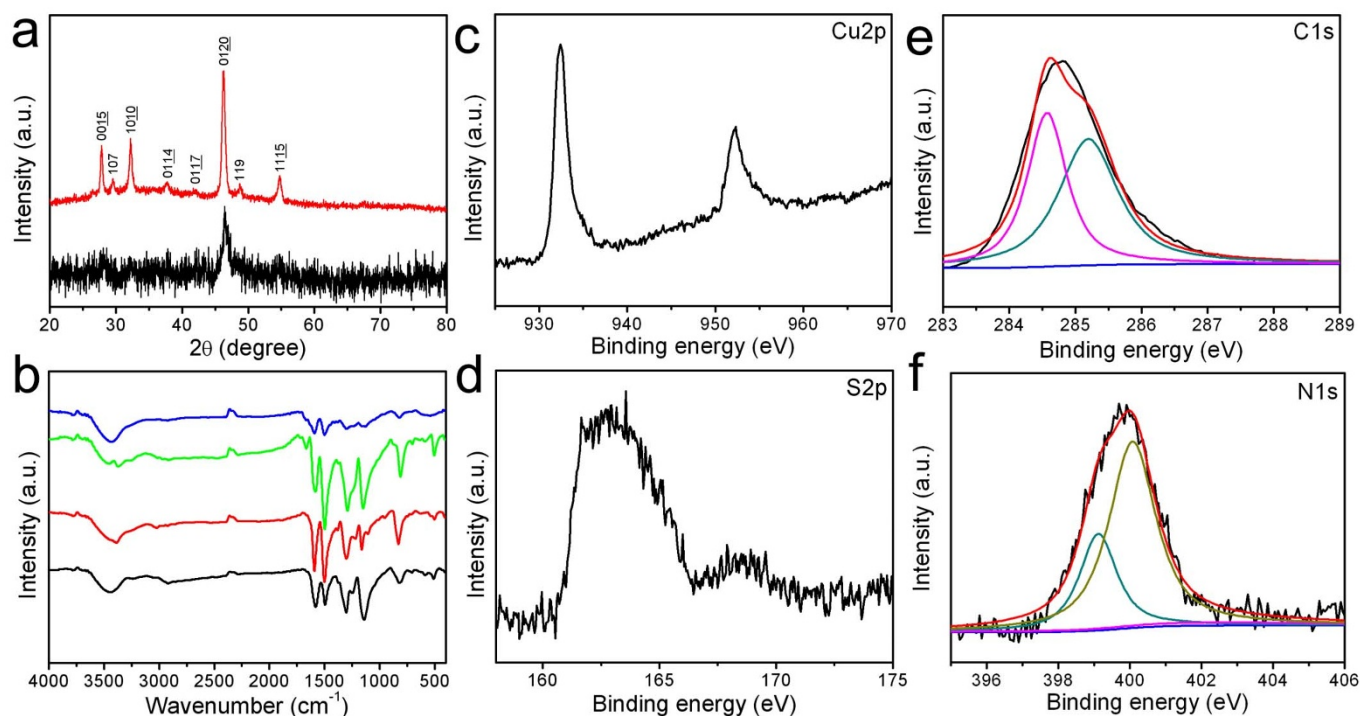


Figure 2 | Surface composition of the PANI/Cu₉S₅ composite nanowires. (a) XRD patterns of pristine Cu₉S₅ nanocrystals (red) and the as-prepared PANI/Cu₉S₅ composite nanowires (black). (b) FTIR spectra of HCl doped PANI nanowires (black), dedoped PANI nanowires with NH₃·H₂O (red), MAA doped PANI nanowires (green) and PANI/Cu₉S₅ composite nanowires (blue). XPS spectra of the as-synthesized PANI/Cu₉S₅ composite nanowires: (c) Cu2p, (d) S2p, (e) C1s and (f) N1s.

(0120), (1115) have also been observed in the pattern of the as-prepared PANI/Cu₉S₅ composite nanowires, indicating the formation of Cu₉S₅ nanocrystals on the surface of PANI nanowires. We also estimated the size of Cu₉S₅ nanocrystals in accordance with the Scherrer's equation, and the average particle size of the Cu₉S₅ nanocrystals was calculated to be about 7.5 nm, which is consistent with the results originated from the TEM images.

Figure 2b shows the FTIR spectra of HCl doped PANI nanowires, dedoped PANI nanowires, MAA doped PANI nanowires and PANI/Cu₉S₅ composite nanowires, respectively. It was found that the characteristic peaks at 1581, 1495, 1304, 1244, 1142, 821 cm⁻¹ which are corresponding to C=C stretching of the quinonoid and benzenoid rings, C-N and C=N stretching vibrations, N=Q=N (where Q denotes the quinonoid ring) bending vibration and the in-plane bending of C-H, respectively, were clearly observed for HCl doped PANI nanowires⁴⁵. After dedoping by aqueous ammonia, the characteristic peaks of C=C stretching of the quinonoid and benzenoid rings shift to 1591 and 1500 cm⁻¹. And these two peaks shift to 1581 and 1498 cm⁻¹ after doping with MAA. And a new peak at 1664 cm⁻¹ appears for the MAA doped PANI nanowires, which is corresponding to the C=O stretching vibrations of MAA dopant. For PANI/Cu₉S₅ composite nanowires, the characteristic peaks were observed at 1591, 1500, 1300, 1130 and 822 cm⁻¹, indicating that the strong interactions between PANI nanowires and Cu₉S₅ nanocrystals.

Insight information of the surface chemical composition of the as-prepared PANI/Cu₉S₅ composite nanowires has been characterized by XPS analysis. As shown in Figure 2c, two strong peaks at 932.4 and 952.3 eV for Cu 2p_{3/2} and Cu 2p_{1/2}, respectively, were clearly observed. The binding energy for Cu 2p_{3/2} in the Cu(2p) core level spectrum is close to the previous report of Cu⁺⁴⁹. In addition, a weak broad peak at about 945.0 eV are also observed, which could be attributed to the Cu²⁺⁵⁰. These results suggested that both Cu⁺ and Cu²⁺ ions existed in the PANI/Cu₉S₅ composite nanowires. Figure 2d shows the S 2p spectrum of PANI/Cu₉S₅ composite nanowires. The binding energy of S 2p appears at about 162.9 eV, which is generally

attributed to the formation of Cu-S bond. And another weak peak centered at about 168.7 eV could be ascribed to the oxidized sulfur species such as sulfonate⁵¹. On the other hand, the C 1s of PANI in PANI/Cu₉S₅ composite nanowires has also been detected and could be deconvoluted into two components (Figure 2e). The peak at about 284.6 eV is attributed to C-C bond, while the other peak at about 285.2 eV is related to C-N bond. Similarly, the N1s spectrum could also be deconvoluted into two components, with binding energy at 400.1 and 399.1 eV, respectively (Figure 2f). The former peak is attributed to neutral nitrogen moieties in PANI⁵². The later signal at 399.1 eV is usually ascribed to uncharged deprotonated imine (=N-) atoms⁵². This result indicated that the doping degree was low in the PANI/Cu₉S₅ composite nanowires.

The formation of the MAA doped PANI nanowires and PANI/Cu₉S₅ composite nanowires has been proved by UV-vis absorption spectra. As shown in Figure 3a, HCl doped PANI nanowires exhibited characteristic color in green. After dedoping by ammonia water, the color turned to blue. Then it became back to light green after again doping with MAA. This result indicated that MAA had been doped in the PANI chains. The UV-vis absorption spectrum of the HCl doped PANI nanowires showed three characteristic absorption bands at around 360, 425 and > 800 nm (Figure 3b). The first absorption peak could be ascribed to the π-π* electron transition within benzenoid segments. The other two absorption peaks at 425 and > 800 nm are attributing to the polaron to π* electron transition and the π to the localized polaron band, respectively⁵³. For the dedoped PANI nanowires, the obvious peak centered at about 670 nm is corresponding to the benzenoid to quinonoid excitonic transition, which is the characteristic band of the dedoped state of the PANI nanowires⁵³. As for the MAA doped PANI nanowires, the characteristic peaks of the π-π* electron transition, polaron-π* electron transition and π-localized polaron band were observed at 358, 450 and > 800 nm, indicating that PANI nanowires are in doped state. The UV-vis absorption spectrum of PANI/Cu₉S₅ composite nanowires showed the characteristic peaks at about 333 and 630 nm,

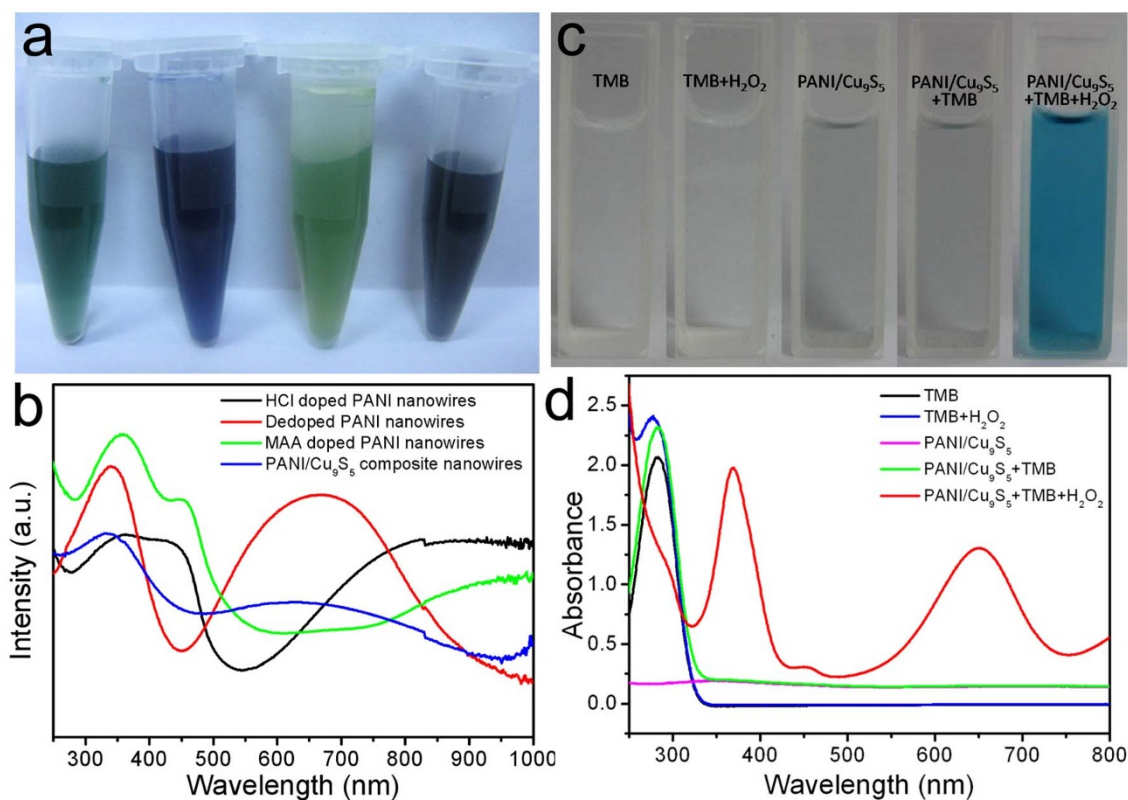


Figure 3 | Absorption spectra property and peroxidase-like catalytic activity of the PANI/Cu₉S₅ composite nanowires. (a) Photographs (from left to right) and (b) UV-vis absorption spectra of aqueous dispersions of HCl doped PANI nanowires (black), dedoped PANI nanowires (red), MAA doped PANI nanowires (green) and PANI/Cu₉S₅ composite nanowires (blue). (c) Photographs (from left to right) and (d) UV-vis spectra of TMB solution (black line), TMB-H₂O₂ (blue line), PANI/Cu₉S₅ solution (purple line), PANI/Cu₉S₅ + TMB (green line) and PANI/Cu₉S₅ + TMB + H₂O₂ (red line) in pH 4.0 acetate buffer at room temperature ([TMB]: 0.1 mM; [H₂O₂]: 65 mM; [PANI/Cu₉S₅]: 20 µg/mL).

indicating the low doping level of the PANI in the composite nanowires.

It is well known that some transition metal compound nanoparticles such as Fe₃O₄, FeS and CuS process a peroxidase-like activity^{14,28,30}. In this study, we evaluated the catalytic activity of the PANI/Cu₉S₅ composite nanowires by using a peroxidase-like catalytic reaction involving the oxidation of a peroxidase substrate TMB in the presence of H₂O₂. Similar to HRP, PANI/Cu₉S₅ composite nanowires could quickly catalyze the oxidation of TMB in the presence of H₂O₂ to produce a typical blue color in only several minutes, showing their good peroxidase-like activity. Control experiments were also performed to demonstrate that the peroxidase-like activity was attributed to the nanocatalysts of PANI/Cu₉S₅ composite nanowires. As shown in Figure 3c, the TMB + H₂O₂ system without PANI/Cu₉S₅ composite nanowires was colorless, and also no blue color was generated for the PANI/Cu₉S₅ composite nanowires + TMB system under experimental conditions. This result suggested that neither H₂O₂ nor PANI/Cu₉S₅ composite nanowires alone could catalyze the oxidation of TMB. UV-vis spectra have also been used to evaluate the peroxidase-like activity of PANI/Cu₉S₅ composite nanowires (Figure 3d). It was seen that no obvious adsorption peaks ranging from 330 to 750 nm were observed for TMB solution, PANI/Cu₉S₅ composite nanowires dispersions, TMB + H₂O₂ system and PANI/Cu₉S₅ composite nanowires + TMB system. However, three strong adsorption peaks centered at 369, 453, and 652 nm appeared for the PANI/Cu₉S₅ composite nanowires + TMB + H₂O₂ system, which originates from the oxidation of TMB. This result revealed that PANI/Cu₉S₅ composite nanowires could catalyze the oxidation of TMB in the presence of H₂O₂. It is well known that Cu²⁺ and Fe³⁺ are common Fenton reagents, which could also efficiently catalyze the oxidation of TMB in the presence of H₂O₂. To

rule out the possibility that the Cu²⁺ leaching from PANI/Cu₉S₅ composite nanowires act as the catalysts for the oxidation of TMB, we also performed a comparison experiment to test the peroxidase-like activity of the leaching solution. It was found that no obvious change of absorbance was observed when the leaching solution was used as the catalysts under the same reaction conditions (Figure S3). These results suggested that the peroxidase-like activity was due to the PANI/Cu₉S₅ composite nanowires.

Discussion

As comparisons, we have evaluated the peroxidase activity of PANI/Cu₉S₅ composite nanowires, Cu₉S₅ nanocrystals, PANI nanowires and even the physical mixture of Cu₉S₅ nanocrystals and PANI nanowires, respectively. As shown in Figure 4a and b, free PANI nanowires almost showed no catalytic activity, and Cu₉S₅ nanocrystals alone had a low catalytic activity. The physical mixture of Cu₉S₅ nanocrystals and PANI nanowires showed a similar catalytic activity with that of pristine Cu₉S₅ nanocrystals. However, the PANI/Cu₉S₅ composite nanowires exhibited a surprising high activity. The catalytic activity of the PANI/Cu₉S₅ composite nanowires processed a factor of about 30 fold higher than that of Cu₉S₅ nanocrystals and more than 1000 fold excess higher than that of PANI nanowires. The high catalytic activity might be due to the small size of the Cu₉S₅ nanocrystals on the surface of PANI nanowires. And the synergetic coupling effects between PANI nanowires and Cu₉S₅ nanocrystals in the PANI/Cu₉S₅ composite nanowires might also play an important role on mimicking peroxidases. It has been reported that the interfaces is important to achieve a better activity and selectivity during the catalytic reactions^{36,37}. Therefore, the synergetic catalytic effect in the composites should be due to the strong contact between PANI

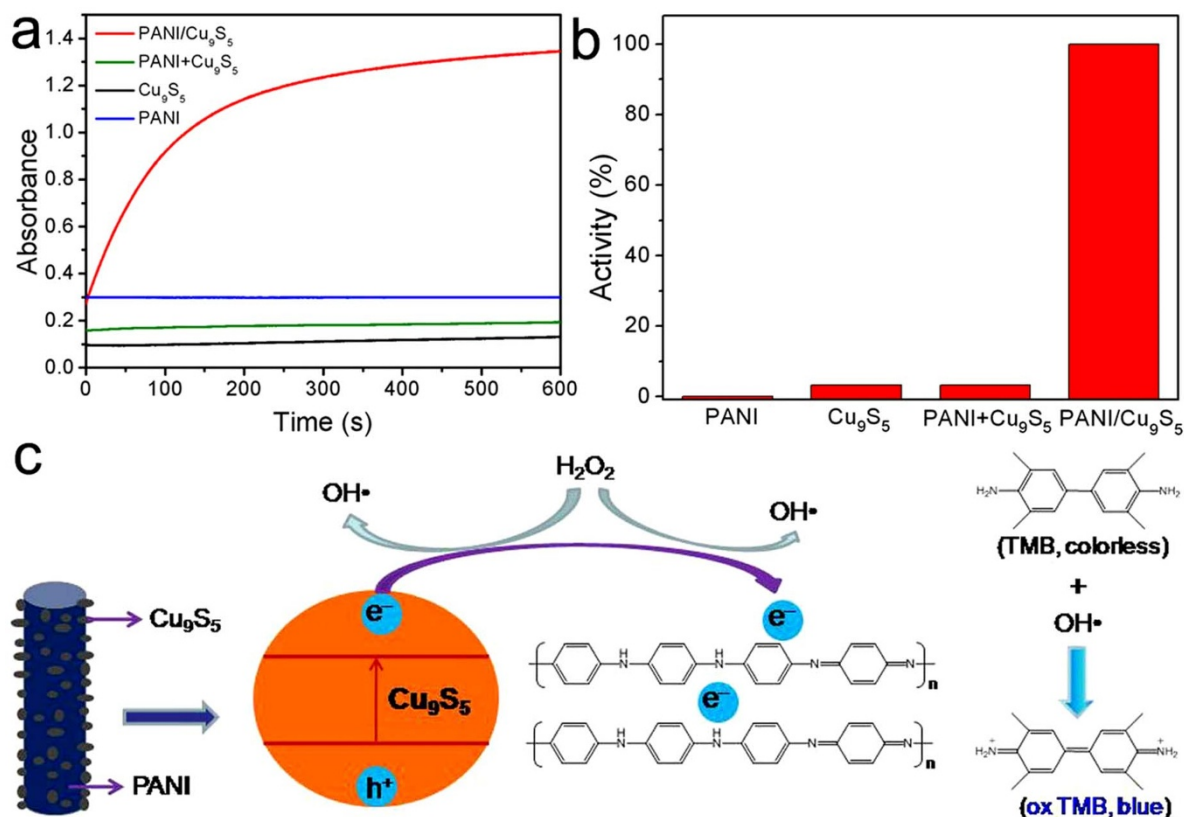


Figure 4 | Synergetic catalytic effect and the mechanism of the PANI/Cu₉S₅ composite nanowires toward the oxidation of TMB. (a) The time-dependent absorbance changes at 652 nm in the presence of pristine Cu₉S₅ nanocrystals, PANI nanowires, the physical mixture of PANI nanowires and Cu₉S₅ nanocrystals, and the as-prepared PANI/Cu₉S₅ composite nanowires in pH 4.0 acetate buffer (0.1 M NaAc-HAc) at room temperature; (b) Comparison of the catalytic activities of PANI nanowires, pristine Cu₉S₅ nanocrystals, the physical mixture of PANI nanowires and Cu₉S₅ nanocrystals, and PANI/Cu₉S₅ composite nanowires under the same conditions. The difference of the absorbance between 10 and 0 min stands for the activity and the maximum point was set as 100%. (c) A possible mechanism of the synergetic catalytic effect of the PANI/Cu₉S₅ composite nanowires toward the oxidation of TMB.

nanowires and Cu₉S₅ nanocrystals. An early report has shown that Au/graphene hybrid with strong covalent interfacial exhibited a synergetic catalytic effect in peroxidase-like catalysis⁴¹. In this paper, we have synthesized Cu₉S₅ nanocrystals on the surface of PANI nanowires by using the dopant of PANI nanowires as the sulfur source, producing a strong contact between the two nanocomponents, which enhances the catalytic activity for the oxidation of TMB. In order to verify the synergetic catalytic effect between PANI nanowires and Cu₉S₅ nanocrystals, we have also synthesized multi-walled carbon nanotubes (MWCNT)/Cu₉S₅ composite nanotubes using a hydrothermal reaction and studied their catalytic activity toward the oxidation of TMB for mimicking peroxidases. TEM image showed that Cu₉S₅ nanocrystals were well dispersed on the surface of MWCNT nanotubes with a very small size, most of which was in the range of 5–30 nm (Figure S4). However, the as-synthesized MWCNT/Cu₉S₅ composite nanotubes showed a low catalytic activity toward the oxidation of TMB compared with that of PANI/Cu₉S₅ composite nanowires (Figure S5). This result further proved that the synergetic catalytic effect between PANI nanowires and Cu₉S₅ nanocrystals contributed the high catalytic activity of PANI/Cu₉S₅ composite nanowires for the oxidation of TMB.

A possible mechanism for the enhanced catalytic activity of the PANI/Cu₉S₅ composite nanowires toward the oxidation of TMB has been demonstrated. Based on the previous reports, the blue color product should be due to the oxidation of TMB by OH[•]^{54,55}. Cu(II) on the surface of Cu₉S₅ nanocrystals might produce OH[•] by the Fenton reaction between Cu(II) and H₂O₂³⁰. However, this pathway

to produce OH[•] could not explain the enhanced catalytic activity of the PANI/Cu₉S₅ composite nanowires compared to that of Cu₉S₅ nanocrystals. We think that the adsorbed H₂O₂ could also be catalyzed by the PANI/Cu₉S₅ heterostructures. As shown in Figure 4c, when PANI was coupled with a narrow band gap semiconductor such as Cu₉S₅ under visible light irradiation, the photogenerated electrons excited by Cu₉S₅ will transfer from Cu₉S₅ to PANI, which effectively prevent the recombination of the electron-hole pairs. And H₂O₂ is a good electron scavenger to form OH[•] on the surface of composite nanowires, which largely enhanced the oxidation ability of TMB⁵⁵. As a result, the PANI/Cu₉S₅ composite nanowires exhibited an enhanced catalytic activity compared to the individual Cu₉S₅ nanocrystals and PANI nanowires alone.

In summary, PANI/Cu₉S₅ composite nanowires have been fabricated under a hydrothermal reaction between MAA doped PANI nanowires and copper chloride. This method affords an effective route to decorate Cu₉S₅ nanocrystals on the surface of PANI nanowires with a strong contact. The obtained Cu₉S₅ nanocrystals were well dispersed on the surface of PANI nanowires. The as-synthesized PANI/Cu₉S₅ composite nanowires show a high catalytic activity towards the oxidation of TMB for mimicking peroxidases. The catalytic activity of the PANI/Cu₉S₅ composite nanowires is much higher than that of Cu₉S₅ nanocrystals and PANI nanowires alone. The synergetic catalytic effect should be attributed to the strong interactions between PANI nanowires and Cu₉S₅ nanocrystals. It was expected that the PANI/Cu₉S₅ composite nanowires could have great potential practical applications in catalysis and bioassays.



Methods

Chemicals and materials. Aniline was purchased from Xilong Chemical Co. Ltd and was distilled under reduced pressure before use. MAA was purchased from Aladdin. Copper chloride ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$) and TMB were purchased from Sinopharm group chemical reagent Co. Ltd. Other reagents such as ammonium peroxydisulfate (APS), hydrochloric acid (HCl), ammonia solution ($\text{NH}_3 \cdot \text{H}_2\text{O}$), hydrogen peroxide (H_2O_2) and ethanol were of analytical grade and were used as received without purification. Distilled water was used in all experiments.

Preparation of MAA doped PANI nanowires. Firstly, HCl doped PANI nanowires was prepared using a modified rapid-mixing reaction method^{56,57}. In a typical procedure, an aqueous solution of 0.3 mL aniline monomer in 10 mL of 1.0 M HCl and another aqueous solution of 0.18 g of ammonium peroxydisulfate in 10 mL of 1.0 M HCl were prepared and mixed rapidly. After shaking for about 30 s, the mixture was left for 2 h. The as-synthesized green precipitate of PANI nanowires doped with HCl was centrifuged and washed with distilled water for at least three times.

For the preparation of dedoped PANI nanowires, the as-synthesized PANI nanowires was dispersed in 1.0 M $\text{NH}_3 \cdot \text{H}_2\text{O}$ and stirred for about 8 h. The green PANI nanowires doped with HCl immediately changed to blue after the addition of $\text{NH}_3 \cdot \text{H}_2\text{O}$. The dedoped PANI nanowires was centrifuged and washed with distilled water for at least two times. For the preparation of PANI nanowires doped with MAA, the obtained dedoped PANI nanowires was then dispersed into a MAA solution for about 12 h. Then the MAA doped PANI nanowires was centrifuged and washed with distilled water. Finally, the MAA doped PANI nanowires were dispersed in water for use.

Preparation of PANI/Cu₉S₅ composite nanowires. PANI/Cu₉S₅ composite nanowires were prepared by mixing MAA doped PANI nanowires and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ under a hydrothermal reaction. In a typical procedure, 1 mL of aqueous solution containing 51 mg $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ was added into 30 mL of water which containing 15 mg of MAA doped PANI nanowires. After that, the mixed solution was transferred into a 45 mL Teflon-lined stainless steel autoclave at 140 °C for 12 h. Finally, the solid product was collected by centrifuge, washing with water and ethanol, and then dried in vacuum at 30 °C for one night.

Investigation of the peroxidase-like activity of the PANI/Cu₉S₅ composite nanowires. To evaluate the peroxidase-like activity of the obtained PANI/Cu₉S₅ composite nanowires, the catalytic oxidation of TMB in the presence of H_2O_2 was tested. In a typical experiment, 20 μL of 30% H_2O_2 and 20 μL of 15 mM TMB solution in DMSO solvent (prepared freshly) were added to 0.1 M acetate buffer (pH 4.0). Then, 20 μL of PANI/Cu₉S₅ composite nanowires suspension in water (3.0 mg/mL) was added into the above mixture. The blue color that developed during the process of the reaction was monitored in time by recording the absorption spectra in a scanning kinetics mode.

Characterization. TEM experiments were performed on JEM-1200 EX (JEOL) electron microscopes with an acceleration voltage of 100 kV. HRTEM imaging and energy dispersive X-ray (EDX) analysis were performed on a FEI Tecnai G2 F20 high-resolution transmission electron microscope operating at 200 kV. XRD patterns are obtained with a PANalytical B.V. Empyrean diffractometer using $\text{CuK}\alpha$ radiation. FTIR spectra of KBr powder-pressed pellets were recorded on a BRUKER VECTOR 22 Spectrometer. UV-vis spectra were recorded on a Shimadzu UV-3101 and 2501 PC spectrometer. Analysis of the X-ray photoelectron spectra (XPS) was performed on a Thermo Scientific ESCALAB250 measurement.

- Wulff, G. Enzyme-like catalysis by molecularly imprinted polymers. *Chem. Rev.* **102**, 1–27 (2002).
- Levine, L. A. & Williams, M. E. Inorganic biomimetic structures. *Curr. Opin. Chem. Biol.* **13**, 669–677 (2009).
- Kotov, N. A. Inorganic nanoparticles as protein mimics. *Science* **330**, 188–189 (2010).
- Wang, Q. *et al.* Supramolecular-hydrogel-encapsulated hemin as an artificial. *Angew. Chem. Int. Ed.* **46**, 4285–4289 (2007).
- Fruk, L. & Niemeyer, C. M. Covalent hemin-DNA adducts for generating a novel class of artificial heme enzymes. *Angew. Chem. Int. Ed.* **44**, 2603–2606 (2005).
- Aissaoui, H., Bachmann, R., Schweiger, A. & Woggon, W. D. On the origin of the low-spin character of cytochrome P450(cam) in the resting state: investigations of enzyme models with pulse EPR and ENDOR spectroscopy. *Angew. Chem. Int. Ed.* **37**, 2998–3002 (1998).
- Genfa, Z. & Dasgupta, P. K. Hemin as a peroxidase substitute in hydrogen peroxide determinations. *Anal. Chem.* **64**, 517–522 (1992).
- Wang, Q. L., Liu, Z. H., Cai, R. X. & Lu, G. X. Highly sensitive determination of hydrogen peroxide with hemoglobin as catalyst. *Chin. J. Anal. Chem.* **30**, 928–931 (2002).
- Liu, Z. H., Cai, R. X., Mao, L. Y., Huang, H. P. & Ma, W. H. Highly sensitive spectrofluorimetric determination of hydrogen peroxide with beta-cyclodextrin-hemin as catalyst. *Analyst* **124**, 173–176 (1999).
- Sono, M., Roach, M. P., Coulter, E. D. & Dawson, J. H. Heme-containing oxygenases. *Chem. Rev.* **96**, 2841–2887 (1996).

- Bonarlaw, R. P. & Sanders, J. K. M. Polyol recognition by a steroid-capped porphyrin. Enhancement and modulation of misfit guest binding by added water or methanol. *J. Am. Chem. Soc.* **117**, 259–271 (1995).
- Ci, Y. X., Zheng, Y. G., Tie, J. K. & Chang, W. B. Chemiluminescence investigation of the interaction of metalloporphyrins with nucleic acids. *Anal. Chim. Acta* **282**, 695–701 (1993).
- Haruta, M. When gold is not noble: catalysis by nanoparticles. *Chem. Rec.* **3**, 75–87 (2003).
- Gao, L. Z. *et al.* Intrinsic peroxidase-like activity of ferromagnetic nanoparticles. *Nat. Nanotechnol.* **2**, 577–583 (2007).
- Wei, H. & Wang, E. Fe_3O_4 magnetic nanoparticles as peroxidase mimetics and their applications in H_2O_2 and glucose detection. *Anal. Chem.* **80**, 2250–2254 (2008).
- Liu, S., Lu, F., Xing, R. & Zhu, J. J. Structural effects of Fe_3O_4 nanocrystals on peroxidase-like activity. *Chem. Eur. J.* **17**, 620–625 (2011).
- Mu, J. S., Wang, Y., Zhao, M. & Zhang, L. Intrinsic peroxidase-like activity and catalase-like activity of Co_3O_4 nanoparticles. *Chem. Commun.* **48**, 2540–2542 (2012).
- Chen, W. *et al.* Peroxidase-like activity of water-soluble cupric oxide nanoparticles and its analytical application for detection of hydrogen peroxide and glucose. *Analyst* **137**, 1706–1712 (2012).
- Asati, A., Santra, S., Kaittanis, C., Nath, S. & Perez, J. M. Oxidase-like activity of polymer-coated cerium oxide nanoparticles. *Angew. Chem. Int. Ed.* **48**, 2308–2312 (2009).
- Andre, R. *et al.* V_2O_5 nanowires with an intrinsic restigiou-like activity. *Adv. Funct. Mater.* **21**, 501–509 (2011).
- Jv, Y., Li, B. X. & Cao, R. Positively-charged gold nanoparticles as peroxidase mimic and their application in hydrogen peroxide and glucose detection. *Chem. Commun.* **46**, 8017–8019 (2010).
- He, W. *et al.* Design of AgM bimetallic alloy nanostructures (M = Au, Pd, Pt) with tunable morphology and peroxidase-like activity. *Chem. Mater.* **22**, 2988–2994 (2010).
- Kwon, T., Min, M., Lee, H. & Kim, B. J. Facile preparation of water soluble CuPt nanorods with controlled aspect ratio and study on their catalytic properties in water. *J. Mater. Chem.* **21**, 11956–11960 (2011).
- He, W. *et al.* Au@Pt nanostructures as oxidase and peroxidase mimetics for use in immunoassays. *Biomaterials* **32**, 1139–1147 (2011).
- Song, Y., Qu, K., Zhao, C., Ren, J. & Qu, X. Graphene oxide: intrinsic peroxidase catalytic activity and its application to glucose detection. *Adv. Mater.* **22**, 2206–2210 (2010).
- Song, Y. *et al.* Label-free colorimetric detection of single nucleotide polymorphism by using single-walled carbon nanotube intrinsic peroxidase-like activity. *Chem. Eur. J.* **16**, 3617–3621 (2010).
- Shi, W. *et al.* Carbon nanodots as peroxidase mimetics and their applications to glucose detection. *Chem. Commun.* **47**, 6695–6697 (2011).
- Dai, Z., Liu, S., Bao, J. & Ju, H. Nanostructured FeS as a mimic peroxidase for biocatalysis and biosensing. *Chem. Eur. J.* **15**, 4321–4326 (2009).
- Dutta, A. K. *et al.* Synthesis of FeS and FeSe nanoparticles from a single source precursor: A study of their photocatalytic activity, peroxidase-like behavior, and electrochemical sensing of H_2O_2 . *ACS Appl. Mater. Interfaces* **4**, 1919–1927 (2012).
- He, W. *et al.* Understanding the formation of CuS concave superstructures with peroxidase-like activity. *Nanoscale* **4**, 3501–3506 (2012).
- Maji, S. K. *et al.* Peroxidase-like behavior, amperometric biosensing of hydrogen peroxide and photocatalytic activity by cadmium sulfide nanoparticles. *J. Mol. Catal. A: Chem.* **358**, 1–9 (2012).
- Luo, W. *et al.* Ultrasensitive fluorometric determination of hydrogen peroxide and glucose by using multiferroic BiFeO_3 nanoparticles as a catalyst. *Talanta* **81**, 901–907 (2010).
- Shi, W., Zhang, X., He, S. & Huang, Y. CoFe_2O_4 magnetic nanoparticles as a peroxidase mimic mediated chemiluminescence for hydrogen peroxide and glucose. *Chem. Commun.* **47**, 10785–10787 (2011).
- Tian, J., Liu, S., Luo, Y. & Sun, X. Fe(III)-based coordination polymer nanoparticles: peroxidase-like catalytic activity and their application to hydrogen peroxide and glucose detection. *Catal. Sci. Technol.* **2**, 432–436 (2012).
- Liu, S., Wang, L., Zhai, J., Luo, Y. & Sun, X. Carboxyl functionalized mesoporous polymer: A novel peroxidase-like catalyst for H_2O_2 detection. *Anal. Methods* **3**, 1475–1477 (2011).
- Zhou, Z., Kooi, S., Flytzani-Stephanopoulos, M. & Saltsburg, H. The Role of the Interface in CO Oxidation on Au/CeO₂ Multilayer Nanotowers. *Adv. Funct. Mater.* **18**, 2801–2807 (2008).
- Yamada, Y. *et al.* Nanocrystal bilayer for tandem catalysis. *Nat. Chem.* **3**, 372–376 (2011).
- Guo, Y. *et al.* Hemin-graphene hybrid nanosheets with intrinsic peroxidase-like activity for label-free colorimetric detection of single-nucleotide polymorphism. *ACS Nano* **2**, 1282–1290 (2011).
- Zuo, X. *et al.* Design of a carbon nanotube/magnetic nanoparticle-based peroxidase-like nanocomplex and its application for highly efficient catalytic oxidation of phenols. *Nano Res.* **2**, 617–623 (2009).
- Dong, Y. *et al.* Graphene oxide- Fe_3O_4 magnetic nanocomposites with peroxidase-like activity for colorimetric detection of glucose. *Nanoscale* **4**, 3969–3976 (2012).



41. Liu, M., Zhao, H., Chen, S., Yu, H. & Quan, X. Stimuli-responsive peroxidase mimicking at a smart graphene interface. *Chem. Commun.* **48**, 7055–7057 (2012).
42. MacDiarmid, A. G. Synthetic Metals: A novel role for organic polymers. *Angew. Chem. Int. Ed.* **40**, 2581–2590 (2001).
43. Li, D., Huang, J. & Kaner, R. B. Polyaniline nanofibers: A unique polymer nanostructure for versatile applications. *Acc. Chem. Res.* **42**, 135–145 (2009).
44. Lu, X., Zhang, W. J., Wang, C., Wen, T. C. & Wei, Y. One-dimensional conducting polymer nanocomposites: Synthesis, properties and applications. *Prog. Polym. Sci.* **36**, 671–712 (2011).
45. Lu, X. *et al.* Preparation and characterization of polyaniline microwires containing CdS nanoparticles. *Chem. Commun.* 1522–1523 (2004).
46. Raut, B. T. *et al.* New process for fabrication of polyaniline–CdS nanocomposites: Structural, morphological and optoelectronic investigations. *J. Phys. Chem. Solids* **74**, 236–244 (2013).
47. Ameen, S., Akhtar, M. S., Kim, Y. S. & Shin, H. S. Synthesis and electrochemical impedance properties of CdS nanoparticles decorated polyaniline nanorods. *Chem. Eng. J.* **181–182**, 806–812 (2012).
48. Shan, J. *et al.* Synthesis and characterization of copper sulfide nanocrystallites with low sintering temperatures. *J. Mater. Chem.* **18**, 3200–3208 (2008).
49. Hu, H., Liu, Z., Yang, B., Chen, X. & Qian, Y. Template-mediated growth of Cu_3SnS_4 nanoshell tubes. *J. Cryst. Growth* **294**, 226–234 (2005).
50. Roy, P., Mondal, K. & Srivastava, S. K. Synthesis of twinned CuS nanorods by a simple wet chemical method. *Cryst. Growth Des.* **8**, 1530–1534 (2008).
51. Laffineur, F., Delhalle, J., Guittard, S., Geribaldi, S. & Mekhalif, Z. Mechanically polished copper surfaces modified with n-dodecanethiol and 3-perfluorooctylpropanethiol. *Colloids Surf. A* **198–200**, 817–827 (2002).
52. Atanasoska, L., Naoi, K. & Smyrl, W. H. XPS studies on conducting polymers: polypyrrole films doped with perchlorate and polymeric anions. *Chem. Mater.* **4**, 988–994 (1992).
53. Stejskal, J., Kratochvil, P. & Radhakrishnan, N. The formation of polyaniline and the UV-vis absorption spectra. *Synth. Met.* **61**, 225–231 (1993).
54. Gao, L., Wu, J. & Gao, D. Enzyme-controlled self-assembly and transformation of nanostructures in a tetramethylbenzidine/horseradish peroxidase/ H_2O_2 System. *ACS Nano* **5**, 6736–6742 (2011).
55. Zhao, M. *et al.* Controlled synthesis of spinel ZnFe_2O_4 decorated ZnO heterostructures as peroxidase mimetics for enhanced colorimetric biosensing. *Chem. Commun.* **49**, 7656–7658 (2013).
56. Huang, J. X. & Kaner, R. B. Nanofiber formation in the chemical polymerization of aniline: A mechanistic study. *Angew. Chem. Int. Ed.* **43**, 5817–5821 (2004).
57. Hang, J., Li, L. Y. & Guo, R. Novel approach to controllable synthesis of gold nanoparticles supported on polyaniline nanofibers. *Macromolecules* **43**, 10636–10644 (2010).

Acknowledgments

X.F.L. acknowledges the funding support from the National Natural Science Foundation of China (51273075), Jilin Science and Technology Department project (201115014) and Open Project of State Key Laboratory of Supramolecular Structure and Materials (sklssm201221). C.W. thanks the National Key Technology Research and Development Program (2013BAC01B02) and the National Natural Science Foundation of China (No. 21274052).

Author contributions

X.F.L. supervised the project, planned and performed the experiments, collected and analysed the data, and wrote the paper. X.J.B. performed the experiments, collected and analysed the data. Z.C.L. was responsible for TEM measurement and analysis. D.M.C. helped with synthesis of the materials and collected the data. C.W. supervised the project and analysed the data.

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: Lu, X.-F., Bian, X.-J., Li, Z.-C., Chao, D.-M. & Wang, C. A facile strategy to decorate Cu_3SnS_4 nanocrystals on polyaniline nanowires and their synergetic catalytic properties. *Sci. Rep.* **3**, 2955; DOI:10.1038/srep02955 (2013).



This work is licensed under a Creative Commons Attribution-NonCommercial-NoDerivs 3.0 Unported license. To view a copy of this license, visit <http://creativecommons.org/licenses/by-nc-nd/3.0>