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Multifunctional cellulosic paper based on quaternized chitosan and gold nanoparticle-reduced graphene oxide via electrostatic self-assembly

Yunzhi Ling^a, Xiaoyun Li^a, Shuwei Zhou^a, Xiaoying Wang^a*, Runcang Sun^{a,b}

Abstract: The surface of the negatively charged paper fiber was coated with quaternized chitosan (QCS) by electrostatic self-assembly to form a homogeneous positive coating due to the highly positive charge and excellent film-forming property of QCS. The gold chloride acid acted as precursor to prepare the gold nanoparticle (AuNP) on the graphene oxide (GO) sheet. Then, this negatively charged AuNP-loaded graphene oxide sheet was directly absorbed by QCS on the surface of fiber via further electrostatic self-assembly in water. Finally, AuNP-reduced graphene oxide/QCS/cellulose composite paper (AuNP-rGO/QCS/Cellulose) was fabricated after papermaking and following reduction by hydrogen iodide vapor. XRD, Raman spectra, XPS and FE-SEM results of the composite papers showed that electrostatic self-assembly made graphene oxide sheets tightly wrap paper fibers and graphene oxide was reduced, thus being beneficial to the formation of a more admirable graphene conductive network. Notably, AuNP-rGO/QCS/Cellulose composite paper to our best knowledge. Besides, this composite paper also presented excellent performance in photothermal conversion and catalysis of nitrophenol. This kind of paper may have promising applications as electric devices, sensors and catalyst.

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1. Introduction

Graphene, a flat two-dimensional monolayer of sp² bonded carbon atoms¹, has been widely studied because of its special structure and exceptional properties, including excellent thermal and electrical conductivity, good thermal stability as well as high mechanical strength²⁻⁶. Recent studies indicate that coating cellulose fiber with graphene is considered as an ideal approach to form flexible, foldable and tough paper which exhibits high electrochemical and mechanical activities⁷. Generally, graphene-cellulose paper is prepared by two ways. One is a simple blending process of dispersing chemically synthesized graphene nanosheets into a cellulosic pulp, followed by filtration⁸. Another is surface coating of graphene nanosheets onto paper substrate, followed by vacuum drying process⁹. However, both methods ignore the problem that the intrinsic van der Waals interaction between layers of graphene easily brings about agglomeration, which leads to insolubility in water¹⁰. The hydrophobicity of graphene would hinder its integration with cellulose fiber in suspension, and there is no strong bond linking graphene and cellulose fiber. As a result, conventional graphene-cellulose paper has drawbacks in homogenization and stabilization^{8,9}. From this point, graphene oxide (GO) has been given much attention, since it can be dispersed in water due to oxygen functional groups, such as hydroxyl, epoxy, carbonyl, and carboxyl groups¹¹. Chemically reduced GO (rGO) sheets can obtain an increased conductivity compared with GO sheets owing to the restoration of the conjugated network in the rGO sheets¹².

But paper fibers¹³ and GO sheets¹⁴ are known to be negatively charged in aqueous suspensions, it is impossible to integrate paper fibers with GO sheets firmly and to form compact electrical network structure because of the mutual repulsion. Therefore, finding a positively charged intermediary serving as an adhesive can be essential for improving the adsorption of GO sheets onto paper fibers.

Quaternized chitosan (QCS) is endowed with numerous positively charged quaternary ammonium groups¹⁵. Moreover, due to the outstanding film-forming ability, QCS is able to generate an even layer of positive-charged coating on surface of paper fibers when fibers are immersed in QCS solution¹⁶. It can deduce that positively charged QCS-coated cellulose fibers attract the negatively charged GO sheets, and the preferable film-forming characteristic of QCS further contributes to the uniform wrapping of GO sheets. For these reasons, QCS, in this study, performs as "glue" to link GO sheets to cellulose fibers via electrostatic self-assembly.

In addition, recent reports have explored that the coupling of nano noble metals onto graphene surface tends to demonstrate synergistic properties and diverse functionalities aimed at specific applications, which provides a promising alternative to endow graphene novel potential¹⁷. For the sake of acquiring better conductive, photothermal conversion ability and catalytic property, chloroauric acid was added to prepare AuNPs loading on GO sheets.

In this work, we fabricated a novel multifunctional paper based on AuNP-rGO/QCS/Cellulose in six main consecutive steps as illustrated in Scheme 1: (1) Negatively charged cellulose fibers were dispersed in water; (2) Cellulose fibers electrostatically interacted with QCS molecules by being immersed in QCS solution and then were covered with positive charges on the surface; (3) Au-loaded GO nanosheets was coated on the QCS-functionalized cellulose fibers via electrostatic self-assembly; (4) After self-assembly process, an even layer of Au-loaded GO nanosheet coating was formed; (5) AuNP-GO/QCS/Cellulose composite experienced paper-making process; (6) Multifunctional /QCS/Cellulose paper was obtained using a low-temperature vapour reduction method with hydroiodic (HI) acid as reducing agent. Finally, electrical, photothermal, mechanical, flexible and catalytic abilities of this multifunctional composite cellulosic paper were evaluated.

2. Experimental

Materials

HI acid (55%) and graphite flake (particle size < 150 μm) were purchased from Aladdin-reagent Inc. QCS was purchased from Tianhua Co. Ltd.(Shandong, China), with the DS of quaternary ammonium groups at 0.92. GO was prepared from natural graphite



Scheme 1 Preparation course of AuNP-rGO/QCS/cellulose composite paper

flake by the modified Hummers method¹⁸. Pulp fiber was prepared in our laboratory with eucalyptus chips, the beating degree was measured at 42 °SR after beating process. Other chemicals were all analytical grade.

Preparation of Cellulosic paper

0.2 g wood pulp was added to 100 mL deionized water, followed by vigorous stirring for 10 min to form homogeneous suspension. Then the mixture was filtered by an 80 mm sintered glass filter and vacuumized. The cellulosic paper was obtained by peeling the paper from filter cloth and then through pressing and drying in a laboratory sheet dryer.

Preparation of QCS/Cellulose paper

The QCS powder was dissolved in deionized water to prepare 0.5 wt% QCS solution and then filtered through a 0.22 µm Millipore filter. Afterwards, the cellulose fibers were immersed in the asprepared QCS solution for 10 min at room temperature with vigorous stirring. The QCS-coated cellulose fibers were obtained after being dried in drying oven and washed with deionized water to remove the residuary QCS molecules. Paper-making procedures were the same as that of cellulose paper.

Preparation of rGO/Cellulose paper

The as-prepared cellulose fibers were soaked in the 200 mL GO solution (5 mg/mL) which was dispersed by ultrasonication for 60 min before use. Stirring for 5 min later, the mixture experienced the same paper-making procedures. After paper-making process, the GO/Cellulose paper was placed in a glass vessel which contained the mixture of 2mL HI and 5mL acetic acid, then the vessel was placed in a water bath at 40 °C for 15 min according to the report ¹⁹. Finally, the rGO/Cellulose paper was obtained after being rinsed by saturated

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NaHCO₃ solution, deionized water, and methanol and then was dried at room temperature.

Preparation of rGO/QCS/Cellulose paper

The preparation processes were quiet similar with that of rGO/Cellulose paper except for the cellulose fibers, which should be replaced by QCS-coated cellulose fibers.

Preparation of AuNP-rGO/QCS/Cellulose paper

Firstly, the synthesis of Au-loaded GO nanocomposites was according to the reduction of Gold chloride by sodium citrate²⁰. Typically, 5 mL HAuCl₄ solution (20 mg/mL) was added to 50 mL GO aqueous suspension (2 mg/mL). The resultant suspension was aged for 1 h to promote the interaction between gold ions and the GO surfaces. Subsequently, the suspension was heated until 80 °C and then 10 mL sodium citrate (50 mL/mg) was added dropwise. The reaction was kept at this temperature for 1h. The preparation procedure of AuNP-rGO/QCS/Cellulose paper was similar with that of rGO/QCS/Cellulose paper apart from the GO suspension, which was replaced by AuNP-GO suspension.

Characterizations

The morphologies and structures of composite papers were investigated by a field emission scanning electron microscopy (Hitachi, Japan). The chemical structures were analyzed by Raman spectroscopy with a 514 nm incident light and X-ray photoelectron analysis (Kratos, UK) using Mg K α (h γ =1253.6 eV) in steps of 0.1 eV. The XRD patterns of composite papers were investigated by using a D8 advance X-ray diffractometer (Bruker, Germany) with a Cu K α radiation (λ = 0.15418 nm) at 40 kV and 50 mA. The tensile test was carried out by a micro tensile tester (Donghua, China) with a rate of 2 mm/min. TGA were carried out on a TGA Q500 (TA, America) from room temperature to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

Measurement of conductivity

The sheet resistance (R_s , Ω/aq) of composite paper was measured by a four-probe method using a multi-electrical measurement system (SDY-5, Guangzhou, China) and the corresponding volume conductivity (σ , S/cm) was calculated by the formula: $\sigma = 1/(R_s t)$, where t (cm) is the paper thickness. *Measurement of photothermal conversion*

Photothermal conversion properties were tested by a 808 nm infrared diode laser with a power density at 4 W/cm² (Changchun New Industries Optoelectronics Technology Co., Ltd.) and a thermometer (UNI-T 1310, UNI-T Electronic Corp.).

Catalysis of 4-nitrophenol by AuNP-rGO/QCS/Cellulose paper

To test the catalytic activity of AuNP-rGO/QCS/Cellulose paper, reduction of 4-NP was monitored as follows. 4-nitrophenol (2 mL, 0.2 mM) solution was added to a standard cuvette containing fresh sodium borohydride (1 mL, 0.03 M), and then AuNPrGO/QCS/Cellulose paper was soaked in the cuvette to catalyze the reduction of 4-NP. The process of reduction was monitored by using a UV-Vis spectrometer (Hitachi U-2001, Japan) in the range of 200 nm ~ 500 nm. The kinetic study was performed by measuring the change in intensity of the absorbance at 400 nm.

3. Results and discussion

Characterization of AuNP-rGO/QCS/Cellulose paper



Fig. 1 XRD spectra of (a) graphite and GO and (b) three kinds of papers; (c) Raman spectra of three kinds of papers; (d) XPS survey spectra of three kinds of papers, and high-resolution C1s core level spectra of (e) GO/QCS/Cellulose paper and (f) rGO/QCS/Cellulose paper. (Three kinds of papers: (I -green curve) GO/QCS/Cellulose paper; (II -blue curve) rGO/QCS/Cellulose paper; (III-pink curve) AuNP-rGO/QCS/Cellulose paper)

Fig. 1(a) shows XRD spectra of graphite and GO. In Fig. 1(a), the pristine graphite has a sharp and strong peak at 26.4 $^{\circ}$, indicating the stacking of graphene layers in graphite. For GO, only a minor peak at 10.2 $^{\circ}$ can be observed. The results reveal the formation of various oxygen-containing groups such as hydroxyl and carboxyl during the chemical oxidation, thus disrupting the ordered structure of graphite layers²¹.

As shown in Fig. 1(b), we can easily find the peak of GO around 10.2 ° as well as the characteristic peaks of cellulose in curve (I), suggesting that the GO/QCS/Cellulose paper contains a certain amount of GO. After HI reduction, the peak of GO disappears both in curves (II) and (III), which confirms the reduction of GO^{22} . But at

the same time, the characteristic peak of rGO which should be similar to that of graphene around 26.4 ° does not come out. This may be ascribed to the overlap with (200) plane of the typical cellulose I crystalline structure²³. In the pattern of the AuNP-rGO/QCS/Cellulose paper (curve III), we can observe additional peaks at 20=38.3, 44.5, 64.6, 77.6 and 81.7° corresponding to the (111), (200), (220), (311), and (222) planes of Au, indicating the existence of AuNPs²⁴.

Raman spectra of three kinds of papers in Fig.1(c) all show the G bands at ~1590 cm⁻¹ and D bands at ~1350 cm⁻¹. D band is the symmetry A_{1g} mode and G band is the E_{2g} mode of sp² carbon atoms.²⁵ Changes in the I_D/I_G ratio indicate the variation of the electronic conjugation state of the GO during reduction²⁶. It is worth noting that the I_D/I_G ratio increased from 0.89 to 1.68 and 1.61, which further proves the GO in composite paper was chemically reduced.

The XPS spectra of three papers are presented in Fig. 1(d). The variation of C/O ratio reveals the change of elements in paper surfaces. Compared with the C/O ratio of 1.63 in GO/QCS/Cellulose paper, C/O ratios for rGO/QCS/Cellulose paper and AuNPrGO/QCS/Cellulose paper are 3.80 and 3.71, respectively, further indicating the highly efficient reduction by HI vapor method. Moreover, GO reduction by HI acid leaves some iodine within the paper, so we can easily find the peaks of I_{3d} and I_{4d} in both of curves II and III²⁷. In curve III, a new peak corresponding to Au_{4f} is observed near 85.0 eV, suggesting that the AuNPs were coated on the surface of rGO sheets. High resolution XPS spectra of C 1s is used to evaluate the removal of oxygen-containing group before (Fig. 1(e)) and after (Fig. 1(f)) reduction. The C 1s spectrum of the original GO/QCS/Cellulose paper (Fig. 1(e)) is composed of C-O (286.4 eV), C-N (285.8 eV), C-O (286.7 eV), C=O (287.6 eV) and C(O)O (288.4 eV), and the major bond ascribes to C-O bond. While after reduction, the intensity of C-C&C=C peak rises significantly, replacing the dominance of oxygen-containing groups peaks in Fig. 1(f). It further confirms the elimination of oxygen functional groups on GO sheets. The presence of C-N could be ascribed to QCS coating.

Based on the above analysis, we can draw conclusions that GO was reduced and we successfully obtained the AuNP-rGO/QCS/Cellulose paper. The AuNP-rGO content in AuNP-rGO/QCS/Cellulose paper was calculated around 4.16% by using TGA (Fig. S1 in Supporting Information).

Morphological analysis of AuNP-rGO/QCS/Cellulose paper



Fig. 2 SEM images of (a) pure cellulose fiber; (b) QCS/Cellulose fiber; (c) rGO/Cellulose fiber; (d) rGO/QCS/Cellulose fiber; (e) AuNP-rGO/QCS/Cellulose fiber; and (f) the enlarged view of AuNPrGO/QCS/Cellulose fiber

Fig. 2(a) and (b) demonstrate the morphology change from pure cellulose fiber to QCS-coated fiber. The pure cellulose fibers experiencing the beating process were splitted into millions of tiny fibrils. While those tiny fibrils disappeared after immersion in QCS solution, and the surface of fibers became smooth, which is mainly owing to the excellent film-forming ability of QCS and the electrostatic interaction between cellulose and QCS. Fig. 2(c), 2(d) show SEM images for rGO/Cellulose paper, and 2(e) rGO/QCS/Cellulose paper and AuNP-rGO/QCS/Cellulose fiber, respectively. Fig. 2(c) shows that lamellate rGO sheets unevenly dispersed in fiber substrate rather than wrapped fibers, since both of them are negatively charged. By contrast, in the presence of QCS as "glue" in Fig. 2(d), a layer of positive-charged QCS coating is beneficial to attract negative-charged GO sheets, which is favorable to form compact conductive network structure. rGO sheets in rGO/QCS/Cellulose fiber are able to twine and to cover fibers, so that a wire-like network can be formed. In Fig. 2(e), AuNP-rGO sheet wrapping paper fiber is also observed and its enlarged view is shown in Fig. 2(f), revealing the existence of neat AuNP on rGO sheets. To get more detailed information of the AuNP-GO composites, we examined the composites by TEM and EDS analyses. Compared with pure GO sheet (Fig. S2 a), AuNP-GO sheet (Fig. S2 b) is uniformly decorated with many small Au nanoparticles without aggregation. The existence of Au peaks in the EDS spectrum (Fig. S2 c) further supports AuNPs coating on GO layers.

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Mechanical properties of the AuNP-rGO/QCS/Cellulose paper

As shown in Fig. 3(a), the AuNP-rGO/QCS/Cellulose paper is flexible and tough with typical metallic luster, which can be bent and freely restored. To evaluate the reinforcement of QCS and graphene sheets in AuNP-rGO/QCS/Cellulose paper, tensile tests were performed, as shown in Fig.3(b). In comparison with pure cellulose



Fig.3 (a) Photographs of AuNP-rGO/QCS/Cellulose paper demonstrating its flexibility; (b) Stress-strain plots of five different composite papers

paper, both QCS/Cellulose paper and rGO/Cellulose paper display a higher tensile strength at 15.5 and 14.1 MPa, respectively. Regarding the QCS/Cellulose paper, the reason is that QCS is able to form a layer of uniform film on fiber surface so as to pose a positive effect on binding force between fibers.²⁸ As for rGO/Cellulose paper, the increased tensile strength may be attributed to the mechanical locking of rGO sheets on cellulose fibers, making it resistant to the inter-fiber slide.8 Because of the joint enhancement effect of rGO AuNP-rGO/QCS/Cellulose and OCS. the paper and rGO/QCS/Cellulose paper show similar tensile strength around 17.3 MPa and approximate strain at break of 1.8%, which respectively were 2.2 folds and 1.7 folds higher than those of the pure cellulose paper. The similarity of those two papers in terms of stress-strain curve demonstrates that introducing AuNPs has less effect on mechanical property of paper.

Conductive property of AuNP-rGO/QCS/Cellulose paper

The electrical conductivities of five different composite papers are shown in Fig. 4(a). As measured, pure cellulose paper as well as QCS/Cellulose paper is not electrically conductive. The rGO/Cellulose which is the simple mixture of cellulose fiber and rGO sheets shows a low electrical conductivity at 156.2 S/m. Interestingly, rGO/QCS/Cellulose paper and AuNPrGO/QCS/Cellulose paper possess remarkably high electrical conductivity with 834.4 and 853.4 S/m, respectively. To our best knowledge, these values are the highest yet in the reported conductive graphene-based cellulosic paper^{7, 8, 29, 30}. The dramatic increase in conductive value may be owing to two aspects. First, the efficient reduction method offers great promotion with the conductivity. HI-acetic acid reduction method can achieve a much higher reducing ability than those methods with hydrazine and NaBH₄ as reducing agents.²⁷ More importantly, due to the effect of



Fig. 4 (a) Electrical conductivities of five different composite papers;(b) Optical image of a light bulb connected with AuNPrGO/QCS/Cellulose paper.

electrostatic self-assembly, an even layer of positive-charged QCS membrane on fiber surface attracts negative-charged GO sheets, enforcing GO sheets to wrap fibers tightly and equably. Furthermore, we also find that the incorporation of AuNP appears slight improvement in conductivity of AuNP-rGO/QCS/Cellulose paper (853.4 S/m in comparison with 834.4 S/m), which can be ascribed to the conductivity of AuNP.³¹ Fig. 4 (b) shows the optical image of a light bulb with folded AuNP-rGO/QCS/Cellulose paper. The lighting bulb further proves the paper's excellent electrical conducting property.

Photothermal activity of AuNP-rGO/QCS/Cellulose paper

Photothermal conversion by GO or rGO has also been extensively studied, and most of studies are associated with photothermal therapy application^{32, 33}. In addition to graphene-based materials, the well-known photothermal effect of AuNP also enables the absorbed light to be converted to heat because of surface plasmon resonance^{34, 35}. The coupling of the AuNP with GO or rGO can enhance the photothermal effects of the composite paper and significantly raise the paper's temperature.³⁶

Fig. 5 compares the extent of temperature rise for five different papers. All the graphene-containing papers show significant photothermal effects than QCS/Cellulose and Cellulose paper. When exposed to the 808 nm infrared diode laser irradiation with a power density of 4 W/cm⁻², the AuNP-rGO/QCS/Cellulose paper displays the highest temperature (90.5 °C) as well as the highest rise rate (3.9 °C/S). In absence of AuNP, the rGO/QCS/Cellulose paper only reaches 82 °C, indicating that AuNP on the rGO sheet surface can play a synergistic effect. Lack of QCS as a media, the temperature rise of rGO/Cellulose paper is the lowest, with the temperature at 72 °C. This is due to the fact that without QCS as a media, there is no function of electrostatic self-assembly absorbing sufficient rGO sheet on cellulose fiber surface.



Fig. 5 Temperature profiles of five different composite papers under the 808 nm laser irradiation with a power density of 4 W/cm^2

Catalytic properties of AuNP-rGO/QCS/Cellulose paper



Fig. 6 (a) UV-Vis absorption spectra of 4-nitrophenol at 3 min time interval; (b) The influence of temperature on the reaction rate; (c) The reusable performance of the AuNP-rGO/QCS/Cellulose paper

Though the reduction by NaBH₄ from 4-NP to 4-aminophenol (4-AP) is thermodynamically favorable, its kinetics is restricted in the absence of a catalyst³⁷. In our study, the color and the absorbance value of 4-NP and NaBH₄ solution remained same even for a couple of days in the absence of the AuNP-rGO/QCS/Cellulose paper, indicating that the reaction did not proceed without a catalyst. This catalytic process after the addition of AuNP-rGO/QCS/Cellulose paper was monitored by UV-Vis spectroscopy. Fig. 6(a) shows the change of the UV-Vis spectra along with time in the presence of AuNP-rGO/QCS/Cellulose paper. The intensity of the peak attributed to 4-nitrophenol (around 400 nm) decreases, while there is

a concomitant appearance of a new peak at 300 nm, indicating the formation of reduction product, 4-AP. After being catalyzed for 30 minutes, the color of 4-NP solution was completely vanished (seen in the inset map of Fig. 6(a)), which means that 4-NP was basically converted into 4-AP, suggesting that our AuNP-rGO/QCS/Cellulose paper is endowed with high catalytic property. However, the total adsorption rate of rGO/QCS/Cellulose composite without AuNPs on 4-NP was 2.7 % (shown in Fig. S3), and the comparative test of Au/QCS/Cellulose composite without graphene spent a longer catalytic time of 45 minutes achieving the full reduction of 4-NP (seen in Fig. S4). Therefore, the high catalytic activity of AuNPrGO/QCS/Cellulose paper may be ascribed to two facts, one is the efficient catalytic efficiency of AuNP due to its high surface energy³⁸. another is the two dimensional structure of rGO sheet, which has a high affinity for the adsorption of 4-NP due to $\pi-\pi$ stacking interactions, ³⁹ as demonstrated in Fig. S3. So a higher concentration of 4-NP near AuNP-rGO could be conducive to higher catalytic efficiency.

The temperature-dependent kinetic studies for the catalytic reduction of 4-NP were also evaluated. As shown in Fig. 6b. the catalytic reduction of 4-NP was carried out at 20 °C, 25 °C, 30 °C, 35 °C and 40 °C, respectively. The rate constants at different temperatures were measured from the plots of ln (A_t/A_0) versus time. It is found that the catalytic performance of AuNP-rGO/QCS/Cellulose paper enhanced with the rise of reaction temperatures. Activation energy (*E*a), an important parameter for all chemical reactions, can reflect the temperature dependency of the rate constants and the value of Ea can be calculated at 49.27 kJ/mol by using the Arrhenius equation.

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{2}$$

Where *A* is a constant, *k* is the rate constant of the reaction at temperature *T*, *R* is the universal gas constant. The Ea value of the catalytic paper is relatively large, illustrating that the rate constant is determined by reaction temperature in the present catalytic system.⁴⁰ It is well known that the unprotected nano noble metals are susceptible to irreversible aggregation in solution due to their small size, resulting in a remarkable decline in their catalytic activities. To address this problem, one of the effective strategies is the introduction of metal nanoparticles on/into solid supports (such as graphene) to form composite catalysts ⁴¹. In this study, the reusability of AuNP-rGO/QCS/Cellulose paper was performed by repeated immersion in a freshly mixed solution of 4-NP and NaBH₄.

As can be seen in Fig. 6(c), AuNP-rGO/QCS/Cellulose paper remains comparatively high conversion efficiency without a visible decrease even after running for 10 cycles.

4. Conclusions

In summary, we report a feasible route to fabricate composite cellulosic paper based on AuNP-rGO using QCS as glue by electrostatic self-assembly. AuNP-rGO/QCS/Cellulose paper presents the currently known highest conductivity of graphene-based cellolusic paper. Moreover, this paper possesses relatively high tensile strength and excellent photothermal conversion, implying its potential application in optical heating sources and photothermal therapy membranes. The efficient catalytic ability and excellent reusable performance indicate that AuNP-rGO/QCS/Cellulose paper can be used as ideal catalytic substrate materials. This facile and large scale fabrication of multifunctional AuNP-rGO/QCS/Cellulose paper may not only implicate a referable route to functionalize graphene-based cellulosic materials but also satisfy requirements for practical applications.

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Notes and references

^{*a*} State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, 510640, China. E-mail address: xyw@scut.edu.cn, Tel and Fax: +86-20-87111861

^b Beijing Key Laboratory of Lignocellulosic Chemistry, Beijing Forestry University, Beijing, 100083, China

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