A New Photoelectric Ink based on Nanocellulose/CdS Quantum Dots for Screen-printing

Aimin tang^{a,*}, Yuan liu^a, Qinwen wang^a, Ruisong chen^a, Wangyu liu^b, Zhiqiang fang^a, Lishi wang^c

a State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, Guangzhou, P. R. China

b School of Mechanical and Automotive Engineering, South China University of Technology, Wushan RD No. 381, 510640 Guangzhou, P. R. China

c School of Chemical Science and Engineering, South China University of Technology, Guangzhou, 510640, P. R. China

Abstract: CdS quantum dots with excellent photoelectrical properties embedded in nanocellulose could be exploited for use in photoelectrical ink. In this work, nanocellulose/CdS quantum dot composites were fabricated by controlling the carboxylate content of the nanocellulose and the molar ratio of Cd²⁺/–COOH. New photoelectric inks were prepared based on the composites, in which the CdS quantum dots acted as the pigment and the nanocellulose as the binder. The results of the photocurrent of the composites showed that the photocurrent could be tailored by the carboxylate content and the molar ratio of Cd²⁺/–COOH. And the photocurrent could be as high as 2 μ A. The surface tension of the photoelectric ink was 27.80 $\pm$ 0.03 mN/m and its viscosity was 30.3 mPa s. The photoelectric ink was stable with excellent fluidity and rheology, it could therefore be applied to screen-printing and three-dimensional (3D) printing.

Keywords

CdS quantum dots; Nanocellulose/CdS; Photoelectric ink; Photocurrent; Viscosity; Screen-printing

1. Introduction

Printed electronics (PEs) offer an attractive alternative to conventional technologies by enabling the creation of large-area, flexible devices at low cost and high efficiency (Ahn, B.Y. et al. 2009). PEs has been employed in antennas, RFID (Potyailo & Morris, 2007), WLAN, and wireless sensor networks (Lakafosis, Rida, Vyas, Yang, Nikolaou & Tentzeris, 2010) in terms of their competitive advantages. In recent years, conducting polymers, organic materials, and inorganic semiconductors (Menard et al., 2007; Sun & Rogers, 2007) have aroused tremendous interest, and they can be used in luminescence devices, flexible displays, storage, flexible photovoltaic cells, batteries, electronic tags, electronic paper, sensors, intelligent devices, and intelligent textiles. Nowadays,

* Corresponding author. Tel.: +86-20-87111225; fax: +86-20-87111288.
E-mail address: amtang@scut.edu.cn.

gold, silver, and copper particles and even many novel carbon nanotubes and graphene can be used as conductive fillers in conductive ink.

Recently, environmental pollution on a global scale has aroused tremendous attention. The development and use of green, ecological materials are being driven by a conversion from petrochemical-based materials to environmentally friendly biopolymers (Yang, Yu, Fan, Sun, Tang & Yang, 2011). Nanocellulose, which is derived from abundant renewable plants, has been employed in various fields, such as in paper manufacturing as a coating or a reinforcement agent (Brodin, F.W., 2014), biomedical science (Markstedt, Mantas, Tournier, Martínez Ávila, Hägg & Gatenholm, 2015; Rees, Powell, Chinga-Carrasco, Gethin, Syverud & Thomas, 2014), and flexible displays (Zhu, H., Fang, Z., Preston, C., Li, Y. & Hu, L. 2014) . Its high modulus(Saito et al., 2009), high tensile strength, low cost, low weight, biocompatibility, and biodegradability make it one of the most useful biomaterials in the world. Recently, three-dimensional (3D) printing has aroused much attention in various fields. It was reported (Markstedt, Mantas, Tournier, Martínez Ávila, Hägg & Gatenholm, 2015; Rees, Powell, Chinga-Carrasco, Gethin, Syverud & Thomas, 2014) that nanocellulose was employed in the biomedical field based on 3D printing. Markstedt et al. fabricated a novel bioink that combines the outstanding shear-thinning properties of nanofibrillated cellulose (NFC) with the fast cross-linking ability of alginate for 3D bioprinting of living cellular soft tissue (Markstedt, Mantas, Tournier, Martínez Ávila, Hägg & Gatenholm, 2015). Rees et al. explored the application of nanocellulose as a bioink for modifying film surfaces by a bioprinting process and nanocellulose bioink was thus used for printing 3D porous structures. However, because it cannot support bacterial growth (Rees, Powell, Chinga-Carrasco, Gethin, Syverud & Thomas, 2014), bioinks based on nanocellulose also need to be developed. However, functional nanocomposites that can be applied as bioinks based on nanocellulose have seldom been reported. In recent years, a variety of nanocellulose/nanoparticle (Padalkar et al., 2010) nanocomposites that retain both the excellent properties of nanoparticles and the intrinsic advantages of nanocellulose have been fabricated. The nanoparticles were absorbed by the abundant hydroxyl groups of nanocellulose and sufficient carboxylate groups. Nanocellulose and cellulose derivatives were reported(Koga, Saito, Kitaoka, Nogi, Suganuma & Isogai, 2013; Magdassi, Bassa, Vinetsky & Kamyshny, 2003), which were employed in water-based ink. Magdassi et al. (Magdassi, Bassa, Vinetsky & Kamyshny, 2003) synthesized an ink-jet ink in which silver acted as the pigment and carboxymethyl cellulose acted as both a stabilizing agent and as a binder. Koga et al. (Koga, Saito, Kitaoka, Nogi, Suganuma & Isogai, 2013) fabricated ultra-strong, transparent, conductive, and printable

2,2,6,6-tetramethylpiperidine-1-oxyl(TEMPO)-oxidized cellulose nanofibril (TOCN)/single-walled carbon nanotube (CNT) nanocomposites, in which the TOCNs were used as the dispersed medium and an effective matrix. Although many conductive nanoparticles were studied to fabricate the conductive ink by absorbing these conductive nanoparticles into the nanocellulose, investigation of photoelectrical ink based on nanocellulose/photoelectrical nanoparticles has been minimal.

CdS quantum dots, which are typical II–IV narrow-band semiconductors, have received much attention in terms of their unique photoelectrical characteristics according to the quantum confinement effect, making them applicable as photoelectrical sensors (Wang, Yu, Xu & Chen, 2009; Xia et al., 2015) or solar cells (Lin, Lin, Meng & Wang, 2014; Ren et al., 2011). Because of their high surface activity, CdS quantum dots agglomerate easily in aqueous solutions. Up to now, many polymers have been used to synthesize CdS/polymer nanocomposites, including silk fibroin (Han, J., Su, H., Dong, Q., Zhang, D., Ma, X. & Zhang, C. 2010), bovine serum albumin (Cui, Zhang, Sun, Hu & Liu, 2015), chitosan(Jiang, Zhu, Yao, Fu & Guan, 2012), and bacterial cellulose, in an effort to avoid agglomeration. Nanocellulose/CdS quantum dot nanocomposites that could effectively disperse the CdS quantum dots well and retain the intrinsic properties of the CdS quantum dots have also been reported. Yang et al. (Yang, Yu, Fan, Sun, Tang & Yang, 2011) synthesized CdS/ bacterial cellulose nanofiber (BCF) hybrid nanofibers in which BCF was the dispersing medium. Li and his colleagues reported that CdS nanoparticles were synthesized and stabilized on unique bacterial cellulose (BC) nanofibers in situ (Li et al., 2009). However, the synthesis of BC nanofibers did not lend itself to a scalable production method. Nanofibril cellulose (NFC), which is derived from plants and prepared by a TEMPO–alkaline medium, is a low-cost and abundant material for fabricating NFC/CdS quantum dot nanocomposites in situ. More importantly, the nanofibril cellulose fabricated by TEMPO-alkaline medium contains enough carboxyl to anchor the cadmium ions by chemical absorption. Therefore, the size of the CdS quantum dots can be sufficiently controlled.

In this work, NFC/CdS quantum dot nanocomposites were synthesized as in situ composites according to our previous research (Tang, Yao, Xu & Wu, 2013) . The NFC/CdS quantum dot nanocomposites exhibited photoelectrical properties and avoided the agglomeration of CdS particles by using NFC as the matrix and dispersing medium. Furthermore, photoelectrical and environmentally friendly water-based inks were fabricated using the CdS quantum dots as the pigment and the NFC as the binder. The photocurrent of the NFC/CdS quantum dot nanocomposites was tailored by controlling the carboxylate groups and the molar ratio of $\text{Cd}^{2+}/\text{--COOH}$. The

surface tension, viscosity, rheology, and zeta potential of the photoelectrical ink were also investigated. The employment of this novel, environmentally friendly photoelectrical ink may represent an enormous breakthrough in the PE and 3D printing fields.

2. Experimental method

2.1 Experimental materials

Brazil Prime Bleached Eucalyptus Kraft Pulp was used as the raw material. The α -cellulose content of the pulp was 86.8%. TEMPO [lot No. 10159254, Alfa-Aesar (Tianjin) Chemical Reagent Co. Ltd., Tianjin, China], sodium hypochlorite, sodium chlorite, absolute ethyl alcohol, hydrogen peroxide, cadmium chloride, sodium sulfide, sodium dodecyl benzene sulfonate (SDBS), and other chemicals were of laboratory grade.

2.2 Preparation of the photoelectric ink based on the NFC/CdS quantum dots

2.2.1 Preparation of the NFC/CdS quantum dot nanocomposites

The TEMPO-oxidized cellulose was prepared by alkaline TEMPO-mediated oxidation according to Saito (Saito, Kimura, Nishiyama & Isogai, 2007). The TEMPO-mediated oxidized cellulose samples were used to prepare nanofibril cellulose via ultrasonication. The oxidized cellulose was diluted with de-ionized water to obtain a 0.5% (w/w) suspension. The solution was then mixed by a magnetic stirring apparatus to obtain a uniform slurry. The NFC/CdS quantum dot nanocomposite was prepared according to our previous work (Tang, Yao, Xu & Wu, 2013, Su & Tang, 2011). When the molar ratio of Cd^{2+} :-COOH was 0.5, a 0.02 mol CdCl_2 solution diluted to 50 mL was added into the NFC suspension (0.3% w/w) according to the carboxylate content. The suspension was stirred for 60 min at 20 °C. Subsequently, the suspension was transferred to the ultrasonic instrument for additional stirring for 60 min at 20 °C. The same amount of Na_2S (0.02 mol) solution was then added to the suspension, changing the solution color from white to yellow. The suspension was further washed with deionized water and finally kept under dark conditions for further application. When the carboxylate content was 0.80 mmol/g, the NFC/CdS quantum dot nanocomposite was synthesized by controlling the molar ratio of Cd^{2+} :-COOH by the same method.

2.2.2 Preparation of the photoelectric ink

The prepared NFC/CdS quantum dot nanocomposites (0.80 mmol/g, Cd^{2+} :-COOH = 0.33, 0.50, 1.0, 2.0) were diluted to 0.2%, and then 2% SDBS as a surfactant was added. Thus, a photoelectric ink was obtained.

2.3 Characterization of the photoelectric inks based on the NFC/CdS quantum dot nanoco

nanocomposites

The morphology of the NFC/CdS nanocomposites was characterized by a Hitachi H-7650 transmission electron microscope (TEM). The powder X-ray diffraction (XRD) patterns of the NFC/CdS quantum dot nanocomposites were recorded on a Bruker D8 Advance X-ray diffractometer. From the XRD pattern, the diameter of the CdS quantum dots was obtained by the Scherrer equation (Wu, Wang, Xiao & Huang, 2008).

$$D = (k\lambda)/(\beta \cos\theta) \quad (1)$$

where k , λ , β , and θ represent the shape factor, X-ray wavelength, full width at half maximum (FWHM), and the diffraction angle, respectively.

The photocurrent of the NFC/CdS nanocomposites was measured by an electrochemical workstation (Tang, Yao, Xu & Wu, 2013). A 10 μ L sample was deposited on indium–tin oxide (ITO) glass, which was cleaned using a solution with equal amounts of hydrogen peroxide (30%) and potassium hydroxide (1 mol), followed by rinsing with deionized water for 5 min. The ITO glass with the sample as the positive pole and the Pt electrode as the negative pole and a saturated calomel electrode (SCE) as the reference electrode were immersed in a sodium sulfate (0.2 mol) solution.

The saturated adsorption amount of Cd^{2+} to NFC was determined by atomic absorption spectroscopy. The samples that were saturated adsorption with Cd^{2+} were carbonized in a crucible with 5% nitric acid. After carbonizing, the crucible with the sample was burning for 4 h at 575 ± 25 °C in a muffle furnace. The sample was wetted with several drops of water and 5 mL of nitric acid (5%) and then dried in an electric furnace. The above process was repeated twice. Then all samples were diluted to 0.1–0.5 $\mu\text{g/ml}$.

The zeta potential of the photoelectric inks was measured by a Zetasizer NanoZS instrument, the surface tension was measured by a Dataphysics DCAT 21 surface tension meter, and the viscosity was obtained by a ThermoScientific HAKKE MARSIII system.

3. Results and discussion

3.1 Characterization of the NFC/CdS quantum dot nanocomposites

The morphology of the NFC/CdS quantum dot nanocomposites was investigated by TEM. The carboxylate content of the NFC of the tested samples was 0.80 mmol/g and the molar ratio of Cd^{2+} /–COOH was 0.5. From **Figure 1**, it is clear that the nanocellulose fibers overlapped to form a 3D porous network; the diameters of the nanocellulose fibers were approximately 10 nm [see **Figure 1(a)**]. **Inset of Figure 1(a), the black dots indicate the morphology of**

the CdS quantum dots. The diameters of the CdS quantum dots were 7.6 nm measured by the software of Nanomeasure. It can also be seen from Figure 1 that the CdS quantum dots were dispersed on the nanocellulose fibers homogeneously.

From the XRD spectrum of the nanocomposite (see **Figure 2**), the peaks at $2\theta = 22.6^\circ$, 15.6° , and 34.6° are assigned to the (002), (101), and (004) planes, respectively, of cellulose I, revealing that the cellulose I crystal structure was perfectly preserved. Apart from these diffractions of nanocellulose, three distinct peaks at $2\theta = 26.3^\circ$, 44.0° , and 52.0° correspond to the (111), (220), and (311) planes, respectively, of cubic CdS (Ruan, Huang & Zhang, 2005). The XRD pattern of the nanocomposite indicated the formation of the CdS quantum dots on the NFC matrix. The diameter of the CdS quantum dots was 10.9 nm, which was calculated by using the Equation (1). This value obtained by the Equation(1) was larger than the result of TEM. The reason maybe that the XRD peaks broaden and their widths become larger as the particles become smaller according to the reference due to the size effect(Luo, Bai, Yang & Cai, 2015).

Both the TEM and XRD analyses indicated that the NFC/CdS quantum dot nanocomposites were successfully fabricated.

Fig. 1. TEM photographs of nanocellulose/CdS composites. Inset of (a) is a partial enlargement of (a). (b) Size distribution of CdS quantum dots

Fig. 2.

XRD spectrum of NFC/CdS quantum dot nanocomposites.

3.2 Influence of carboxylate content on nanocomposite photocurrent

To prepare the photoelectric ink, we first investigated the influence of the carboxylate content on the photocurrent of the nanocomposites at a $\text{Cd}^{2+}/\text{--COOH}$ molar ratio of 0.5 (Figure 3). From Figure 3, the photocurrent increased from 0.3 μA to 1.5 μA with increasing NFC carboxylate content from 0.48 mmol/g to 0.98 mmol/g. Simultaneously, the Cd^{2+} content of the nanocomposite increased from 1.26% to 3.13%. It is clear that the NFC carboxylate content had a noticeable influence on the photocurrent. The reason was that the number of CdS quantum dots dispersed on the NFC increased with increasing NFC carboxylate content. The results also indicated that carboxyl groups were the active sites for Cd^{2+} adsorption. Therefore, with the same molar ratio of $\text{Cd}^{2+}/\text{--COOH}$, nanocellulose fibrils with a higher carboxylate content could immobilize more CdS quantum dots. The generation mechanism of the CdS quantum dot photocurrent can be explained by the fact that electrons are excited from the valence band to the conduction band, forming electron-hole pairs, when the material absorbs photons with energies higher than that of its band gap. Then the electrons are transferred to the surface of the ITO glass, generating the photocurrent (Wang, Yu, Xu & Chen, 2009). Therefore, it is obvious that the photocurrent of the NFC/CdS quantum dot nanocomposites increased with increasing carboxylate content.

Fig. 3.

Photocurrent and cadmium content of nanocellulose/CdS quantum dot nanocomposites with different carboxylate contents (mmol/g of nanocellulose).

3.3 Photocurrent-tunable NFC/CdS quantum dot nanocomposites by controlling the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$

Furthermore, we investigated the influence of the $\text{Cd}^{2+}/\text{-COOH}$ molar ratio on the photocurrent of the nanocomposites at an NFC carboxylate content of 0.80 mmol/g (Figure 4). From Figure 4, we can see that the Cd^{2+} content of the nanocomposites increased from 0.93 to 5.05% with increasing $\text{Cd}^{2+}/\text{-COOH}$ molar ratio from 0.3 to 2. Also, the photocurrent increased from 0.3 to 2 μA as the $\text{Cd}^{2+}/\text{-COOH}$ molar ratio increased. The reason for these results was that there were more CdS quantum dots dispersed on the NFCs with increasing $\text{Cd}^{2+}/\text{-COOH}$ molar ratio. The results agreed with the Cd^{2+} content. From Figure 4, the Cd^{2+} content sharply increased with increasing molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ from 1 to 2. However, when the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ was 1, the photocurrent was 1.8 μA , which was almost equal to the highest photocurrent at a $\text{Cd}^{2+}/\text{-COOH}$ molar ratio of 2. Under ultraviolet (UV) irradiation, electron-hole pairs were formed. With an increase in the number of CdS quantum dots, the number of electron-hole pairs increased. However, the CdS quantum dots corroded under illumination. If there are many holes that cannot be scavenged properly, these holes may improve the recombination of the electron-hole pairs, thus hindering photocurrent generation according to the photocurrent mechanism (Wang, Yu, Xu & Chen, 2009). In addition, the NFC/CdS quantum dots agglomerated easily with the

increased molar ratio of $\text{Cd}^{2+}/\text{-COOH}$. Therefore, there should be a limit to the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ in the fabrication of NFC/CdS quantum dots nanocomposites using in-situ composites.

Fig. 4.

Photocurrent and cadmium content of nanocellulose/ CdS composites with different molar ratios of cadmium to carboxyl.

3.4 Synthesis of the photoelectrical ink based on the NFC/CdS quantum dot nanocomposites

3.4.1 Average size and zeta potential-tunable photoelectrical ink by controlling the molar ratio of

$\text{Cd}^{2+}/\text{-COOH}$

The photoelectric inks were fabricated according to section 2.2.2. The inset in Figure 5 from left to right shows images of the photoelectrical inks with molar ratios of carboxyl to cadmium of 0.5, 1, 2, and 3. The colors of the samples from left to right gradually changed from being colorless to a weak yellow, lemon yellow, and orange. From the results, we confirmed that the prepared NFC/CdS quantum dot nanocomposites had photoelectric characteristics. The average particle size was investigated by the Malvern ParticleSizer system. As seen in Figure 5, the average size increased from 239.6 nm to 1111 nm as the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ increased from the 0.3 to 2. The reason was that the number of CdS quantum dots dispersed on the nanocellulose fibers increased with increasing molar ratio, such that the average size of the nanocomposites increased. It is necessary to point out that the particles investigated by the Malvern ParticleSizer were spherical, and so the results would be larger than the real value.

The zeta potential of the photoelectric inks was obtained by a Zetasizer NanoZS instrument. The zeta potential is the potential difference between the dispersion medium and the stationary layer of fluid attached to the dispersed particle. Zeta potential is a key indicator of the stability of colloidal dispersions. Here, the zeta potential is a measure of the stability of the samples. Because the absolute value of the zeta potential of the photoelectric inks was smaller than 15 mV, the samples were unstable and apt to agglomerate (Khoury ,2010) . The zeta potential is influenced by the charge of the particles in the solution; in the current study, the cadmium ions were positive and -COO^- was negative. The Zeta potential of NFC solution was -43.2 mv with the carboxylate content of 0.8 mmol/g. And the zeta potential absolute value increased from 25.1 to 58.6 with increasing molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ from 0.33 to 1.0 and then decreased to 0.332 at a molar ratio of 2.0. When the molar ratio was 2.0, the zeta potential absolute value was decreased to 0.332, which indicated the absorption of more CdS quantum dots on the NFC. When the carboxylate content was 0.80 mmol/g and the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ was 1, the zeta potential was -58.6 mV. The stability of NFC/CdS quantum dots nanocomposites may be concerned with the co-action of the electrostatic repulsion and steric hindrance effect(Li et al., 2015; Martins et al., 2012). Here the electrostatic repulsion of the ink is related with the carboxylate content of NFC, and the steric hindrance is caused by CdS quantum dots. It is thus obvious that when the carboxylate content was 0.80 mmol/g and the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ was 1, the ink was well dispersed and stable. Thus, the NFC/CdS quantum dot nanocomposite could remain stable for a long time, which is an important factor for ink (Khoury ,2010) . Therefore, a new stable photoelectric ink was prepared based on the NFC/CdS quantum dots, in which the CdS quantum dots acted as the pigment and NFC as the binder. To further study the characteristics of the photoelectric ink, the nanocomposite with an NFC carboxylate content of 0.80 mmol/g and a $\text{Cd}^{2+}/\text{-COOH}$ molar ratio of 1 was chosen for further characterization.

Fig. 5.

Average size, zeta potential, and dispersion states for the nanocellulose/CdS composites with different molar ratios of cadmium to carboxyl in the ink. The inset in Figure 5 from left to right show the samples with molar ratios of cadmium to carboxyl of 0.33, 0.5, 1.0, and 2.0.

3.4.2 Morphology of the photoelectrical ink based on the NFC/CdS quantum dot nanocomposites with the molar ratio of cadmium to carboxyl of 1

The morphology of the photoelectric ink was characterized by TEM (Figure 6). The photoelectric ink solution was well dispersed with particles 200 nm in length and 50 nm in width. Conventional pigments in ink-jet inks contain particles 100–400 nm in size¹³. This solution was thus most suitable to be employed as ink.

Fig. 6.

TEM photographs of cellulose nanofiber electro-optical ink with the molar ratio of cadmium to carboxyl of 1.

3.4.3 Surface tension and viscosity of the photoelectrical ink based on the NFC/CdS quantum dot nanocomposites with the molar ratio of cadmium to carboxyl of 1

The photoelectric ink surface tension was obtained and the results are shown in Table 1. Compared to the NFC/CdS quantum dot nanocomposites, the photoelectric ink surface tension decreased from 71.22 ± 0.03 mN/m to 27.80 ± 0.03 mN/m. Thus, the surface tension of the ink was less than that of the matrix and could therefore

avoid shrinkage and mesh clogging. The photoelectric ink viscosity was investigated and the results are shown in Figure 7(a). The photoelectric ink and the NFC/CdS quantum dot nanocomposites had high viscosity and was shear thinning. When the shear rate was almost 0 s^{-1} , the viscosity of the photoelectric ink and the nanocellulose/CdS quantum dot nanocomposites were approximately 750 mPa s and 150 mPa s, respectively. These results indicate that it is essential to add SDBS to the NFC/CdS quantum dot nanocomposites. Also, the addition of the SDBS could effectively improve the viscosity of the NFC/CdS quantum dot nanocomposites, which is favorable for screen printing. The photoelectric ink and the nanocomposites had viscosities of 30.3 mPa s and 8.61 mPa s at a shear rate of 100 s^{-1} . The viscosity of the NFC/CdS quantum dot nanocomposites sharply decreased to 8.61 mPa s at a shear rate of 10 s^{-1} . However, the viscosity of the photoelectric ink, with SDBS added into the nanocomposites, decreased to 30.3 mPa s at a shear rate of 20 s^{-1} . The results obviously show that the addition of the surfactant could significantly improve the viscosity. It has been reported²⁹ that ink with a viscosity of 1 or 10 Pa s could print high-resolution, conductive patterns by screen printing (Hyun, Secor, Hersam, Frisbie & Francis, 2015). Although the photoelectric ink viscosity was improved by adding the surfactant, it was still lower than that of the ink for screen printing (Hyun, Secor, Hersam, Frisbie & Francis, 2015). It's reported that the rheological properties of NFC solutions can be influenced by the dry content (Naderi, Lindström & Sundström, 2014) and oxidation extent (Besbes, Alila & Boufi, 2011). Therefore the viscosity of the photoelectric ink can be improved by increasing the concentration of the NFC/CdS quantum dots nanocomposites and decreasing the oxidation extent of the NFC solutions. It also can be improved by adding thickener (Dong, Chen, 2014), so that make the ink form network structure and improve the viscosity of the ink. These methods should be applied in our future work. To reveal the influence of adding SDBS to the composite on photocurrent, we measured the photocurrent of the composite and the photoelectric ink with the carboxylate content at 0.80 mmol/g and the molar ratio of the carboxyl to the cadmium at 2 respectively. From figure 7(b), the photocurrent of the composite was $0.70 \mu\text{A}$ and the photocurrent of photoelectric ink was $0.84 \mu\text{A}$. The improvement of the photocurrent of the photoelectric ink may be due to the increasing area of the generating photon by adding SDBS. The surface energy of photoelectric ink with SDBS decreased, which was benefit to spread on ITO.

Table 1.

Base performance of nanocellulose photoelectric ink with and without surfactants.

	NFC/CdS nanocomposites	Photoelectric ink
Photocurrent (μA)	0.70	0.84
Surface tension (mN/m)	71.22 ± 0.03	27.80 ± 0.03
Viscosity (mPa s)	8.61	30.3

Fig. 7.

(a) Rheological behavior of nanocellulose photoelectric ink that the molar ratio of cadmium to carboxyl was 1 with and without surfactants. Upside of (b) was the photocurrent of NFC/CdS quantum dots; below of (b) was the photocurrent of photoelectric ink.

Conclusion

NFC/CdS quantum dot nanocomposites were successfully fabricated by an in situ composite. The XRD pattern of the NFC/CdS quantum dot nanocomposite indicated the formation of cubic CdS quantum dots on the NFC matrix, and TEM photographs clearly showed the CdS quantum dots dispersed homogeneously on the nanofibril cellulose fibers. The photocurrent of these nanocomposites can be tailored by controlling the carboxylate content and the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$. The photocurrent of the nanocellulose/CdS quantum dot composites increased from 0.3 to 1.5 μA as the carboxylate content increased from 0.48 to 0.98 mmol/g, and the nanocomposites photocurrent also increased from 0.3 to 2 μA as the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ increased from 0.33 to 2, at a carboxylate content of 0.8 mol/g. The nanocomposites photocurrent was as high as 2 μA . Photoelectrical inks that retained the photoelectrical properties were then synthesized. The results also indicate that there should be a limit on the molar ratio of $\text{Cd}^{2+}/\text{-COOH}$ in the fabrication of NFC/CdS quantum dot nanocomposites by in-situ composites. The photoelectric ink surface tension was 27.80 ± 0.03 mN/m and its viscosity was 30.3 mPa s. In conclusion, the photoelectrical ink solution had excellent stability, and the surface tension and viscosity were close to those of screen-printing ink. The photoelectrical properties of the ink make it potentially applicable to the PEs and 3D-printing fields.

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