



## Natural rubber particle modified fabrics with catalytic activity and hydrophobicity

Jinlong Tao<sup>a,b</sup>, Bin Tang<sup>b,c,\*</sup>, Puwang Li<sup>a</sup>, Dongning He<sup>a</sup>, Lusheng Liao<sup>a</sup>, Zheng Peng<sup>a</sup>, Xungai Wang<sup>b,c,\*\*</sup>

<sup>a</sup> Chinese Agricultural Ministry Key Laboratory of Tropical Crop Product Processing, Agricultural Product Processing Research Institute, Chinese Academy of Tropical Agricultural Sciences, Zhanjiang 524001, China

<sup>b</sup> Deakin University, Institute for Frontier Materials, Geelong, VIC 3216, Australia

<sup>c</sup> Wuhan Textile University, National Engineering Laboratory for Advanced Textile Processing and Clean Production, Wuhan 430073, China

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### ABSTRACT

We report a novel and facile approach to fabricate functional fabrics using environment-friendly waterborne natural rubber latex (NRL) containing in-situ synthesized gold nanoparticles (AuNPs). AuNPs were prepared and decorated on the surface of the natural rubber particles (NRPs) by heating, forming a dual-scale hierarchical architecture. The hybrid particles of NRPs and AuNPs (AuNP@NRP) were coated on cotton and hydrophilic polyester fabric surfaces, endowing the fabrics with catalytic and hydrophobic features. The treated fabrics with low loadings of AuNP@NRP exhibited high catalytic activity for the reduction of 4-nitrophenol (4-NP) by NaBH<sub>4</sub> and could be reused, after easy separation from the catalytic reaction system, with excellent durability. In addition, the hydrophobicity of fabrics increased as coating cycles increased. The obtained hydrophobic fabrics were used for oil/water separation, showing high separation efficiency (> 96%).

### 1. Introduction

Various strategies have been developed to impart fabrics with functional properties such as antibacterial activity, electric conductivity, UV protection, flame retarding and self-cleaning [1–5]. One of the most efficient approaches for fabricating functional fabrics is to incorporate nanoparticles on their surface, which can be completed by modifying either the fabric surface or the nanoparticle fillers, or a combination of both [6–8]. In addition, there is an increasing requirement from consumers and manufacturers that the functional textiles should be low-cost, environment-friendly, and preferably based on sustainable raw materials.

Cotton, as a traditional natural fibrous material, has been widely used in textile industry due to its abundance, degradability and eco-friendliness [9–11]. A number of methods including in-situ preparation and assembling strategy have been attempted to develop multi-functional cotton products, endowing them with properties such as catalytic activity and hydrophobicity. For example, a catalytic fabric containing Pd nanoparticles was developed by incorporating polydopamine on cotton fiber surface, acting as a reducing agent for the growth of Pd nanoparticles [12]. Yang et al. developed an approach to

prepare functional textile by assembling various gold nanoparticles with positive charges to the cotton fiber surface through electrostatic interaction and the treated fabric had good catalytic performance for chemical reactions [13]. In addition, cotton fabric has also been used as a supporting material for fabricating hydrophobic or super-hydrophobic materials, which are usually achieved through a combination of appropriate surface roughness and materials with a low surface energy [14]. Recently, special wettability materials based on eco-friendly natural biomass have been developed. Gao and co-workers reported an oil/water separation material with high adsorption capacity and excellent recyclability, which was prepared by directly carbonizing polar catkins [15]. Besides, a potato residue coated stainless steel mesh without any further chemical modification was used for oil/water separation by spraying waste potato residue powders and water polyurethane mixtures on the mesh [16]. Though a variety of approaches have been successfully established to fabricate catalytic and high hydrophobic textiles [17–20], it is still of great importance to develop facile, inexpensive and eco-friendly processing routes.

Natural rubber latex (NRL) is a principle feedstock of rubber material used for fabricating tires, dipping goods and coating products in the conventional transportation field and the hygienic and medical

\* Corresponding author. Deakin University, Institute for Frontier Materials, Geelong, VIC 3216, Australia.

\*\* Corresponding author. Deakin University, Institute for Frontier Materials, Geelong, VIC 3216, Australia.

E-mail addresses: [bin.tang@deakin.edu.au](mailto:bin.tang@deakin.edu.au) (B. Tang), [xungai.wang@deakin.edu.au](mailto:xungai.wang@deakin.edu.au) (X. Wang).

sectors [21–23]. As a natural bio-based polymer, NRL is gradually becoming an attractive candidate for preparing functional nanocomposite because of its excellent elasticity, film-forming properties and sustainability. It has been demonstrated that NRL can be used as a structure-directing agent to synthesize stable mesostructured titania exhibiting high photocatalytic activity for the degradation of phenol and rhodamine B under solar light [24]. Natural rubber-based hollow latex particles have also been developed by Wichaita et al. through seeded emulsion polymerization polymer on natural rubber seed [25]. The results showed that the large surface areas of these natural rubber-based hollow nanocomposites with a 3.5 nm pore diameter were suited as delivery vehicle systems. Xia et al. developed a novel conductive natural rubber nanocomposites based on graphene oxide through assembling and latex mixing, fabricating an efficient conductive network due to the assembly of graphene on the surface of rubber latex particles [26]. It is apparent that waterborne NRL is an environment friendly material in comparison to synthetic polymer. To the best of our knowledge, little has been reported on functionalization of textiles with modified NRL nanocomposites.

Herein, we developed a novel and facile approach to fabricate multifunctional fabrics using natural rubber particles (NRPs) combining with gold nanoparticles (AuNPs). The hybrid particles of NRP and AuNPs (AuNP@NRP) were fabricated through in-situ synthesis of AuNPs in natural rubber latex matrix by heat reduction of  $\text{HAuCl}_4$  without additional reducing or capping agent. Fabrics were successfully modified with AuNP@NRP using a conventional “dip and dry” approach. Optical features, surface morphologies and wettability properties were analyzed with various characterization techniques. The effect of the coating cycles on the catalysis and wettability of the fabrics was investigated. The treated fabrics not only exhibited notable catalytic activity, but also demonstrated remarkable hydrophobic property. Furthermore, the hydrophobic fabrics treated with AuNP@NRP were used as oil/water separation materials to good effect. Many hydrophobic or superhydrophobic materials have been developed for oil/water separation. However, most of them were prepared using hazardous chemicals. The present work is focused on developing environmentally friendly and facile approach to fabricate novel functional material for oil/water separation. Both natural rubber and cotton are sustainable. Also, the obtained material in this study work exhibited good performance for oil/water separation, comparable with the most published work.

## 2. Experimental section

### 2.1. Materials

Tetrachloroauric (III) acid trihydrate ( $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , > 99%), 4-nitrophenol ( $\geq 99\%$ ), and sodium borohydride ( $\text{NaBH}_4$  > 98%) were

purchased from Sigma-Aldrich. All chemicals were analytic grade reagents, and used without further purification. Cotton and polyester fabrics were obtained from Spotlight Australia. Pre vulcanized NRL was obtained from a local retailer, the dry rubber content of the NRL was around 60 wt%. They were used as received.

### 2.2. Instruments

Ultraviolet–visible (UV–vis) absorption spectra of solutions were obtained with a Varian Cary 3E UV–vis spectrophotometer. UV–vis reflectance absorption spectra were obtained from a Varian Cary 5000UV-VIS-NIR spectrophotometer with a diffuse reflectance accessory (DRA-2500). Scanning electron microscopy (SEM) measurements were performed with a Supra 55 VP field emission SEM. Transmission electron microscopy (TEM) images were obtained using a JEOL JEM-2100 with an acceleration voltage of 200 kV. An IRIS Intrepid IIXSP inductively coupling plasma atomic emission spectrometer (ICP-AES) instrument was employed to determine the gold content of different samples. X-ray diffraction (XRD) analysis was performed on the Panalytical X'Pert Powder instrument at a voltage of 45 kV and a current of 20 mA. XRD data were collected with  $2\theta$  range of  $10^\circ$ – $80^\circ$  and a scanning rate of  $2^\circ/\text{min}$  at a step of  $0.01^\circ$ . X-ray photoelectron spectroscopy (XPS) measurements were carried out on a Kratos XSAM800 XPS system with  $\text{K}\alpha$  source and a charge neutralizer. Fourier transform infrared spectra (FTIR) were measured with a PerkinElmer Fourier transform infrared spectrometer (FTIR-1730) in attenuated total reflection (ATR) mode. The water contact angle of the fabrics was tested using a contact angle meter (KSV CAM101).

### 2.3. In-situ synthesis of AuNP@NRP

The AuNP@NRP hybrid latex was prepared through heating  $\text{HAuCl}_4$  and natural rubber latex. Briefly, 2.0 ml of colloid suspension of natural rubber latex (5.0 wt%) was added into the conical flask containing an aqueous  $\text{HAuCl}_4$  solution (198 mL,  $5.88 \times 10^{-4}$  M) in water bath at  $90^\circ\text{C}$  and was shaken for 40 min. Finally, the nanocomposite of AuNP@NRP were obtained.

### 2.4. Surface modification of the fabrics with AuNP@NRP

The AuNP@NRP colloid suspension was used to modify the fabrics including cotton and hydrophilic polyester fabric using “dip and dry” method, as shown in Fig. 1. Firstly, cotton fabrics were dipped into the AuNP@NRP colloid and shaken for 2 min, followed by heating in the oven at  $100^\circ\text{C}$  for 10 min, which was defined as one circle. Afterwards, the fabrics with different loadings of AuNP@NRP can be obtained by repeated “dip and dry” coating cycles. The obtained cotton fabric samples were denoted as CRAu1 ~ CRAu9 for 1–9 coating cycles

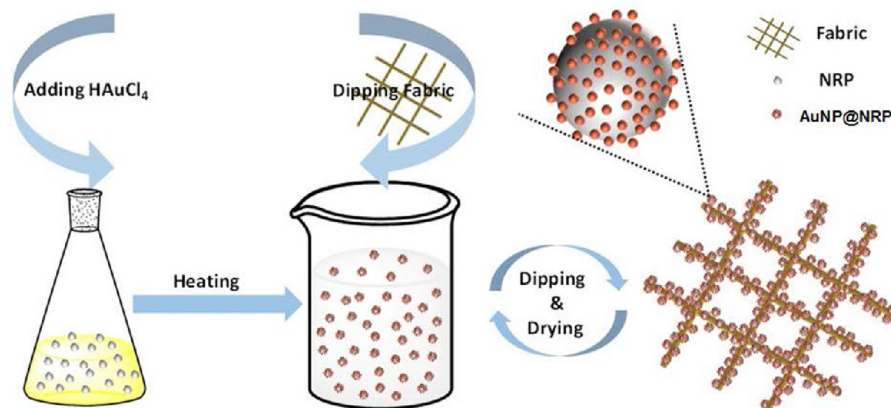


Fig. 1. Schematic view of preparation process of functional fabrics based on AuNP@NRP nanocomposite using a “dip and dry” method.

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