

# Cotton Fabric Immobilized ZnO-NR@GO and ZnO-NR@AuNP and Their Photocatalytic Application

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## ABSTRACT

The present study demonstrates immobilization of the ZnO nanorod (ZnO-NR) on the cotton fabric (CF) and further functionalization with gold nanoparticles (AuNPs) and graphene oxides (GO). Graphene oxide (GO) was synthesized from graphite flakes and AuNPs was synthesized *ex-situ* using citrate method. These GO and AuNPs are further deposited on ZnO-NR immobilized on CF thereby generating CF@ZnO-NR, CF@ZnO-NR@GO, and CF@ZnO-NR@AuNP composites. The morphology of these deposited nanostructures were verified by scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), and Fourier transformed infrared spectroscopy (FTIR). The photocatalytic degradation of dye molecules by these composites were assessed by UV-visible spectroscopy. CF immobilized composites materials exhibited good catalytic activity with excellent recyclability.

**Keywords:** Cotton fabric, graphene oxide, ZnO nanorod, AuNPs, and SEM

## 1 INTRODUCTION

The photocatalytic properties of metal oxide based materials namely TiO<sub>2</sub>, ZnO and CdS have been explored extensively in recent years [1; 2; 3]. These metal oxide based photocatalyst have tremendous potential for transforming energy of photon into chemical energy and thereby cause degradation of water and air based organic pollutants [1; 2; 3]. Among these photocatalysts, ZnO turns out to be most favorable due to large band gap (3.37 eV), large excitation binding energy (ca. 60 meV), high photosensitivity, chemical stability and non-toxic nature [4]. However, the immediate recombination of the photo-generated electrons and holes is a major setback in achieving enhanced photocatalytic activity of the ZnO [4]. In order to enhance the photocatalytic activity effort are under way so that the photogenerated electron hole pair do not recombine rapidly [4]. In these efforts ZnO was coupled with noble metals such as gold and platinum [5], graphene [4], polymeric material [6], carbon nanotubes [7] etc. Among these combination of ZnO and graphene showed maximum photocatalytic activity due to the high surface area and high electron conductivity of graphene [8]. Various synthetic methods have been employed in order to fabricate ZnO-graphene composite such as electrochemical

deposition [9], chemical vapor deposition (CVD) [10], and hydrothermal synthesis [11].

In this work we have synthesized graphene oxide (GO) [12; 13] and AuNPs [14] utilizing traditional methods and then further deposited on ZnO-NR immobilized on cotton fabric (CF) [15] by dip-coating method. The composite materials thus generated were assessed for photocatalytic degradation of Trypan Blue (TryB) in aqueous solution in presence of UV light.

## 2 EXPERIMENTAL

### 2.1 Materials

Sodium tetrachloroaurate(III) dihydrate (99%), graphite flakes, sodium nitrate (99%), TryB powder and sodium borohydride (99%) were purchased from Sigma-Aldrich; Sodium hydroxide, zinc acetate dihydrate, zinc nitrate hexahydrate, hexamethylenetetramine, sodium citrate dihydrate, potassium permanganate (98%), sulfuric acid (98%), hydrogen peroxide (30%), and triethylamine were purchased from Fisher Scientific. Isopropyl alcohol and Triton X-100 were purchased from VWR analyticals. All chemicals and solvents were used without further purification. 100% cotton fabrics are purchased from walmart. The DI water in all experiments was Milli-Q water (18 MΩ cm, Millipore).

### 2.2 Synthesis of Graphene oxide (GO)

Graphene oxide (GO) was synthesized with modification of Hummers method [12; 13]. 0.5 g of graphite and 0.5 g of NaNO<sub>3</sub> were stirred in an ice bath in presence of 23 mL of sulfuric acid. 3.0 g of KMnO<sub>4</sub> was added and the mixture was stirred at 35 °C water bath for an hour. The thick paste thus formed was stirred for additional 30 minutes at 35 °C in presence of extra 40 mL of water. After that 100 mL of water was added followed by slow addition of 3 mL of 30% H<sub>2</sub>O<sub>2</sub>. The color of the solution turned yellow from brown. The mixture was filtered warm and washed with 100 mL of water. The yielded filter cake was dispersed in water by ultra sonication. All the larger graphite particles were removed by 3-5 times low speed centrifugation at 1000 rpm for 2 minutes. Finally the supernatant was centrifuged two more times at 8000 rpm for 15 minutes to get rid of small pieces of GO and water soluble impurities. The obtained GO was dispersed in water by vortex for further use.

### 2.3 Surface cleaning of Cotton Fabrics

Cotton fabric surface cleaning was done by following literature method [15]. Before deposition of ZnO nanorod, cotton fabrics were cut into 2 cm x 2 cm pieces. In 100 mL DI water 25 g of NaOH, 7.5 g of Triton X-100 and 3.75 g

of sodium citrate were added and after dissolution of the solids 1000 mL of additional DI water was added. After addition of cotton swatches the mixture was stirred at 100 °C for an hour. Then the cotton swatches were taken out of the cold mixture and thoroughly cleaned with excess DI water several times and then air dried.

#### 2.4 ZnO Seed Solution

ZnO seed solution was prepared by following literature method [15]. 1.10 g of zinc acetate dihydrate was added to 50.0 mL of isopropyl alcohol and stirred vigorously at 85 °C for 15 min. After that 700 µL of triethanolamine was added dropwise and the resulting clear solution was stirred at 85 °C for another 10 min. The solution was then incubated at room temperature for 3 hrs without stirring.

#### 2.5 ZnO Growth Solution

ZnO growth solution was prepared by following literature method [15]. 7.71 g of hexamethylenetetramine first dissolved in 550 mL of DI water. To this solution 16.4 g of zinc nitrate hexahydrate was added and resulting mixture was stirred for 24 hrs at room temperature. The final pH of the resulting solution was maintained at 6.11.

#### 2.6 ZnO-NR Growth on Fibers

Surface cleaned cotton swatches were first dip-coated with the ZnO seed solution for 5 min and then rinsed with ethanol. Dip-coated swatches were then dried in the oven at 90 °C for 1 hr and then left in air for 12 hours. These swatches were then immersed into a 500 mL growth solution and incubated at 95 °C for 8 hrs in the oven. The beaker was further incubated at room temperature for 12 hrs before the swatches were taken out of the growth solution and rinsed thoroughly with DI water several times and then air dried at room temperature. The procedure was adopted from literature method [15].

#### 2.7 Synthesis of AuNPs

AuNPs was synthesized following literature method [14]. About 3.5 nm size AuNPs was prepared by mixing a 20 mL  $2.5 \times 10^{-4}$  M NaAuCl<sub>4</sub> and 2.5 mL of  $2.5 \times 10^{-4}$  M trisodium citrate in an erlenmeyer flask and adding 0.6 mL of 0.1 M ice cold NaBH<sub>4</sub> solution with constant stirring. The solution color turned pink immediately and allowed to stir for another 2 hrs and after that stored at room temperature until further use.

#### 2.8 Fabrication of CF immobilized ZnO-NR

The CF immobilized ZnO-NR were further fabricated with GO, AuNPs and a combination of GO and AuNPs. CF@ZnO-NR@GO composites were obtained simply by dip-coating the CF@ZnO-NR composites in GO aqueous solution and then dried at 60 °C. CF@ZnO-NR@AuNP composites were prepared by dip-coating the CF@ZnO-NR composites in an *ex-situ* synthesized colloidal AuNP-citrate solution for 24 hrs. Finally CF@ZnO-NR@AuNP@GO composites were fabricated by dip-coating the CF@ZnO-NR@AuNP composites in GO aqueous solution and then dried at 60 °C. The digital pictures of all the composite materials are illustrated in Figure 1.

#### 2.9 UV-visible and FTIR Spectroscopic Studies

The absorption spectra of GO and AuNPs samples were recorded using a Cary 4000 UV-visible spectrophotometer. FTIR spectroscopy was performed using Perkin-Elmer FTIR Spectra 100 spectrometer fitted with diamond ATR. The spectra were further processed and plotted with Origin 8.0 software.

#### 2.10 SEM and EDX analysis

SEM images were collected using JOEL JSM-5800LV scanning electron microscope equipped with Bruker Esprit 1.9 microanalysis software. This is also connected to an EDX detector and EDX line analysis data were obtained by using the back-scattered detector at a working distance of 10-12 mm at 15.0 kV of accelerating voltage.

#### 2.11 Photocatalytic Degradation Experiment

For the photocatalytic degradation experiment 20 µM TryB solution was prepared in DI water. 15 watt UV-Bench lamp emitting at 365 nm was used to irradiate the reaction mixture. One piece of composite material was immersed into a 5.0 mL of 20 µM of TryB in 20 mL sintered glass vial on a hot plate with constant stirring. The whole process was carried out in an enclosed wooden box and progress of the degradation process was monitored by measuring the absorbance of the reaction mixture at a regular time interval using a UV-visible spectrophotometer.

### 3 RESULTS AND DISCUSSION

In this report we demonstrated fabrication of CF with ZnO forming CF@ZnO-seed and CF@ZnO-NR composites. CF@ZnO-NR was further modified to CF@ZnO-NR@GO composite by dip-coating in GO solution and to CF@ZnO-NR@AuNP by dip-coating in AuNPs-citrate colloidal solution synthesized *ex-situ*. CF@ZnO-NR@AuNP was then modified to CF@ZnO-NR@AuNP@GO by dip-coating in GO solution and drying at 60 °C. The digital pictures of all these composites are shown in Figure 1.

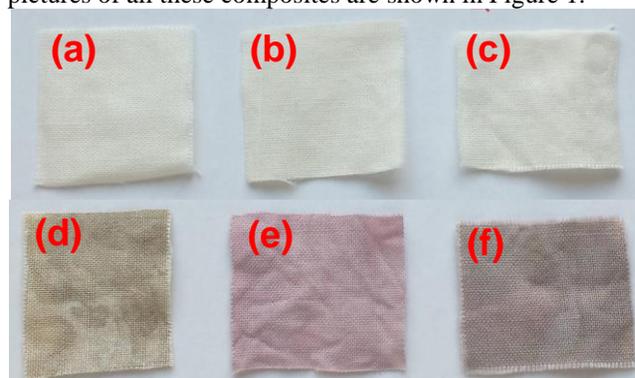


Figure 1: Digital photographs of (a) empty CF, (b) CF@ZnO-seed, (c) CF@ZnO-NR, (d) CF@ZnO-NR@GO, (e) CF@ZnO-NR@AuNP, and (f) CF@ZnO-NR@AuNP@GO composites.

### 3.1 Characterization of the composites by FTIR Spectroscopy

FTIR spectroscopic data for all the above mentioned cotton fabric[16] based composite materials are shown in Figure 2. A broad peak was observed at  $3309\text{ cm}^{-1}$  corresponding to O-H stretch. This signal is relatively broader for CF@ZnO-NR@AuNP@GO composite. Another broad signal is observed at  $2894\text{ cm}^{-1}$  due to C-H stretching. In this case the symmetric and asymmetric stretching mode of  $-\text{CH}_2-$  are not distinct. The adsorbed water signal appears at  $1638\text{ cm}^{-1}$ . Other peaks of these spectra are at  $1427$ ,  $1314$ ,  $1158$ , and  $1025\text{ cm}^{-1}$  corresponding to C-H bending, O-H deformation, C-O-C asymmetric stretching, and C-O stretching.

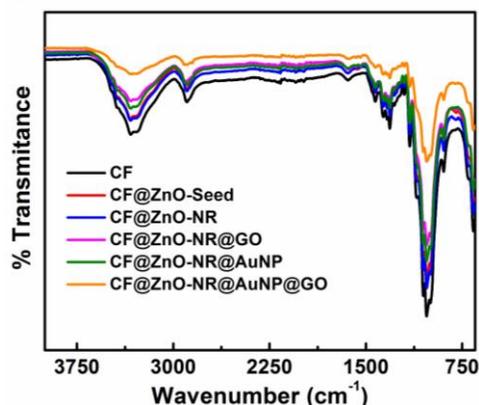


Figure 2: FTIR spectra of empty CF (black line), CF@ZnO-Seed (red line), CF@ZnO-NR (blue line), CF@ZnO-NR@GO (pink line), CF@ZnO-NR@AuNP (green line), and CF@ZnO-NR@AuNP@GO (orange line).

### 3.2 Photocatalytic Reaction by the Composites

The photocatalytic degradation of  $20\text{ }\mu\text{M}$  TryB was evaluated in presence of a 15 watt UV lamp emitting at  $365\text{ nm}$ .  $5.0\text{ mL}$   $20\text{ }\mu\text{M}$  TryB solution was inserted into  $20\text{ mL}$  glass vials and the liquid was stirred under the UV lamp inside an enclosed wooden box in presence or absence of the designed composite materials. A  $2\text{ cm} \times 2\text{ cm}$  composite material was inserted into the reaction solution as shown in Figure 3. The reaction was monitored time to time by UV-visible absorption spectroscopic measurement. The digital pictures of the reaction solutions with and without photocatalyst at 1 hour and at 24 hours are shown in Figure 3. The vial (a) is control, containing only  $20\text{ }\mu\text{M}$  TryB. Rest of the vials contain  $20\text{ }\mu\text{M}$  TryB and (b) empty CF or (c) CF@ZnO-Seed or (d) CF@ZnO-NR or (e) CF@ZnO-NR@GO or (f) CF@ZnO-NR@AuNP or (g) CF@ZnO-NR@AuNP@GO. It was observed that after 24 hours the solution color of all the vials turned colorless except of vial (a1) (no catalyst, control) and (b1) (empty CF) as illustrated in Figure 3.

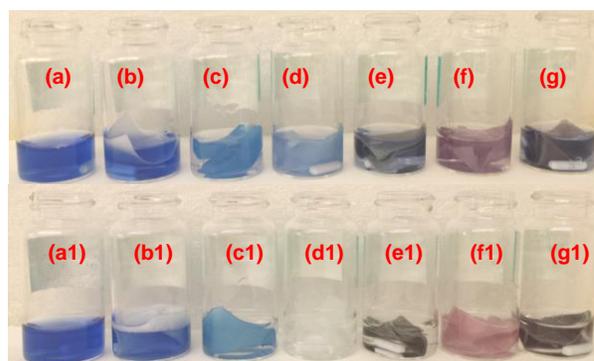


Figure 3: Digital photographs of the photocatalytic degradation process of  $20\text{ }\mu\text{M}$  TryB after 1 hour (a-g) and 24 hour (a1-g1) under  $365\text{ nm}$  UV lamp and in presence and absence of photocatalyst.

Figure 4 depicts the UV-visible absorption spectra of the  $20\text{ }\mu\text{M}$  TryB dye in aqueous solution after 1 hour in presence and absence of composite photocatalysts under UV light. It appears that the absorption maxima at  $592\text{ nm}$  decreases most in presence of CF@ZnO-seed composite. However, with close observation it was found that TryB gets extensively adsorbed to the CF@ZnO-seed composite and composite color turned blue. Besides this the CF@ZnO-NR@AuNP performs best among all other composites.

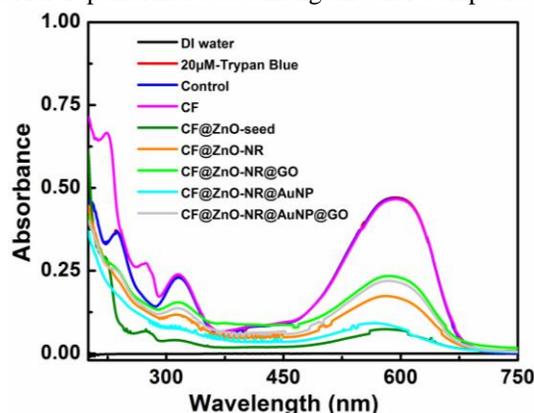


Figure 4: Evaluation of photocatalytic degradation of  $20\text{ }\mu\text{M}$  TryB after 1 hour by UV-visible absorption spectroscopy under  $365\text{ nm}$  UV lamp and in presence and absence of photocatalyst. The  $20\text{ }\mu\text{M}$  TryB spectrum (red line) is in absence of UV light and control spectrum (blue line) is in presence of UV light.

Figure 5 represents the UV-visible absorption spectra of the  $20\text{ }\mu\text{M}$  TryB dye in aqueous solution after 5 hour in presence and absence of composite photocatalyst under UV light. It is observed that the absorption maxima at  $592\text{ nm}$  decreases most in presence of CF@ZnO-NR@AuNP composite. The second best result was found with CF@ZnO-NR composite. On the other hand composites CF@ZnO-NR@GO and CF@ZnO-NR@AuNP@GO performs moderately well.

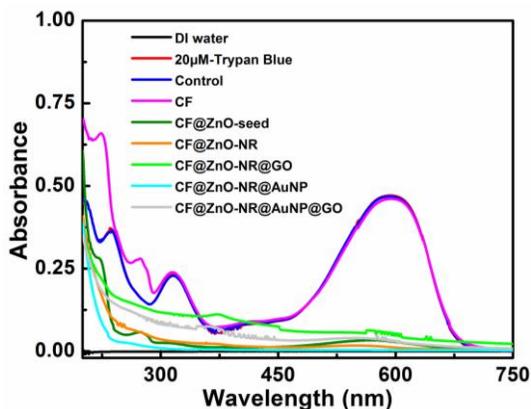


Figure 5: Evaluation of photocatalytic degradation of of 20  $\mu\text{M}$  TryB after 5 hour by UV-visible absorption spectroscopy under 365 nm UV lamp and in presence and absence of photocatalyst. The 20  $\mu\text{M}$  TryB spectrum (red line) is in absence of UV light and control spectrum (blue line) is in presence of UV light.

## 4 CONCLUSIONS

In summary, we have successfully fabricated surface cleaned cotton fabrics into several different composite materials namely CF@ZnO-seed, CF@ZnO-NR, CF@ZnO-NR@GO, CF@ZnO-NR@AuNP, and CF@ZnO-NR@AuNP@GO. The FTIR data were almost indistinguishable as the fibers in the fabric are still intact. Only in case of CF@ZnO-NR@AuNP@GO we have observed some broadening of the FTIR signals. Almost all the composites materials effectively performed in photocatalytic degradation of TryB except for CF@ZnO-seed. In this case most of the dye gets adsorbed to the material. Composites CF@ZnO-NR and CF@ZnO-NR@AuNP performed best as photocatalysts. No dye degradation was observed in absence of catalyst or in presence of only UV light and CF. The SEM and EDX analysis are in progress.

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