

**STUDIES ON MULTI-FUNCTIONAL
PROPERTIES OF DOPED TiO₂ NANOPARTICLE
COATED COTTON FABRIC**

ANU MISHRA



**DEPARTMENT OF TEXTILE TECHNOLOGY
INDIAN INSTITUTE OF TECHNOLOGY DELHI
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PROPERTIES OF DOPED TiO₂ NANOPARTICLE
COATED COTTON FABRIC**

by

ANU MISHRA

Department of Textile Technology

Submitted

in fulfilment of the requirements of the degree of Doctor of Philosophy

to the



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**Dedicated to my Parents, Grandparents
&
All family members**

CERTIFICATE

This is to certify that the thesis titled **Studies on Multi-functional Properties of Doped TiO₂ Nanoparticle Coated Cotton Fabric**, being submitted by **Mr. Anu Mishra** to the Indian Institute of Technology Delhi, for the award of the degree of **Doctor of Philosophy**, is a record of bonafide research work carried out by him. He has worked under my guidance and supervision and fulfilled the requirements for submission of the thesis which has attained the standard required for a Ph.D. degree of this institute.

The results contained in this thesis have not been submitted, in part or in full, to any other university or institute for the award of any degree or diploma.

Dr. Bhupendra Singh Butola

Associate Professor

Date:

Department of Textile Technology

Indian Institute of Technology Delhi

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Anu Mishra

Abstract

Development of textiles with multifunctional properties for creation of high value added products is being explored by smart manufacturers for quality conscious customers. Traditionally organic agents and finishes have been used for imparting functionalities to the textiles like antimicrobial, UV protection, water repellency, flame retardancy etc. In recent times however, focus has shifted to inorganic finishes, typically metal salts and oxides to impart some functional properties.

One of the widely explored inorganic compounds is TiO_2 , which is well known for its photocatalytic activity in UV light. Its ability to destroy organic matter by oxidation in UV light radiation has been exploited in self-cleaning, dye decolorization, antimicrobial activity and removal of toxic organic compounds from water. In the last decade, researchers have started applying TiO_2 on textiles for imparting functional properties like self-cleaning, UV protection, dye decolorization etc. The TiO_2 has been found to be much more effective in nanoparticle (NP) form than as bulk deposition.

In this study, TiO_2 has been deposited in NP form on cotton fabric by sol-gel technique. Titanium tetraisopropoxide (TTIP) has been used as a precursor for in-situ deposition of TiO_2 NP on woven cotton fabric. Three different process routes, namely pad-dry-cure, pad-dry-hydrothermal and pad-dry-solvothermal were chosen for in-situ application of TiO_2 NP on cotton fabric and effect of various parameters on properties like UV protection, self-cleaning as well as wash durability was examined. The study shows that very low levels of TiO_2 deposition ($\sim 0.1\%$ owf) are sufficient to impart reasonable level of UV protection to cotton fabric. Prolonged high temperature thermal treatment in water ($\sim 120^\circ\text{C}$, 3 h) is needed to convert the deposited TiO_2 coating to crystalline NP form. Only when the deposited TiO_2 gets converted to crystalline anatase NP form, it develops significant self-cleaning and wash durable properties.

Although TiO_2 is one of the most effective photocatalyst available, its band gap ensures that the photocatalytic activity is witnessed only in presence of UV light. Since UV radiation is only a small fraction of overall solar radiation, it can be converted to a much more effective manner if the photocatalytic effect can be extended to visible part of the spectrum. This is possible by reducing the band gap and one of the popular ways of doing it is doping of TiO_2 with various elements.

In this study TiO_2 was doped with silver and it was found that it has the ability to reduce the band gap of TiO_2 from 3.25 eV to 3.14 eV. This allows TiO_2 to be effective as a photocatalyst in visible part of the solar radiation also. Such silver doped TiO_2 NP coated cotton fabric composites were used for decolorization of Rhodamine B (RhB) dye solution in water. It was found that cotton fabric coated with silver doped TiO_2 NPs was able to provide $\sim 94\%$ and 91% decolorization of RhB dye solutions after 8 h exposure to UV and visible light radiations respectively. Similar trend was observed with self-cleaning of methylene blue (MB) dye stains.

One of the highly effective antibacterial inorganic materials is silver. Silver is a highly potent inorganic antibacterial material and has been used by mankind in various forms. However, due to its very high surface area and hence effectiveness, nano-silver is being widely used nowadays. In this study, silver has been used in a novel way to convert TiO_2 NP coated cotton into effective antibacterial form. Silver salt has been used at very low concentrations (100 ppm) during hydrothermal treatment of TiO_2 NP coated fabric to dope it. Doping was confirmed by spectroscopic studies and this resulted in imparting valuable broad spectrum antibacterial properties to cotton.

The enhancement of dye decolorization and stain removal property can be brought about by use of highly crystalline mixed crystal forms of TiO_2 NP. One such product is P-25 from Degussa (Anatase:Rutile/80:20), which is highly crystalline nanoparti-

cles (NPs) of TiO_2 , with mixed crystalline forms and a size of ~ 25 nm. Although these NPs have high catalytic power, they do not have high affinity for cotton. A novel approach was used to exploit the high catalytic power of P-25 NPs on cotton and at the same time ensuring durability of their deposition. These NPs were introduced in the hydrothermal bath of cotton fabric coated with an amorphous coating of TiO_2 . During the hydrothermal stage, the P-25 NPs get embedded in the amorphous layer, which itself becomes crystalline and hence durable. It was found that the cotton fabric in which P-25 NPs were applied on TiO_2 coated cotton during hydrothermal treatment, exhibited the highest dye decolorization and self-cleaning attributes. The hydrothermal route also imparted reasonable wash durability to deposited P-25 NPs.

सार

आजकल गुणवत्ता में विश्वास रखने वाले ग्राहकों के लिए स्मार्ट वस्त्र निर्माता, बहुआयामी वस्त्रों का विकास कर रहे हैं। परंपरागत रूप से, कार्बनिक रसायनों का उपयोग करके वस्त्रों को जीवाणु रोधी, अग्निरुधी एवं विकिरण रोधी बनाया जाता रहा है। किन्तु पिछले लगभग एक दशक से अकार्बनिक रसायनों (धातु लवण अथवा ऑक्साइड) का उपयोग भी वस्त्रों की गुणवत्ता बढ़ाने में किया जा रहा है। कार्बनिक रसायनों की तुलना में अकार्बनिक रसायन कई कारणों से अधिक श्रेष्ठ सिद्ध हुए हैं। संक्षेपण में आसानी, बहु-कार्यक्षमता, उपयोग के उपरान्त आसान तरीके से निस्तारण के साथ- साथ अकार्बनिक रसायन, पर्यावरण को नुकसान भी कम पहुँचाते हैं। इसके अतिरिक्त, अकार्बनिक तत्वों से बने जीवाणु रोधी रसायनों की जीवाणुओं के प्रति प्रतिरोधकता भी लम्बे समय तक रहती है।

धरती पर विद्यमान अनेकानेक अकार्बनिक यौगिकों के बीच टाइटेनियम डाइऑक्साइड नामक यौगिक का अपना विशेष स्थान है। यह यौगिक पराबैगनी प्रकाश में अपनी उत्प्रेरक क्षमता के लिए जाना जाता है। पराबैगनी प्रकाश में ऑक्सीकरण द्वारा हानिकारक पदार्थों को नष्ट करने की क्षमता एवं किसी भी सतह को स्वतः साफ़ बनाये रखने की इसकी क्षमता अति महत्वपूर्ण है। पिछले एक दशक से वस्त्र वैज्ञानिकों ने भी इस यौगिक का उपयोग हानिकारक पराबैगनी किरणों से बचाव, वस्त्र को स्वतः स्वच्छ रखने एवं जीवाणु रोधी बनाने में किया है।

उपलब्ध साहित्य से पता चलता है कि वस्त्रों में टाइटेनियम डाइऑक्साइड की पतली एवं टिकाऊ परत चढ़ाने की प्रक्रिया में कोई व्यवस्थित अध्ययन नहीं हुआ है। इस अध्ययन में टाइटेनियम डाइऑक्साइड को सूती वस्त्र के ऊपर तीन विभिन्न विधियों से लगाया गया है।

प्रयोगों द्वारा पता चलता है कि टाइटेनियम डाइऑक्साइड का बहुत कम स्तर (वस्त्र के भार का ~0.1%) सूती कपड़े के लिए यूवी संरक्षण के उचित स्तर को प्रदान करने के लिए पर्याप्त है। अपने प्री कर्सर (टाइटेनियम टेट्रा-आइसोप्रोपोक्साइड) द्वारा वस्त्र पर टाइटेनियम डाइऑक्साइड की

प्रारंभिक जमावट एक असंगत फिल्म बनाती है। नतीजे बताते हैं कि जमा हुई टाइटेनियम डाइऑक्साइड की परत को क्रिस्टलीय रूप में परिवर्तित करने के लिए पानी में लंबे समय तक उच्च तापमान (हाइड्रोथर्मल उपचार, ~ 120 डिग्री सेल्सियस, 3 घं०) की आवश्यकता होती है। केवल तभी टाइटेनियम डाइऑक्साइड की परत क्रिस्टलीय एनाटेज रूप में परिवर्तित हो जाती है, जो कि टिकाऊपन के साथ स्वतः सफाई का गुण वस्त्र पर (टाइटेनियम डाइऑक्साइड) विकसित करती है। चाँदी एक अत्यधिक प्रभावी जीवाणुरोधी अकार्बनिक अवयव है। यह आम तौर पर विभिन्न प्रकार से उपयोग लाया जाता रहा है। हालांकि, उच्च सतह क्षेत्र और प्रभावशीलता के कारण, आजकल चाँदी के नैनो आकार का व्यापक रूप से उपयोग किया जा रहा है। इस अध्ययन में, टाइटेनियम डाइऑक्साइड लेपित सूती वस्त्र को प्रभावी जीवाणुरोधी रूप में परिवर्तित करने के लिए चाँदी का उपयोग किया गया है। टाइटेनियम डाइऑक्साइड लेपित सूती कपड़े के हाइड्रोथर्मल उपचार के दौरान चाँदी के लवण का उपयोग बहुत कम सांद्रता (100 पीपीएम) पर किया गया है। स्पेक्ट्रोस्कोपिक अध्ययनों द्वारा डोपिंग की पुष्टि हुई और इसके परिणामस्वरूप इस अध्ययन में सूती वस्त्रों में जीवाणुरोधी गुण प्रदान किया गया।

यद्यपि टाइटेनियम डाइऑक्साइड एक अत्यंत प्रभावी प्रकाश उत्प्रेरक है, परन्तु इसका बैंड अंतर इसकी प्रकाश उत्प्रेरक क्षमता केवल यूवी प्रकाश की उपस्थिति में ही निश्चित करता है। चूंकि यूवी विकिरण समग्र सौर विकिरण का केवल एक छोटा सा अंश है, इसलिए इसका उपयोग अधिक प्रभावी तरीके से नहीं किया जा सकता है। टाइटेनियम डाइऑक्साइड के बैंड अंतर को कम करके इसकी प्रकाश उत्प्रेरक क्षमता का प्रभाव सौर स्पेक्ट्रम के दृश्य भाग तक बढ़ाया जा सकता है और इसे करने के लोकप्रिय तरीकों में से एक विभिन्न तत्वों के साथ टाइटेनियम डाइऑक्साइड की डोपिंग है।

अध्ययन से पता चलता है कि चाँदी के साथ टाइटेनियम डाइऑक्साइड की डोपिंग न केवल सूती वस्त्रों को जीवाणुरोधी चरित्र प्रदान करती है, बल्कि यह टाइटेनियम डाइऑक्साइड के बैंड अंतर को

3.25 इलेक्ट्रान वोल्ट से 3.14 इलेक्ट्रान वोल्ट तक कम करने में भी सक्षम है। यह टाइटेनियम डाइऑक्साइड को सौर विकिरण के दृश्य भाग में भी एक प्रभावी प्रकाश उत्प्रेरक के रूप में विकसित करता है। इस प्रकार चाँदी डोपिंग के उपरान्त टाइटेनियम डाइऑक्साइड लेपित सूती कपड़े, पानी में रोडामीन B डाई के रंगीन विलयन को रंगहीन करने के लिए इस्तेमाल किये गए। यह पाया गया कि चाँदी डोपेड टाइटेनियम डाइऑक्साइड के साथ लेपित सूती कपड़े पराबैंगनी एवं दृश्य प्रकाश विकिरण में 8 घंटे के एक्सपोजर के बाद डाई विलयन के रंग को क्रमशः ~ 94% और 91% रंगहीन करने में सफल हुए। इसी तरह की प्रवृत्ति मेथिलीन ब्लू डाई द्वारा लगे दागों की स्वतः सफाई करने में भी देखी गई।

डाई को रंगहीन करने और दाग हटाने की प्रवृत्ति में वृद्धि टाइटेनियम डाइऑक्साइड के क्रिस्टलीय मिश्रित रूपों के उपयोग के द्वारा भी की जा सकती है। ऐसा एक उत्पाद डेगुसा (पी-25) है, जो मिश्रित क्रिस्टलीय रूपों (एनाटेज और रूटाइल) के ~25 नैनोमीटर आकार वाले टाइटेनियम डाइऑक्साइड के अत्यधिक क्रिस्टलीय नैनो कण हैं। हालांकि इन कणों में उच्च उत्प्रेरक शक्ति है, लेकिन इनके पास सूती वस्त्र के साथ स्थायित्व रखने की क्षमता नहीं है। सूती वस्त्र पर पी-25 की उच्च उत्प्रेरक क्षमता का उपयोग एवं इनके जमाव को वस्त्र पर स्थायित्व प्रदान के लिए भी यह अध्ययन किया गया है। इन नैनोकणों को टाइटेनियम डाइऑक्साइड की एक असंगत कोटिंग के साथ लेपित करके सूती कपड़े का हाइड्रोथर्मल उपचार किया गया। हाइड्रोथर्मल उपचार के दौरान, पी-25 कण असंगत परत में स्थापित होकर स्वयं क्रिस्टलीय बनकर वस्त्र पर टिकाऊ हो जाते हैं। अध्ययन में यह पाया गया कि सूती कपड़े (जिसमें पी-25 को हाइड्रोथर्मल उपचार के दौरान टाइटेनियम डाइऑक्साइड लेपित सूती वस्त्र पर लागू किया गया था) ने डाई के विलयन को अधिकतम रंगहीन किया और स्वतः सफाई में भी सर्वोत्तम प्रदर्शन किया। इस प्रकार हाइड्रोथर्मल विधि द्वारा पी-25 कणों को सूती वस्त्रों पर स्थाई रूप से जमा किया जा सकता है।

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