

# Recent Advances of Modified TiO<sub>2</sub> Nanostructure as Heterogeneous Catalyst in Organic Transformations

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**Abstract:** This review highlights the different strategies of modified TiO<sub>2</sub> nanostructure as heterogeneous catalyst in organic transformations. The modification in TiO<sub>2</sub> nanostructure have been achieved by doping with metal and non-metal, composing with other material such as metals, metal oxides, nonoxides, semiconductor and nanostructure carbon materials. The influence of modification in TiO<sub>2</sub> nanostructure on catalytic properties in organic synthesis also discussed. Different modifications of TiO<sub>2</sub> extend the catalyst selectivity and reusability over unmodified TiO<sub>2</sub> nanoparticles. Recent investigations have shown that modified TiO<sub>2</sub> nanostructures utilised as active catalysts or catalyst support in organic transformations including C-C, C-N, C-S, C-O bond formation reactions, multicomponent reactions (MCR), oxidation- reductions.

**Keywords:** Heterogeneous Catalyst, TiO<sub>2</sub> Nanoparticles, Organic Transformations, TiO<sub>2</sub> as Support, Supported Nanoparticles

## I. INTRODUCTION

This A rapid industrialization and urbanization have produced many serious environmental issues during past few decades.<sup>1,2</sup> Therefore researchers have been faced with a new challenge of finding the environment-friendly processes that can reduce or eliminate the dependence of hazardous reagents and solvents. 'Heterogeneous catalysis' is one of most powerful approach to replace or eliminate polluting processes.<sup>3</sup> Heterogeneous catalysis long established in commercial production of fuels, polymers and fibers. In recent years considerable interest has been developed towards the use of the heterogeneous catalyst in the synthesis of advanced intermediate, fine chemicals, and bioactive heterocyclic compounds.<sup>4,5</sup>

Heterocyclic compounds are an important and largest division of organic compounds and played a significant role in the pharmaceutical, agricultural, biological etc. field as they show broad spectrum of biological activity.<sup>6-7</sup> A variety of conventional catalysts were used for synthesis of heterocyclic compounds. However, these protocols suffered one of the drawbacks such as a necessity of excess organic solvent, needs longer reaction time, tedious work up procedures and recovery of catalyst.<sup>8</sup> The solid catalyst was used as a heterogeneous catalyst due to their easy separation and reusability.

Metal oxides are a versatile class of solid catalyst widely utilized in organic/inorganic transformations, water treatment and removal of pollutants.<sup>9-11</sup> In recent years, (TiO<sub>2</sub>) have been paying much more attention due to high chemo-selectivity, environmental compatibility, thermal stability and low cost.<sup>12</sup> In past several reports reviewed on TiO<sub>2</sub> based nanomaterial in numerous areas, including medical research, drug delivery, antibacterial materials, energy storage, self-cleaning and as a catalyst in organic reactions such as condensation, dehydrogenation, hydrogenation, dehydration, and coupling reactions.<sup>13-14</sup> It is widely demonstrated that the physical and chemical modification in TiO<sub>2</sub> were achieved by controlling the particle size to nanometer scale.<sup>15</sup>

Nanocrystalline materials are polycrystalline solids with a grain size of a few nanometers, typically < 100 nm. Nanocrystalline materials are a new class of materials that display distinct electrical, optical, magnetic, catalytic

properties over their bulk counterparts. These features of nanocrystalline material have great impacts in various fields.<sup>16</sup> Nanocrystalline TiO<sub>2</sub> are exceptionally important oxides having applications in preparing gas sensors, electrical devices, fuel cells, piezoelectric devices, chemical absorbent, optical devices, varistors and catalyst.<sup>17-19</sup> The properties nanocrystalline materials can be rationalized by adopting various synthesis and post-synthesis routes.<sup>20,21</sup> Furthermore, it is possible to confirm these modifications by the available characterization techniques. Therefore, development of a morphologically controllable synthesis of nanocrystalline metal oxides by a simple and economical method is an important research

### 1.1 TiO<sub>2</sub>

Titanium dioxide (TiO<sub>2</sub>) is naturally occurring oxides, was discovered in 1795 and commercial production started in the 1920s.<sup>22</sup> TiO<sub>2</sub> powders possess distinctive optical, electrical and catalytic properties. Hence, it is extensively used in paints, paper, textiles, plastics, inks, anti-bacterial agents, corrosion-resistant coatings, water and air purification, self-cleaning surfaces, rechargeable batteries, food additives sensor devices, etc.<sup>23,25</sup> In 1972, Fujishima and Honda revealed the photochemical splitting of water into hydrogen and oxygen with TiO<sub>2</sub>, that led to great attention towards TiO<sub>2</sub> as heterogeneous photo-catalyst.<sup>26</sup> Its properties in the visible and UV portions of the electromagnetic spectrum are especially significant.

### 1.2 Nanocrystalline TiO<sub>2</sub>

The interest in nanocrystalline TiO<sub>2</sub> have been grown extensively due to their outstanding chemical and physical properties, which furnished wide their applications such as optics, sensors, catalysts, pigments photovoltaic cells, photocatalysts. TiO<sub>2</sub> is known for its easy availability, low cost, prolonged chemical stability and nontoxic nature. The use of nanocrystalline TiO<sub>2</sub> in variety of applications was attained by fulfilling requirements in terms of particle size, size distribution, morphology, crystallinity and phase.<sup>13</sup> The desired property of TiO<sub>2</sub> can be achieved by adapting proper synthetic method and reaction condition.<sup>14</sup>

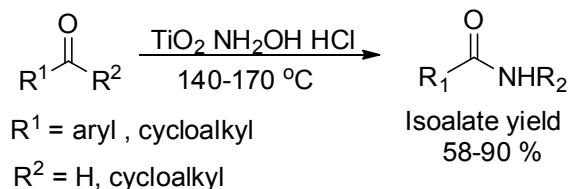
## II. SIGNIFICANCE OF NANOCRYSTALLINE TiO<sub>2</sub> IN ORGANIC TRANSFORMATION

### 2.1 Bare TiO<sub>2</sub> Nanoparticle as Heterogeneous Catalyst

#### 2.1.1. Beckmann Rearrangement

Beckmann rearrangement involves conversion of ketoximes or aldoximes into corresponding amides. It is significant route particularly for manufacturing  $\epsilon$ -caprolactam in the chemical industry. Beckmann rearrangement are usually carried out in presence of strong Lewis or Bronsted acid such as sulfuric acid, phosphorus penta chloride, hydrochloric acid in presence of organic solvents. These routes leads to formation of variety of by-product.

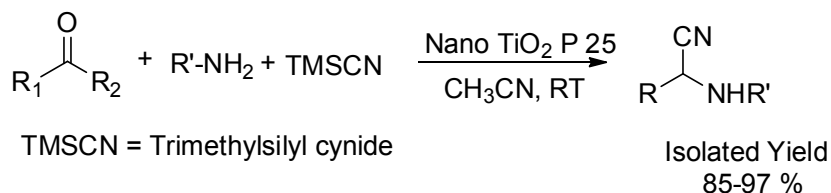
Sharghi, H. *and et al.* examined the TiO<sub>2</sub> as solid catalyst for Beckmann rearrangement of several ketones and aldehydes. It was found ketones and aldehydes reacts NH<sub>2</sub>OH. HCl to give corresponding amides in single step with quantitative yield under solvent free condition.<sup>26</sup> Solvent free condition, simple work-up, use of commercial, available and inexpensive catalyst and high yields, can make this procedure a useful and attractive alternative to the currently available methods.



**Scheme 1:** Beckmann rearrangement

#### 2.1.2 Strecker Reaction

Seyed Meysam Baghbanian *et al.* developed a simple and efficient for the synthesis of  $\alpha$ -amino nitriles from aldehydes, amines and trimethylsilyl cyanide (Me<sub>3</sub>SiCN) in the presence of a catalytic amount of cyanuric acid at room temperature.<sup>28</sup>



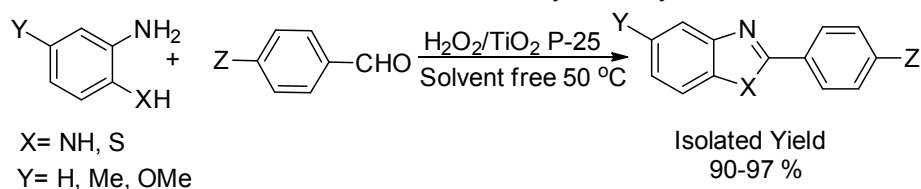
**Scheme 2:** Strecker reaction in malononitrile

Entry	Catalyst (mol%)	Time (min)	Yield <sup>b</sup> ( % )
1	No catalyst	12 h	0
2	5	10 min	55
3	10	10 min	70
4	20	10 min	98
5	25	10 min	98
6	20	15 min	86 <sup>c</sup>
7	20	25 min	90 <sup>d</sup>

TiO<sub>2</sub> P 25 was added to a mixture of 1 mmol of benzaldehyde, 1 mol of aniline, and 1.2 mmol of TMSCN. <sup>b</sup> Isolated yield. <sup>c</sup> In the presence of CHCl<sub>3</sub>. <sup>d</sup> In the presence of THF.

### 2.1.3 Synthesis of Benzimidazole

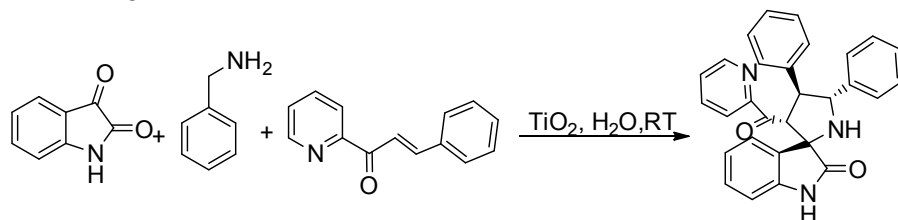
Bahram, K. and *et al.* described an oxidative coupling of *o*-phenylenediamine /*o*-aminothiophenol and aromatic aldehydes were carried out in presence of H<sub>2</sub>O<sub>2</sub>/TiO<sub>2</sub> P-25 NPs (particle size ≈ 21 nm) afford 2-substituted benzimidazole and benzothiazole derivatives (**Scheme 3**).<sup>29</sup> It was observed that the absence of TiO<sub>2</sub>-P25 NPs reaction proceeded very slowly and reaction stopped to formation of imine derivatives, In contrast, the presence of catalytic amount of TiO<sub>2</sub>-P25 NPs leading to formation of desired products. The catalyst can be activate the decomposition of H<sub>2</sub>O<sub>2</sub>. The reaction condition tolerates to both aldehydes bearing electron-withdrawing and electron-donating substituents in excellent yield the desired product. However, the same optimum reaction condition did not give desired 2-substituted benzoxazoles by reaction between 2-aminophenol and aldehydes. The catalyst TiO<sub>2</sub>-P25 NPs is stable and reused upto the 5 consecutive runs without considerable loss of catalytic activity.



**Scheme 3:** Synthesis of benzimidazoles

### 2.2.4. Synthesis of Spiroindole-Pyrrolidine

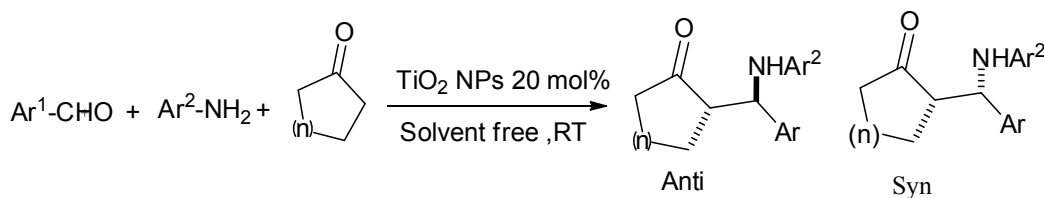
Pambal Ramesh and *et al.* reported TiO<sub>2</sub> NPs as a reusable heterogeneous catalyst for synthesis of spiroindole-pyrrolidine by reacting of 3-aryl-1-(pyridin-2-yl)-prop-2-en-1-one, isatins and benzylamines *via* 1,3-dipolar cycloaddition reaction using water as reaction media.<sup>30</sup>



**Scheme 4:** Synthesis of spiroindole-pyrrolidine by reacting of 3-aryl-1-(pyridin-2-yl)-prop-2-en-1-one,

### 2.2.5. Mannich Reaction

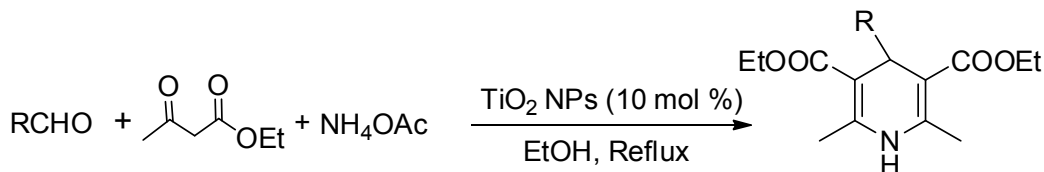
M.Z. Kassaei and *et al.* synthesized spherical shaped pure anatase TiO<sub>2</sub> NPs *via* a sol-gel method. The as synthesized catalyst was used for synthesis of  $\beta$ -aminocarbonyl *via* mannich reaction. It was observed TiO<sub>2</sub> nanoparticle catalysed n under solvent free condition<sup>31</sup>.



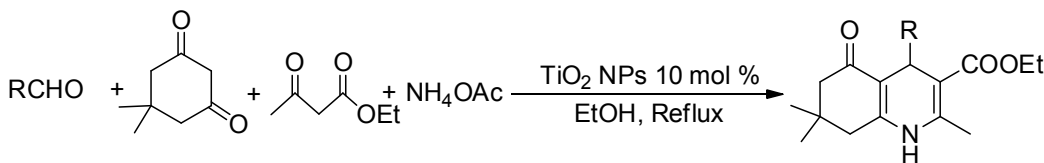
**Scheme 5:** Preparation of  $\beta$ -aminocarbonyl compounds

### 2.4.6. Hantzsch Condensation

1,4-Dihydropyridine and polyhydroquinoline derivatives have been prepared efficiently in a one-pot synthesis *via* Hantzsch condensation using nanosized titanium dioxide as a heterogeneous catalyst<sup>32</sup>. The present methodology offers several advantages such as excellent yields, short reaction times (30–120 min) environmentally benign, and mild reaction conditions. The catalyst can be readily separated from the reaction products and recovered in excellent purity for direct reuse.



**Scheme 6a:** One-pot synthesis of 1,4-DHPs. NPs-nanoparticles



**Scheme 6b:** One-pot synthesis of polyhydroquinoline derivatives

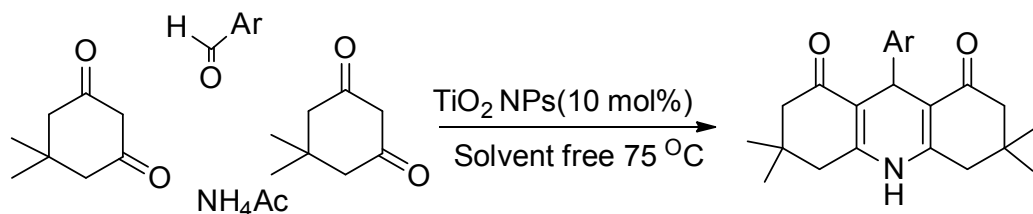
**Table 2:** The efficiency of several classical solvents

Entry	Solvent	Temperature (°C)	Time (h)	Yield <sup>a</sup> (%)
1	—	25	6	60
2	—	80	6	68
3	CH <sub>2</sub> Cl <sub>2</sub>	reflux	6	35
4	CH <sub>3</sub> CN	reflux	6	45
5	toluene	reflux	6	50
6	H <sub>2</sub> O	reflux	6	30
7	H <sub>2</sub> O + EtOH	reflux	6	42
8	EtOH	reflux	1.75	92
9	EtOH	40	6	78
10	EtOH	25	4	45

<sup>a</sup>Yield refers to isolated products.

### 2.5.7. Synthesis of 1,8-dioxo-Decahydroacridine Derivatives

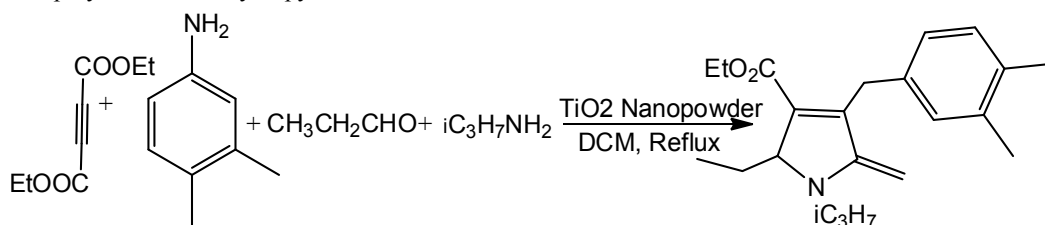
Ardeshir Khazaei and *et al.* studied effect of the rutile and anatase TiO<sub>2</sub> phases for synthesis of 1,8-dioxo-decahydroacridine derivatives under solvent-free condition<sup>33</sup>.



**Scheme 7:** One-pot synthesis of polyhydroquinoline derivatives

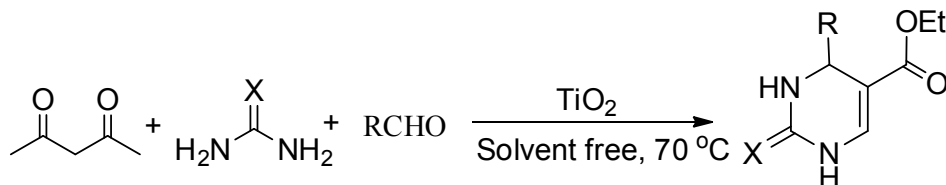
### 2.2.8. Synthesis of substituted 2-oxo dihydropyrroles

Sunil Rana and et al. demonstrated site-selective multicomponent synthesis of substituted 2-oxo dihydropyrroles catalyzed by heterogeneous  $\text{TiO}_2$  nanopowder<sup>34</sup>. The reaction is site-selective with respect to aromatic and aliphatic amines. Environmentally benign reaction procedure, excellent yields, tolerance of varieties of functionalities in the reactants, a wide variety of products and reusability of the catalyst make the methodology highly beneficial for the synthesis of polyfunctional dihydropyrroles.



**Scheme 8:**  $\text{TiO}_2$  nanopowder catalyzed multicomponent synthesis of fully substituted dihydropyrroles

### 2.1.9 Bigilini Reaction



**Scheme 9:**  $\text{TiO}_2$  nanopowder catalyzed Bigilini reaction

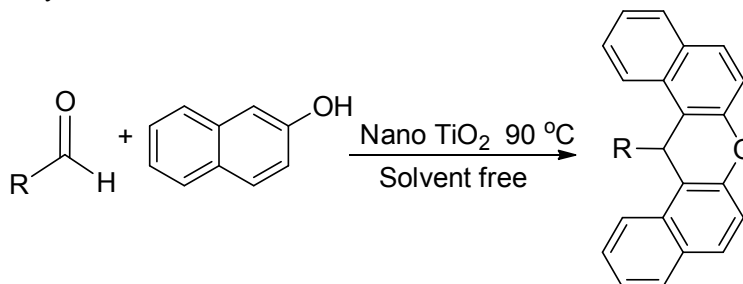
**Table:** Screening of catalysts for the synthesis of multifunctional dihydropyrroles

Entry	Catalyst (10 mol %)	Isolated yield (%)	Time (h)
1	Boric acid + glycerol (1 drop)	60	12
2	$\text{FeCl}_3$	46	12
3	TsOH	58	12
4	AcOH	65	12
5	$\text{SiO}_2$	37	12
6	$\text{Al}_2\text{O}_3$ (acidic)	31	12
7	$\text{H}_3\text{PO}_4\text{-SiO}_2$	66	12
8	$\text{H}_3\text{PW}_{12}\text{O}_{40}$	78	12
9	Commercial $\text{TiO}_2$ (10)	83	12
10	$\text{TiO}_2$ nanopowder (10)	91	12
11	$\text{TiO}_2$ nanopowder (5)	82	12
12	$\text{TiO}_2$ nanopowder (15)	90	12
13	$\text{TiO}_2$ nanopowder (10)	91	3
14	None	Trace	12

Diethyl acetylenedicarboxylate (1 mmol), 3,4-dimethyl aniline (1 mmol), isopropyl amine (1.2 mmol), propionaldehyde (1.1 mmol), and 5 ml DCM were taken in a 25 ml round bottomed flask. The resulting mixture was then refluxed for the mentioned period of time in the presence of various catalysts.

#### 2.1.10. Synthesis of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes

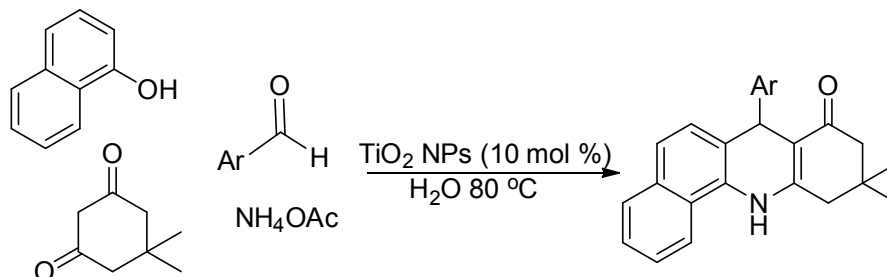
B. F. Mirajalili and *et al.* reported the synthesis of 14-aryl-14H-dibenzo[a,j]xanthene derivatives under heating conditions by reaction between 2-Naphthol and various aldehydes in presence of nano TiO<sub>2</sub>. It was observe the protocol is simple method for the synthesis of 14-aryl or alkyl-14H-dibenzo[a,j] xanthenes using nano-TiO<sub>2</sub> as eco-friendly and efficient catalyst <sup>35</sup>.



**Scheme 10:** Synthesis of 14-aryl or alkyl-14H-dibenzo[a,j]xanthenes

#### 2.2.11 Synthesis of series of tetrahydrobenzo[c]acridinone derivatives

Sharhzad abdolmohammadi *et al.* reported a four component one-pot synthesis of series of tetrahydrobenzo[c]acridinone derivatives in aqueous media using a catalytic amount of titanium dioxide nanoparticles (TiO<sub>2</sub> NPs).(Scheme). The advantages of this novel protocol include the excellent yields, operational simplicity, short reaction time, easy work-up, reusability of the catalyst and an environmentally friendly procedure<sup>36</sup>.

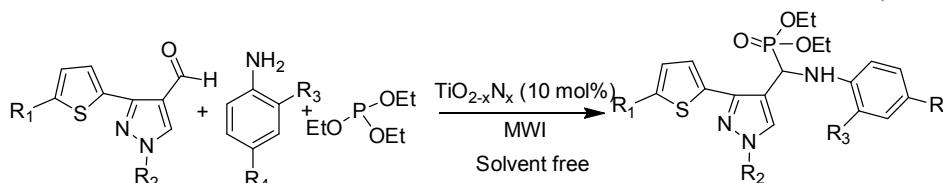


**Scheme 11:** Synthesis of Tetrahydrobenzo[c]acridines

### 2.2 Doped TiO<sub>2</sub> as Heterogeneous Catalyst

#### 2.2.1 Kabachnik-Fields reaction Synthesis of α-aminophosponates

Sachin Kunde *et al.* prepared a series of TiO<sub>2-x</sub>N<sub>x</sub> nanoparticles (NPs) *via* the direct amination method at a relative low temperature <sup>37</sup>. Different proportion of rutile to anatase phases were achieved through simply varying volume ratio of TiCl<sub>4</sub>, methanol, water and triethylamine. They found the prepared TiO<sub>2-x</sub>N<sub>x</sub> (NPs) showed enhanced catalytic activity than commercial available TiO<sub>2</sub> in Kabachnik-Fields reaction under microwave irradiation (**Scheme 11**).



**Scheme 11:** Synthesis of α-aminophosponates

### III. CONCLUSION

In this paper we have reviewed the dependence of catalytic activity in organic transformation with structural modification of TiO<sub>2</sub> nanoparticles. Different modifications of TiO<sub>2</sub> extends the catalyst selectivity and reusability over unmodified TiO<sub>2</sub> nanoparticles. Recent investigations have shown that modified TiO<sub>2</sub> nanostructures utilised as active catalysts or catalyst support in organic transformations including C-C, C-N, C-S, C-O bond formation reactions, multicomponent reactions (MCR), oxidation- reductions.

### ACKNOWLEDGMENT

The authors are grateful Prin. Ganesh Thakur, Mahatma Phule College Panvel, Dist. Raigad for providing research facility. The authors are thankful to parent institute Rayat Shikshan Sanstha, Satara.

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