Sol-gel TiO$_2$ nanostructures single doped with copper and nickel as nanocatalysts for enhanced performance for the Liebeskind–Srogl reaction

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HIGHLIGHTS

• Copper and nickel single-doped TiO$_2$ nanostructures were successfully prepared.
• Structures, elemental compositions and morphologies were characterized.
• The catalytic performance of the Cu-doped and Ni-doped TiO$_2$ nanostructures were evaluated.
• The pyridopyrimidine derivatives was prepared using doped TiO$_2$ nanostructures.

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ABSTRACT

Design of nanostructured catalytic materials plays a strategic role in the synthesis of organic compounds with outstanding physicochemical properties. In this regard, titanium dioxide nanostructures doped with a single metal, namely, nickel and copper, were successfully prepared by a sol-gel method, and their phase structures, elemental compositions and morphologies were extensively characterised. In particular, X-ray diffraction (XRD) diffractograms and Raman spectra mainly revealed a rutile-phase structure for Cu-doped TiO$_2$ and a biphasic anatase–rutile structure for Ni-doped TiO$_2$. In addition, catalytic activities of Cu- and Ni-doped titanium dioxide nanostructures were evaluated for the synthesis of pyridopyrimidine derivatives from sulphur intermediates by the Liebeskind-Srogl reaction under UV illumination. Under the optimized reaction conditions, the target compounds were obtained in a yield of up to 87% by using the Cu-doped TiO$_2$ catalyst and with a slightly lower yield of up to 79% for Ni-doped TiO$_2$ in 12 h. Overall, the catalytic activity of Cu-doped TiO$_2$ was greater than that of Ni-doped TiO$_2$.

1. Introduction

Catalysis is of significance in chemistry as numerous chemical processes involve catalytic reactions. Historically, homogeneous catalysts such as sulphuric acid, potassium hydroxide and metal-complex catalysts are typically used in the synthesis of polymers and medicines, etc. [1]. However, these catalysts are limited by several disadvantages, notably complex separation of the product from the catalyst and the generation of hazardous wastes. In this context, owing to their high activity, non-toxicity, availability and facile reusability, heterogeneous catalysts have emerged as potential candidates that can compete with homogeneous catalysts. In particular, heterogeneous catalysis using semiconductor materials has been widely applied as a promising alternative for the photocatalytic degradation of inorganic and organic pollutants [2]. Among heterogeneous catalysts, TiO$_2$-based materials have attracted substantial interest.

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due to their high activity, stability under UV irradiation and cost-effectiveness [3, 4]. Versatile TiO₂ nanostructures can be prepared by different approaches, including sol-gel, co-precipitation and hydrothermal methods, etc. The properties of the synthesised TiO₂ nanostructures are dependent not only on the synthesis method but also on different processing parameters, such as type of precursor [5, 6], pH [7] and calcination temperature [8], etc.

Moreover, the performance of TiO₂-based nanostructures can be enhanced depending on the desired application via different approaches, including doping with metal and non-metal elements [9, 10] and the formation of composites with various compounds, such as metal oxides [11, 12], graphene [13] and carbon nanotubes [14], etc.

TiO₂-based materials are typically used as environmentally friendly catalysts or catalyst supports in several applications, including the degradation of several pollutants [15, 16], fuel processing [17, 18] and organic synthesis [19, 20].

On the other hand, pyridopyrimidines are recognised as a class of compounds that have attracted increasing interest for biological and chemical applications [21]. Therapeutically, pyridopyrimidines have been reported to exhibit anti-allergic [22, 23], antibacterial [24], insecticidal [25], antiepileptic [26], antihypertensive [27], antihypertensive [28], anticonvulsant [29] and antileishmanial effects [30], as well as antioxidant properties [31] and dihydrofolate reductase or epidermal growth factor receptor inhibitor effects [32–35]. Moreover, some of these scaffolds have been reported to exhibit a strong inhibitory effect against hepatitis C [36].

Furthermore, in organic chemistry, photo-induced synthesis has been reported to exhibit a key role due to its mild reaction conditions and eco-friendly handling [37, 38].

Based on our previous studies on heterocycles and photochemical synthesis [39–47], this study focuses on the evaluation of catalytic activities of Cu- and Ni-doped TiO₂ towards the preparation of pyridopyrimidines (Scheme 1) by the Liebeskind–Srogl method.

2. Experimental

2.1. Reagents and chemicals

Tetrabutyl titanate (TBOT, (C₄H₉O)₄Ti, 98%) was used as the precursor for the sol-gel synthesis of various TiO₂-based samples. Ethanol and hydrochloric acid (HCl, 38%) were used as additives. Copper chloride (CuCl₂) and nickel chloride (NiCl₂) were used to prepare doped TiO₂ samples. All other chemicals were obtained from Aldrich, Fluka, Acros Organics and Shanghai Chemical Reagent Companies. Pre-coated silica gel plates (0.25-mm silica gel, 60G F2540) purchased from Merck (Germany) were used for thin layer chromatography (TLC). UV light was used for the visualisation of TLC plates. Before use, all solvents were distilled under nitrogen.

2.2. Preparation of pure and Cu- and Ni-doped TiO₂ nanostructures

Metal-free and single-metal-doped TiO₂ nanopowders were prepared by a conventional sol-gel strategy as detailed in a previous study with some modifications [48]. Briefly, a mixture of 23 mL of TBOT and 23 mL of ethanol added in each of three beakers was subjected to vigorous agitation for 30 min to obtain a solution referred to as sol. 1. Next, 1 wt% of CuCl₂ and 1 wt% NiCl₂ were separately dissolved in two beakers each containing 23 mL of ethanol, while a third beaker only contained 23 mL of ethanol. Next, 18 mL of a 4.4 M HCl aqueous solution was added to each beaker under vigorous stirring for 15 min to form a solution called sol. 2. The content of each beaker (i.e. sol. 2) was dropwise added to each beaker of sol. 1 under sonication. The obtained mixtures were dried at 40 °C for 4 days. Finally, the collected dry gels were milled and calcined at 600 °C for 2 h.

2.3. Characterisation apparatus

A Rigaku Ultima IV X-ray diffractometer (CuKα radiation source with λ = 1.54056 Å), a SERTENNA II Compact Raman Microscope from Bruker with a laser excitation λ of 532 nm, an Inspex F50 scanning electron microscope (The Netherlands), as well as a Thermo Scientific K-Alpha XPS system (Thermo Fisher Scientific, UK) with an AlKα X-ray source (1486.6 eV), were used for the characterisation of the synthesised TiO₂-based nanopowders.

3. Results and discussion

3.1. Characterisation of metal-free and metal-doped TiO₂ nanostructures

3.1.1. Elemental analysis by XPS

XPS was employed to analyse the element valence states in different TiO₂-based samples. Fig. 1 shows the typical survey spectra. Binding energies were calibrated by using the C1s line at 286 eV as the standard. Ti2p and O1s characteristic peaks of TiO₂ were observed in the survey spectra of different samples.

In addition, the XPS spectrum of Ni–TiO₂ revealed a new peak corresponding to Ni2p, indicating that nickel is effectively incorporated into the TiO₂ nanostructures. Similarly, the XPS survey spectrum of Cu–TiO₂ revealed the presence of a new peak corresponding to the Cu2p doublet, confirming the presence of copper in this sample. To gain additional information about the oxidation states of nickel and copper, high-resolution XPS spectra of Ni2p and Cu 2p were recorded. The Cu2p spectra revealed features typical of the Cu²⁺ state of CuO (Fig. 1b). Specifically, two peaks at 933.15 and 952.58 eV corresponding to the Cu2p₁/₂ and Cu2p₃/₂ spin-orbit splitting components, respectively, in addition to a satellite peak at 941.18, were observed. The Ni2p scan revealed two peaks at 852.68 and 870.38 eV, respectively, separated by 17.7 eV, corresponding to the metallic nickel state Ni⁰, in addition to a satellite peak at 858.93 eV.

3.1.2. Structural examination by XRD

Initially, crystallographic characterisation of as-prepared TiO₂-based samples were examined by XRD. Fig. 2 shows the XRD patterns. In the XRD spectrum of metal-free TiO₂, a set of peaks were observed at 20 values of 27.3°, 36°, 39°, 41°, 44°, 54.3°, 56.5°, 63°, 64°, 68.8° and 69.9°, corresponding to the (110), (101), (200), (111), (120), (211), (220), (130), (002), (311) and (112) planes, respectively (PDF card no: 89-0552). These observed diffractions were consistent with the reported XRD pattern for the pure rutile TiO₂ phase.

Based on the PDF card nos. (89–0552) and (80–1916), in the XRD pattern of Cu–TiO₂, intense peaks were observed at 20 values of 27.4°, 36°, 39.1°, 41.2°, 44°, 54.3°, 56.5°, 62.8°, 63.9° and 68.9°, corresponding to the (110), (101), (200), (111), (120), (211), (220), (130), (002), (311) and (112) planes; this result was in good agreement with the rutile TiO₂ phase structure. On the other hand, weak peaks observed at 20 values of 32.5, 35.5°, 38.7°, 48.6°, 58.3°, 61.46°, 65.7° and 68° corresponded to the (100), (−111), (111), (−202), (202), (−113), (022) and (220) planes, respectively, indicative of the presence of a CuO phase.

On the other hand, according to the PDF card nos. (71–1168) and (89–0552), in the XRD pattern of Ni–TiO₂, peaks were observed at 25.3°,
33°, 38.3° and 48°, corresponding to the anatase phase, in addition to conventional peaks of rutile TiO$_2$. Consequently, unlike that observed in the case of Cu doping, in Ni doping, the anatase crystalline phase of TiO$_2$ supported by the anatase–rutile biphasic structure is partially maintained for Ni–TiO$_2$. This result is possibly related to the substitution of some Ti atoms by Ni in the TiO$_2$ lattice. Ni phases were not identified in this Ni-doped TiO$_2$ sample compared to the Cu-doped sample, suggesting that Ni is uniformly distributed on the TiO$_2$ nanoparticle surface. The anatase to rutile percentage was quantitatively estimated by using the Spurr equation \[ X_A = \frac{100}{1 + 1.256 \left( \frac{I_R}{I_A} \right)} \] where $I_A$ and $I_R$ represent intensities of the fingerprint peaks of the anatase and rutile phases observed at 25.3° and 27.3°, respectively. Accordingly, this ratio was calculated to be 38%. Generally, heterojunction-based photocatalysts, such as anatase–rutile biphasic TiO$_2$, exhibit beneficial features for the enhancement of photocatalytic activity. These systems promote the effective transfer of photoexcited electrons from the conduction band of anatase to that of rutile TiO$_2$, which boosts the separation of electrons and holes. Several studies have demonstrated that the mixture of anatase and rutile TiO$_2$ demonstrates higher photocatalytic efficiency than that of either anatase or rutile TiO$_2$ alone [50–52]. Previously, a synergistic photocatalytic effect towards the degradation of methylene blue has been reported for an anatase-to-rutile ratio between 40% and 80% [53]. Later, calcined Degussa P25 TiO$_2$ at different temperatures has been investigated by XRD, and the anatase-to-rutile fraction has been reported to exhibit temperature dependence. Notably, by the calcination of the sample at 700 °C for 2 h, it contains 26% anatase to 74% rutile and exhibits the highest photodegradation ability for malachite green [54].

In addition to XRD spectra, Raman spectra were recorded to gain additional information about the structural phase of TiO$_2$-based samples. Fig. 3 shows the corresponding Raman spectra. In the Raman spectra of pure TiO$_2$ and Cu–TiO$_2$, three main Raman active bands were observed at 232, 447 and 609 cm$^{-1}$, corresponding to the multiphoton process and $E_g$ and $A_{1g}$ modes of rutile TiO$_2$, respectively [55,56]. Indeed, the two samples exhibited a Raman peak pattern similar to that reported for rutile TiO$_2$, which was consistent with the above-mentioned XRD observations. Furthermore, Raman bands corresponding to copper oxide structures were not identified in the Raman spectrum of Cu-doped TiO$_2$. In the Raman spectrum of Ni-doped TiO$_2$, four bands were observed at 144, 395, 516 and 640 cm$^{-1}$, corresponding to the anatase phase [55,57,58]. In addition, an additional band was observed at 445 cm$^{-1}$, corresponding to the rutile phase of TiO$_2$. Consequently, Ni-doped TiO$_2$ comprises anatase and rutile phases. Overall, doping with Ni apparently hindered the transformation from the anatase phase to the

![Fig. 1.](image1.png) XPS survey spectra of metal-free TiO$_2$ as well as Cu- and Ni-doped TiO$_2$ (a), high-resolution scans of (b) Cu2p and Ni2p (c) peaks.

![Fig. 2.](image2.png) XRD patterns of metal-free TiO$_2$ and Cu- and Ni-doped TiO$_2$.

![Fig. 3.](image3.png) Raman spectrum of metal-free TiO$_2$ and Cu- and Ni-doped TiO$_2$. 

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rutile phase, and Ni phases were absent, indicating that metallic nickel is well dispersed on the TiO$_2$ nanoparticle surfaces. In contrast, doping with Cu apparently promoted the rutile TiO$_2$ phase, in addition to the development of a CuO phase, which was consistent with XPS analysis.

3.1.3. Morphological analysis by SEM

Scanning electron microscopy (SEM) was employed to examine the morphology of metal-free and metal-doped prepared samples. In the SEM image of the metal-free TiO$_2$ sample, capsule-like nanostructures exhibited a porous feature (Fig. 4a). Unlike pure TiO$_2$, Cu–TiO$_2$ (Fig. 4b) comprised roughly spherical nanoparticle aggregates with sizes ranging from 20 nm to 80 nm, reflective of the composite nature of the sample formed by CuO and TiO$_2$ nanoparticles as revealed by XRD. The morphology of Cu–TiO$_2$ was markedly different from that of naked TiO$_2$, which can be explained by the growth of CuO nanoparticles on the TiO$_2$ nanoparticle surface. On the other hand, Ni-doped TiO$_2$ (Fig. 4c) was characterised by the presence of spherical and capsule-like nanostructures, possibly corresponding to the presence of the anatase–rutile biphasic structure as revealed by XRD and Raman analyses.

3.2. Catalytic activity

Basically, pyrido[2,3-d]pyrimidine-4(1H)-thione (2) was prepared from pyrido[2,3-d]pyrimidine-4(1H)-one and Lawesson’s reagent in dioxane under reflux for 1–2 h (Scheme 2) [59].

3.2.1. General reaction procedure

First, a mixture of heterocycle 2 (1.0 eq.), boronic acids (2.2 eq.), a nanocatalyst (5% eq) and copper(I) thiophene-2-carboxylate CuTC (2.2 eq.) in 3 mL of dimethoxyethane (DME) was reacted in a 10-mL reaction vial under UV irradiation. A UV lamp, with a wavelength centred at 300 nm (Philips, TUV 8 W/G5 T5, 0.15 A, 16 mm diameter, The Netherlands), was used as the light source. Reaction follow-up was performed by TLC (100% DCM). Then, the mixture was evaporated, and the purification of the final heterocycle 4 was achieved by chromatography (100% DCM).

3.2.2. Reaction optimisation

Initially, when heterocycle 2 was reacted with phenylboronic acid under an inert atmosphere, in the absence of a catalyst, co-catalyst and light source, a reaction was not observed (Table 1, entry 1). Next, in the presence of versatile catalysts and co-catalysts without the light source, the reaction started, but a product was not obtained (Table 1, entries 2–4). Next, in the presence of a light source (wavelength of 300 nm), the reaction was investigated using different solvents and catalysts at room temperature. In the absence of a co-catalyst, the desired product was not obtained even in the presence of catalysts and under $hv$ light (Table 1, entries 5–7). However, when the reaction was conducted using Cu–TiO$_2$ as the catalyst, CuTC as the co-catalyst and DME as the solvent, the target product was obtained in 84% yield (Table 1, entry 9). Similarly, when Ni–TiO$_2$ was used as the nanocatalyst, the heterocycle was obtained in 75% yield (Table 1, entry 10). Furthermore, by using Pd(PPh$_3$)$_4$ as the homogenous catalyst, heterocycle 4d was obtained in 83% yield (Table 1, entry 8).

Besides, the screening of solvents indicated that the reaction is more productive in DME, with the highest product yield (84%) (Table 1, entries 11–14). This difference might be due to the polarity difference between the used solvents.

Based on the results listed in Table 1, the reaction was investigated using versatile boronic acids. Then, compound 2 was reacted with an equimolar amount of boronic acid with the nanocatalyst (5 mol%) in the presence of CuTC and DME (Table 2).

Boronic acids with electron-donating substituents on the aryl group supported the formation of product 3 from heterocycle 2 in good yields. In contrast, halogen groups such as nitrile, trifluoromethyl and fluoro hindered the production of the heterocycle. Moreover, by using...


**Table 1**

Optimisation of the reaction conditions for the construction of the heterocycle.\(^a\)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Co-catalyst</th>
<th>hv</th>
<th>Solvent</th>
<th>Yields(^b) (Time)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>DME</td>
<td>0 (12 h)</td>
</tr>
<tr>
<td>2</td>
<td>Pd(PPh(_3))(_4)</td>
<td>CuTC</td>
<td>–</td>
<td>DME</td>
<td>0 (12 h)</td>
</tr>
<tr>
<td>3</td>
<td>Cu/TiO(_2)</td>
<td>CuTC</td>
<td>–</td>
<td>DME</td>
<td>0 (24 h)</td>
</tr>
<tr>
<td>4</td>
<td>Ni/TiO(_2)</td>
<td>CuTC</td>
<td>–</td>
<td>DME</td>
<td>0 (24 h)</td>
</tr>
<tr>
<td>5</td>
<td>Pd(PPh(_3))(_4)</td>
<td>–</td>
<td>300 nm</td>
<td>DME</td>
<td>0 (12 h)</td>
</tr>
<tr>
<td>6</td>
<td>Cu/TiO(_2)</td>
<td>–</td>
<td>300 nm</td>
<td>DME</td>
<td>0 (24 h)</td>
</tr>
<tr>
<td>7</td>
<td>Ni/TiO(_2)</td>
<td>–</td>
<td>300 nm</td>
<td>DME</td>
<td>0 (24 h)</td>
</tr>
<tr>
<td>8</td>
<td>Pd(PPh(_3))(_4)</td>
<td>CuTC</td>
<td>300 nm</td>
<td>DME</td>
<td>83% (12 h)</td>
</tr>
<tr>
<td>9</td>
<td>Cu/TiO(_2)</td>
<td>CuTC</td>
<td>300 nm</td>
<td>DME</td>
<td>84% (12 h)</td>
</tr>
<tr>
<td>10</td>
<td>Ni/TiO(_2)</td>
<td>CuTC</td>
<td>300 nm</td>
<td>DME</td>
<td>75% (12 h)</td>
</tr>
<tr>
<td>11</td>
<td>Cu/TiO(_2)</td>
<td>CuTC</td>
<td>300 nm</td>
<td>DMF</td>
<td>22% (12 h)</td>
</tr>
<tr>
<td>12</td>
<td>Cu/TiO(_2)</td>
<td>CuTC</td>
<td>300 nm</td>
<td>DMF</td>
<td>37% (12 h)</td>
</tr>
<tr>
<td>13</td>
<td>Cu/TiO(_2)</td>
<td>CuTC</td>
<td>300 nm</td>
<td>Acetone</td>
<td>05% (12 h)</td>
</tr>
<tr>
<td>14</td>
<td>Cu/TiO(_2)</td>
<td>CuTC</td>
<td>300 nm</td>
<td>THF</td>
<td>32% (12 h)</td>
</tr>
</tbody>
</table>

\(^a\) Yield of the obtained product. Reaction conditions: ArB(OH)\(_2\) (2.2 eq), nanocatalyst (5 mol%), DME (3 mL), co-catalyst (2.2 eq.), hv.

\(^b\) Isolated yields.

furanyloboronic or thienylboronic acid as the reactants, only minor product yields were obtained. Remarkably, compared to Cu\(_2\)TiO\(_3\), Ni-TiO\(_2\) exhibited lower reaction yields, which were possibly attributed to the fact that nickel metal is well dispersed on the TiO\(_2\) surface, as mentioned above, and forms nickel titanate at the sintering temperatures used, which decreases the photocatalytic activity.

**3.2.3. Proposed reaction mechanism**

Based on the performed optimisation experiments, the schematic of the proposed reaction mechanism is shown in Fig. 5. Basically, under UV illumination, electrons jump from the valence band of TiO\(_2\) (band gaps for anatase and rutile of 3.02 and 3.2 eV, respectively) to its conduction band, forming an electron–hole pair. Unfortunately, this pair recombines extremely rapidly within the TiO\(_2\) semiconductor; thus, photoexcited electrons do not participate in the catalytic reaction. Alternatively, besides its potential to lower the band gap, doping is also a useful solution to overcome the issue of electron recombination, either by the trapping of the excited electron when pure metal is loaded on the TiO\(_2\) nanoparticle surface or by forming a heterojunction if metal oxides are developed on the TiO\(_2\) structures, thereby promoting the electron–hole separation and slowing recombination; consequently, interfacial charge transfer is improved. Herein, notably, without the CuTC co-catalyst, the reaction was not completed even when the metal-doped TiO\(_2\) catalyst was used under UV irradiation. This result suggested that, in the first step, CuTC interacted with reactant 2, and the formed complex captured a photogenerated electron. Simultaneously, the generated holes activated the C–B bond of phenylboronic acid, which was transformed to B(OH)\(_2\) by attracting an OH\(^-\) from the basic reaction medium. Finally, when the oxidised arylboronic acids were transferred to the activated reactant 2, the cross-coupling reaction provided the final products by transmetalation and reductive elimination. Currently, additional profound investigations into the reaction mechanism are underway by our group.

**4. Conclusion**

In this study, an efficient and a simple sequential nano-strategy for the synthesis of the pyridopyrimidine heterocycles from boronic acids by the Liebeskind–Srogl coupling using TiO\(_2\) nanocatalysts doped with single metals of Cu and Ni was investigated. In addition, the physico-chemical properties of the prepared doped nanocatalysts were extensively investigated. Ni doping apparently hindered the structural transformation of the TiO\(_2\) phase, and a biphasic anatase–rutile structure was developed, while Cu doping promoted the transformation from the anatase to the rutile phase. Overall, both catalysts exhibited comparable performance; nevertheless, Cu-doped TiO\(_2\) was found to be more effective than Ni-doped TiO\(_2\).

**CRediT authorship contribution statement**

Yassine Riadi: Conception and design of study, acquisition of data, analysis and/or interpretation of data, Writing – original draft, revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published. Mohammed H. Geesi: Acquisition of data, analysis and/or interpretation of data, Writing – original draft, revising the manuscript critically for important intellectual content. Oussama Ouerghi: Acquisition of data, analysis and/or interpretation of data, Writing – original draft, revising the manuscript critically for important intellectual content, Approval of the version of the manuscript to be published.
manuscript to be published. Rachid Azzallou: Writing – original draft, Approval of the version of the manuscript to be published. Oussama Debbi: Writing – original draft, Approval of the version of the manuscript to be published. Saïd Lazar: Writing – original draft, Approval of the version of the manuscript to be published.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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References


