Fabrication and visible light photocatalytic activity of a novel $Ag/TiO_{2-x}N_x$ nanocatalyst†

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A facile and simple synthesis of a conceptually novel $Ag/TiO_{2-x}N_x$ under mild experimental conditions produced a remarkably efficient, stable and recyclable nanophotocatalyst that is functional under visible light.

The scientific community have directed efforts towards the preparation of photocatalysts that are active under solar or artificial visible light irradiation. TiO_2 is one of the most widely used photocatalysts, and it is employed in self-cleaning coatings, photocatalytic processes and environmental remediation processes, especially in the degradation of biorecalcitrant organic contaminants[1,2] due to its good photoactivity, high chemical stability, low cost and non-toxicity.[3] TiO_2 exhibits a high reactivity and chemical stability under ultraviolet (UV) irradiation at a wavelength of 387 nm, whose energy exceeds the band gaps of 3.0 and 3.2 eV for its rutile and anatase crystalline phases, respectively.[1,4] Unfortunately, due to the size of its band gap, TiO_2 is active only under UV irradiation, which comprises less than 5% of solar light energy.[5] Thus, the fabrication of TiO_2 photocatalysts that yield high stability and reactivity under artificial visible and solar light (wavelength > 380 nm) would allow utilization of the solar spectrum and provide photocatalysts that are active during daylight and/or even in ambient illuminated indoor areas.

It is anticipated that noble metals and non-metal species deposited on TiO_2 would show different effects on the photocatalytic activity of TiO_2 under solar and artificial visible light irradiation.[6] According to Sung-Suh and co-authors,[7] there are several mechanisms responsible for such effects: (i) dopants enhance the electron–hole separation by acting as electron traps, (ii) they extend the light absorption into the visible range and (iii) for example, noble metals modify the surface properties of the photocatalyst. Metal dopants affect surface properties by generating a Schottky barrier in the metal in contact with the TiO_2 surface that acts as an electron trap and inhibits e^-–h^+ recombination.[8] Ag is a noble metal that is suitable for numerous industrial applications.[9] It has been reported that silver deposited onto TiO_2 significantly shortens the illumination period and increases the efficiency of the catalyst.[10] Alternatively, *N*-doping is very effective in decreasing the band gap of TiO_2 through mixing of the N 2p and O 2p states, and due to the electronic transitions from the dopant 2p or 3p orbitals to the Ti 3d orbitals.[11] Such doping is also attractive because of the comparable atomic size of nitrogen and oxygen, the small ionization energy, metastable center formation and their remarkable stability.[4] Moreover, TiO_2 doping with non-metals, in conjunction with the use of metal atoms, may exhibit more beneficial effects when compared with a single non-metallic or metallic dopant.

There is a lack of studies utilizing 'green' nanoscience principles to facilitate the metal and non-metal doping of TiO_2 catalysts.[12] Therefore, we present here a one-pot facile synthesis of TiO_2 nanoparticles doped with guanidine nitrate and deposited with silver nitrate to increase their photocatalytic activity in the visible light range.

Fig. 1 a, b and c show SEM, EDS and TEM micrographs of nano $Ag/TiO_{2-x}N_x$, respectively, that allows the location and distribution of the dopants on the TiO_2 to be identified. SEM shows the distribution of the dopants on or inside the TiO_2 lattice (Fig. 1a). The EDS pattern of the $Ag/TiO_{2-x}N_x$ particles can be seen in Fig. 1b. There are eight X-ray peaks associated with O Kα, Mg Kα, Al Kα, Au Kα, Cl Kα, Pd Kα, Ag Kα and Ti Kα; however, the lines for Mg Kα, Al Kα, Au Kα, Cl Kα, Pd Kα are either constituents of the TEM grid used for the analysis, precursors of the synthesis or impurities. Therefore, the results indicate that O, Ag and Ti correspond to the nanoparticles prepared by the aforementioned protocol.

It is evident that the silver and TiO_2 particles are nearly spherical. The density of the silver particles is higher than for the TiO_2;[14] therefore, the TEM image of the silver particles is much darker in comparison with the TiO_2 particles (Fig. 1c).

The average crystallite sizes could be determined from the semi-empirical Sherrer equation ($d = K\lambda/\beta \cos\theta$), taking into account the half-width of the major diffraction peaks, where λ is the X-ray wavelength (0.154 nm), β is the full-width at half-maximum in radians and θ is the Bragg angle in degrees.[15] The mean crystallite size of the samples derived from Sherrer's equation was 29.3 nm for the TiO_2 phase and 28.4 nm for the Ag phase (Fig. 1d). The formed metallic silver particles had strong peaks at 38° (111), 44.6° (200) and 65.7° (220), indicating that Ag was attached to the TiO_2.[14,16] $Ag/TiO_{2-x}N_x$ exhibited strong TiO_2 peaks at 25, 37.8 and 48°. Only traces of the rutile phase were detected in the Degussa P25 sample.

The diffraction peak at 28.3° may be attributed to the deposited Ag particles.[14]

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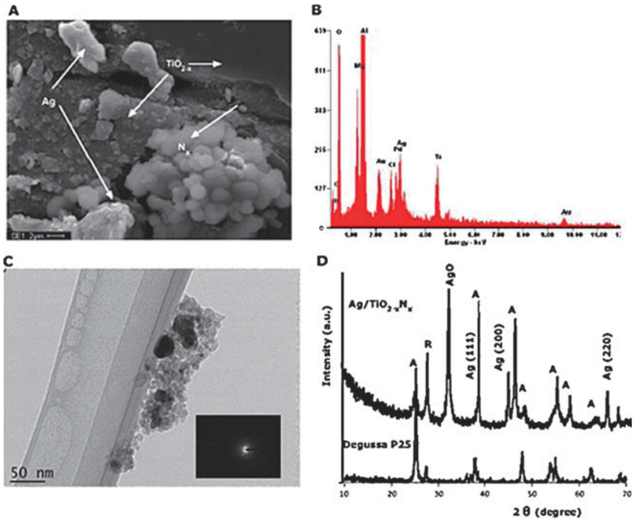

Fig. 1 Characterization of the Ag/$TiO_{2-x}N_x$ catalyst: (A) SEM micrograph, (B) EDS pattern of the Ag/$TiO_{2-x}N_x$ particles, (C) TEM image of the nanoparticles and (D) XRD pattern of the freshly prepared catalyst in comparison to commercially available Degussa P25 (A—anatase, R—rutile).

Fig. 2 depicts the visible light-induced photocatalytic mechanism for nano Ag/$TiO_{2-x}N_x$; the proposed reaction pathway of methyl orange (MO) may be as follows:

(1) Silver ions undergo transformation on the TiO_2 surface at a 450 °C calcination temperature:[16]

$$AgNO_3 \rightarrow Ag_2O \rightarrow Ag \qquad (1)$$

(2) The presence of silver particles and nitrogen helps to efficiently split the electron–hole pairs by attracting the conduction band photoelectrons (Fig. 2). Moreover, the valence band photogenerated holes are able to react with OH^- adsorbed onto the TiO_2 to create hydroxyl radicals ($^\bullet OH$):

$$TiO_2\ (h^+) + H_2O \rightarrow (OH^-) \rightarrow TiO_2 + H^+ + {}^\bullet OH \qquad (2)$$

(3) Furthermore, the conduction band electrons can react with electron acceptors (*e.g.* O_2) producing dioxygen radicals ($^\bullet O_2^-$):[17]

$$TiO_2\ (e^-) + O_2 \rightarrow TiO_2 + {}^\bullet O_2^- \qquad (3)$$

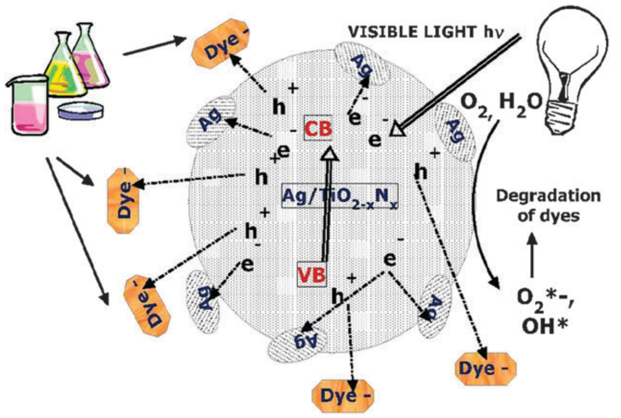

Fig. 2 Proposed visible light-induced photocatalytic mechanism for nano Ag/$TiO_{2-x}N_x$.

(4) In addition, the electron migrates to the surface of the TiO_2 catalyst, where it participates in the reduction of MO (anionic basic form MO^-) in the presence of powerful oxidizing agents:

$$MO^- + 2H^+\ (aq.) + 2e^-\ (TiO_2) \rightarrow ({}^\bullet OH, {}^\bullet O_2^-) \rightarrow H_2MO^- \rightarrow (intermediate) \rightarrow CO_2 + H_2O \qquad (4)$$

Fig. 3 shows the ratio between the concentration of MO (*C*) at a certain time (*t*) and the initial concentration (C_o) over Ag/$TiO_{2-x}N_x$ and $TiO_{2-x}N_x$ catalysts in the presence of the visible light. The reactions were pseudo zeroth order with reaction rates of 0.01×10^{-3} and 3.5×10^{-3} M min^{-1} for the Ag/$TiO_{2-x}N_x$ and $TiO_{2-x}N_x$ catalysts, respectively. Initial tests showed that adsorption onto the Ag/$TiO_{2-x}N_x$ and $TiO_{2-x}N_x$ surfaces was negligible and comprised only 15–20%. The catalyst was calcined at 450 °C and when doped with 5 mol% Ag showed excellent photoactivity; MO was completely degraded in 90 min. In comparison, MO disappeared in 180 min in the presence of the as-prepared $TiO_{2-x}N_x$ catalyst. Also, it has been reported that, unfortunately, much lower initial MO concentrations can be degraded in 160 to 240 min in the presence of Ag/TiO_2 films[18] and Ag/TiO_2 powder catalysts.[19] In addition, the increased photocatalytic activity of Ag/$TiO_{2-x}N_x$ may also be also attributed to the formation of active inorganic radical anions, such as NO_3^-, from the guanidine nitrate.[10]

Moreover, Ag/$TiO_{2-x}N_x$ exhibited an outstanding stability and reusability without any significant loss in catalytic activity (reaction rate constants were 5–15% lower than that of the original catalyst) after five consecutive experimental rounds. However, after a simple regeneration procedure, the catalyst showed a similar photocatalytic activity (reaction rate constants in average 3–5% lower) in comparison to the original Ag/$TiO_{2-x}N_x$.

In conclusion, the simple and facile synthesis of nano Ag/$TiO_{2-x}N_x$ has been demonstrated by utilizing simple precursors to generate an active, stable and reusable photocatalyst that is active in the visible light range. Furthermore, Ag-doped TiO_2 composite materials are known to exhibit a bactericidal activity.[20] Therefore, such attributes of the catalyst may simultaneously be further extended to antimicrobial

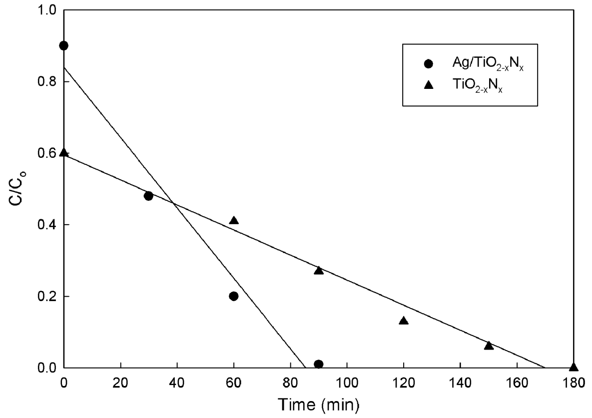

Fig. 3 The ratio between the concentration of MO (*C*) at a certain time (*t*) and the initial concentration (C_o) over Ag/$TiO_{2-x}N_x$ and $TiO_{2-x}N_x$ catalysts in the presence of visible light.

and chemical contamination. In a typical heterogeneous photocatalysis process, surface modification with silver particles and nitrogen significantly alters the surface characteristics, which results in a change in the area exposed to light. Significantly, future applications of these catalysts is anticipated in view of the fact that (i) the catalyst was not poisoned by the various impurities, such as reaction intermediates, and was active in five consecutive runs without any significant loss in activity, and (ii) thermogravimetric analysis showed an excellent thermal stability (see ESI, Fig. S1†).

Additional studies are under way to further optimize the reaction and synthesis conditions, which may subsequently enhance the photocatalytic and antibactericidal activity of novel nano Ag/$TiO_{2-x}N_x$ catalysts.

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Experimental

Photoactive nano TiO_2 powders were prepared at room temperature by a simple sol–gel procedure: (i) Ag/$TiO_{2-x}N_x$ was prepared by dispersing 20 g of a Ti^{4+} salt (digested to 50% in HCl) in 1000 mL of water. Next, 20 g of guanidine nitrate and 5 mol% of $AgNO_3$ were added to the solution, and the vessel's contents magnetically stirred for 30 min. An ammonium hydroxide (NH_4OH, 33 wt%) solution was then added to bring the solution pH to 9 and the reaction mixture stirred at room temperature for 24 h. The product was then dried at 60 °C overnight, powdered, calcined at 450 °C for 2 h and characterized by means of X-ray diffraction (XRD), TEM and SEM-EDS. As synthesized Ag/$TiO_{2-x}N_x$ was coloured yellow, suggesting its ability to absorb light in the visible region.[13] For comparison, $TiO_{2-x}N_x$ was prepared in the same manner without the addition of $AgNO_3$.

XRD patterns were determined by X-ray diffraction using an X'Pert Pro MPD X-ray diffractometer and a Cu-Kα source with a diffraction angle range of $2\theta = 10$ to 70°. The data was collected in steps of 1 ° min^{-1} and a typical angle of 0.5°. SEM observations were performed using an FEI XL30 ESEM operating at 15–20 kV on gold-sputtered samples. TEM micrographs were recorded on an FEI CM20 TEM microscope at an operating voltage of 200 kV.

The photocatalytic activity of nano Ag/$TiO_{2-x}N_x$ was evaluated by the degradation of methyl orange (MO), a relatively toxic, complex and non-biodegradable compound that is classified as a micropollutant and is widely used in the textile industry. Moreover, its activity was compared to $TiO_{2-x}N_x$ fabricated according to the same protocol and Ag/TiO_2 from literature sources. For the photocatalytic experiments, unless specified otherwise, 20 mL (100 ppm) of an MO aqueous solution was placed in a 25 mL glass reactor equipped with a magnetic stirrer. 3 g L^{-1} of the freshly prepared catalyst was dispersed into the solution. The mixture was inserted into a water circulating jacket to cut the infrared radiation and continuously fluxed with O_2. The reaction mixture was stirred magnetically in the dark for 30 min to ensure an adsorption/desorption equilibrium between the contaminant and the catalyst. The photoreactor was irradiated using a 300 W medium pressure metal halogen lamp. MO degradation was monitored by collecting aliquots at regular time intervals (30 min and 1 h, unless indicated otherwise). The aliquots were centrifuged and absorption spectra recorded using a Hewlett Packard 845X UV-vis instrument at a maximum peak of 464 nm.

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