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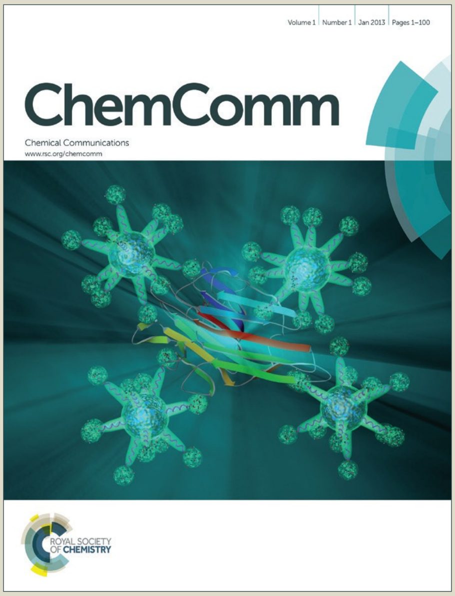

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In-situ Production of Visible Light Absorbing Ti-based Nanoparticles in Solution and in a Photopolymerizable Cationic Matrix

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A novel straightforward approach is proposed to generate *in situ*, under light activation and in aerated media, visible-light absorbing and well-defined titanium-based nanoparticles (NPs) in solution and in an epoxide matrix using titanium derivatives complexes/iodonium salt photoinitiating systems. The nature of the solvent and oxygen play a decisive role, and two mechanisms involved in these syntheses are operative, i.e photofragmentation/addition process (in toluene and isopropanol) and a photoinduced sol-gel reaction (in isopropanol).

The generation of metal nanoparticles NPs (e.g. Ag, Au…) in solution using the reduction of a metallic salt upon a photochemical activation (conventional light sources or laser) has been largely explored (see e.g. [1-7] and references therein). The same holds true in film (but to a lesser extent) as the small size NPs containing matrices possess unique properties; indeed, the simultaneous *in-situ* incorporation of NPs in a photopolymerizable medium extends the range of available polymer materials and could lead to a better control of the NPs[8]. The *in-situ* incorporation of NPs has been achieved in acrylate monomer/oligomer matrices (see e.g. ref[9-15] and references therein). In such media, the photoinitiation step and the NPs formation involves a photoinitiator PI (ra) or a PI/amine AH system that produces two radicals by a homolytic cleavage (rb) or an electron/proton transfer (rc): one is used to initiate the polymerization (rd), the other to reduce a metal salt (re, rf), this last reaction generating a cationic species (re, rf); Ag, Pd, Au NPs have been thus produced. The concomitant *in-situ* incorporation of Ag NPs[8, 16-19], Au NPs[20], and Cu NPs[21] in a photocurable epoxide matrix was also reported. The cationic species formed in such PIs (re, rf) are used to initiate a cationic ring opening polymerization. In solution [1-6], radical sources such as the PIs referred above also lead to the NPs generation.

$\mathrm{PI} \rightarrow {}^1\mathrm{PI}\ (h\nu)$ and ${}^1\mathrm{PI} \rightarrow {}^3\mathrm{PI}$ **(ra)**

${}^3\mathrm{PI} \rightarrow \mathrm{R}^\bullet + \mathrm{R'}^\bullet$ **(rb)**

or ${}^3\mathrm{PI} + \mathrm{AH} \rightarrow \mathrm{PIH}^\bullet + \mathrm{A}^\bullet$ **(rc)**

$\mathrm{R}^\bullet$ (or $\mathrm{A}^\bullet$) + acrylate monomer $\rightarrow$ polymer **(rd)**

$\mathrm{R'}^\bullet + \mathrm{Ag}^+ \rightarrow \mathrm{R'}^+ + \mathrm{Ag}^0$ **(re)**

$\mathrm{PIH}^\bullet + \mathrm{Ag}^+ \rightarrow \mathrm{PI} + \mathrm{H}^+ + \mathrm{Ag}^0$ **(rf)**

H^+ (or $\mathrm{R'}^+$) + epoxide monomer $\rightarrow$ polymer **(rg)**

Recently, a novel strategy involving a bimolecular homolytic substitution reaction (S_H2 process) that converts the peroxyl radicals (inherently present in an aerated medium) into new initiating species using appropriate compounds opened the way to the photochemical *in-situ* incorporation of Zr[22], Ti[23] NPs (starting from e.g. Cp_2ZrCl_2 or Cp_2TiCl_2 in the presence of a UV cleavable photoinitiator and using reactions rh-rj) and Zn fillers[24] in very thin acrylate films in contact with air. This was likely the first photochemical production of Ti-based NPs along with a radical photopolymerization. As known, such NPs[25] are usually thermally produced or elaborated by ion implantation[26], sputtering[27], hydrolyzation of titanium alkoxides by sol-gel method[28], direct hydrolysis of organic or inorganic salt under hydrothermal[29, 30] or solvothermal[31, 32] conditions, for being used in solar energy conversion, as antibacterial agents, environmental remediation, sensing, cosmetics, cleaning air products, industrial photocatalytic processes.

radicals $+ \mathrm{O}_2 \rightarrow$ peroxyls **(rh)**

peroxyl $+ \mathrm{Cp_2TiCl_2} \rightarrow \mathrm{ROOTiCpCl_2} + \mathrm{Cp}\bullet$ **(ri)**

peroxyl $+ \mathrm{ROOTiCpCl_2} \rightarrow\rightarrow\rightarrow$ Ti based NP $(h\nu)$ **(rj)**

Herein, we propose another original strategy for the synthesis of visible-light absorbing Ti-based NPs in solution and in a cationic monomer film that have never been investigated yet: in this latter case, the Ti-based NPs are *in-situ* generated during the cationic polymerization of a diepoxide film that opens the way for developing new polymeric hybrid materials used for organic degradation or catalysis. The strategy lies on the UV light irradiation of titanium isopropoxide (TiOx1)/4-methylphenyl)[4-(2-methylpropyl) phenyl]- hexafluorophosphate (Iod) couples under air in a solvent or in a cationic monomer film (results concerned with a titanium propoxide (TiOx2)/Iod parent system are gathered in the Supporting Information). The role of the kind of solvent, the polymerization profiles, the characterization of the NPs and the involved mechanisms are provided using steady state photolysis, Electron Spin Resonance Spin Trapping ESR-ST and Transmission Electron Microscopy (TEM) experiments and DFT Calculations.

First, titanium-based NPs have been formed from TiOx1/Iod in organic solvents upon irradiation with a Xe-Hg lamp ($250 < \lambda < 800$nm) under air. The solution which is initially colorless becomes red. TEM experiments (Figures 1A and 1B) illustrate the well-defined spherical shape, as well as the nanoscopic size of these NPs (diameters ranging from 5 to 70 nm, mean = 19 nm, SD = 17nm) formed in dry toluene (the irradiation of TiOx1 or TiOx2 alone, as shown in Figure S1 in Supporting Information, does not generate any NPs). Figures 1C and 1D show the EDX spectra acquired in STEM by focusing the electron beam on a single Ti based NP deposited on the supporting membrane of the microscopy grid, respectively. The Ti Kα (~ 4.5 keV), O Kα (~ 0.5 keV) and C Kα (~ 0.25 keV) peaks are significantly increased (Figure 1D). Interestingly, these results reveal the presence of carbon and oxygen atoms into the titanium based NPs. The same holds true with TiOx2/Iod as shown in Figure S2 (Supporting Information).

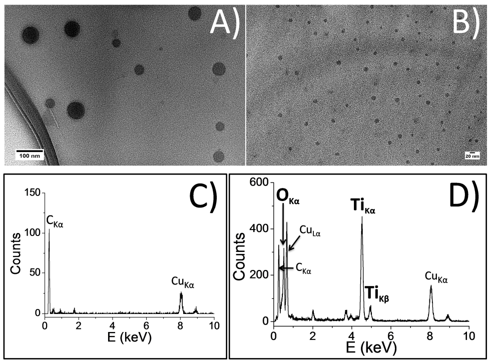

Figure 1. A and B) TEM images of the photoinduced titanium-based nanoparticles obtained from the photolysis of TiOx1/Iod in toluene**.** EDX spectra acquired in STEM on C) the supporting membrane and D) on a single titanium-based nanoparticle. Xe-Hg lamp exposure (polychromatic light). 360s of irradiation. Under air. [TiOx1] = 2.7×10^{-2} M, [Iod]=2.5×10^{-2} M. Note that the Cu and Si signals at ~ 2 keV are artefacts originating from the copper microscopy grid and the silicon X-ray detector.

In a polar and hydroxylic medium (propan-2-ol), the morphologies of the resulting Ti-based NPs differ from those obtained in a non-polar solvent (toluene). TEM images in Figures 2A and 2B, using TiOx1/Iod in aerated propan-2-ol (or TiOx2/Iod in Figures S3-A and S3-B, Supporting Information), display the presence of hybrid Ti networks in addition to the Ti-based NPs (which diameters are ranging from 5 nm to 22 nm, mean = 10 nm and SD = 4 nm). Interestingly, the composition of the resulting Ti-based NPs in propan-2-ol appears as similar as what observed in toluene, i.e. an increase of the carbon atoms in the Ti-based structure is noted (Figure 2C).

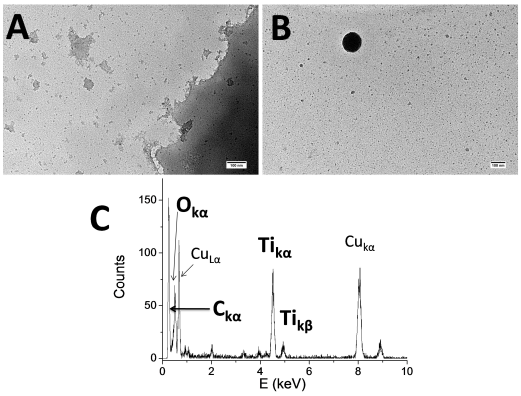

Figure 2. TEM images of hybrid Ti networks (A) in addition to the Ti-based NPs (B) obtained from the photolysis of TiOx1/Iod in propan-2-ol. C) EDX spectra acquired in STEM on a single titanium-based nanoparticle. Xe-Hg lamp exposure. 360s of irradiation. Under air. [TiOx1] = 3.2×10^{-2} M, [Iod] = 3×10^{-2}M.

Second, Iod, TiOx1/Iod and TiOx2/Iod systems have been incorporated into a cationic diepoxide (EPOX) formulation. Upon exposure to the Xe-Hg lamp, the polymerization reaction readily occurs under air (Figure 3A) and almost similar final monomer conversions are reached (evaluated at ~30% after 400s of irradiation, Figure 3A, curves 2 and 3). In the polymer material, well-defined Ti-based NPs are *in-situ* simultaneously formed (Figures 3B and 3C; using TiOx1/Iod). Note that the TiOx1/Iod and TiOx2/Iod couples can also initiate the free radical polymerization of an acrylate (TMPTA) thin film (4 µm thick) under air (Figure S4, curves 2 and 3, Supporting Information). The final color suggests that NPs are formed but this is out of the scope of the present paper.

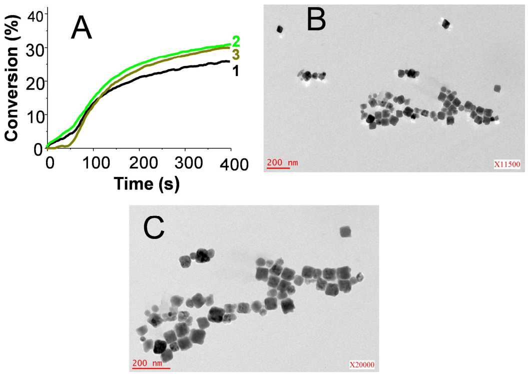

Figure 3. A) Photopolymerization profiles of EPOX. Photoinitiating systems: Iod (3wt%) (1), TiOx1 (1wt%)/Iod (3wt%) (2) TiOx2 (1wt%)/Iod (3wt%) (3). B) and C) TEM images of the photoinduced Ti-based NPs obtained in the final polyether film (using TiOx1 (1wt%)/Iod (3wt%). Xe-Hg lamp exposure (polychromatic light at λ > 300nm). Under air. Thickness of the film = 25 µm.

To better understand the mechanism in the NPs formation, steady state photolysis and ESR ST investigations are done. Photolysis experiments on TiOx1/Iod/spin trap (PBN) in aerated dry toluene lead to a yellowish solution (Figure 4C) whereas, in the absence of PBN, a red colour solution is obtained (Figure 4A), thus revealing the presence of a new absorption band (Nabs) in the 425-600 nm wavelength range after 360s of irradiation. On the opposite, under argon, no significant absorption in the visible range is noted (Figure 4B-2 vs Figure 4B-3). The irradiation of Iod/PBN in oxygen saturated toluene also leads to a yellowing of the solution (Figure 4D) but without Nabs. These results support the occurrence of radical processes. According to the literature [30, 33-35], the red shifts observed during the photolysis and the appearance of Nabs could be ascribed to a band gap narrowing effect brought about doping Ti NPs with carbon. Indeed, these experimental and theoretical works devoted to carbon-doped or carbon-modified TiO_2 materials indicate that doping with carbon is an efficient method to increase the visible-light absorption threshold. The photolysis results concerning TiOx2/Iod/PBN are displayed in Supporting Information (Figure S5). In the photolysis of TiOx2/Iod in propan-2-ol (Figure S6 in SI), the increase of the absorbance and the red-shift of the absorption as a function of the irradiation time is obviously due to the incorporation of carbon atoms into the Ti-based NPs.

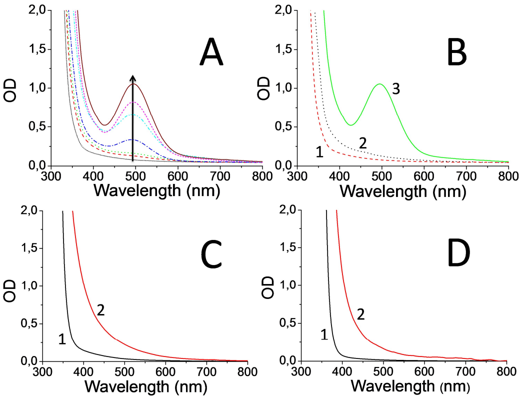

Figure 4. A) Photolysis of TiOx1/Iod under air during 360s of irradiation; B) Effect of the atmosphere on the photolysis of TiOx1/Iod after 0s (1) and 360s (2) under argon or 360s (3) under air; C) Photolysis of TiOx1/Iod/PBN under air after 0s (1) and 360s (2); D) Photolysis of Iod/PBN under air after 0s (1) and 360s (2). Solvent: toluene. Xe-Hg lamp exposure. Experiments at room temperature. [TiOx1] = 2.7x10^{-2}M, [Iod] = 2.5x10^{-2}M.

ESR-ST experiments have also been conducted. When Iod is irradiated alone under argon, the presence of phenyl radicals (Ph•) is clearly supported (Figure 5A; hyperfine coupling constants hfc of the PBN radical adduct: aN = 14.1G and aH = 2.1G in agreement with known reference values[36, 37]). Under oxygen, peroxyl radicals PhOO• resulting from the Ph•/O_2 interaction are observed (Figure 5B; hfc: aN = 13.6 G and aH = 1.6 G in agreement with literature data[38, 39]). The same PhOO• radical species are trapped by PBN when irradiating TiOx1/Iod (Figure 5C). Such a result is obviously explained by the better absorption of Iod in the Iod/TiOx1 mixture (Figure S7, Supporting Information).

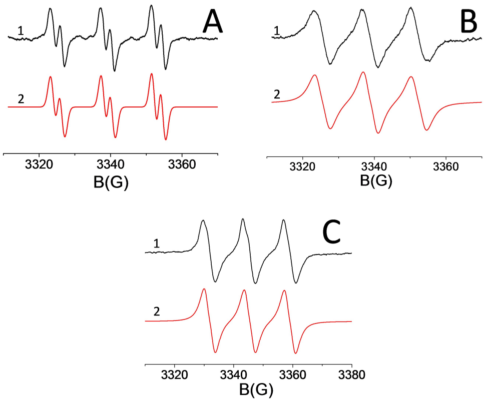

Figure 5. Experimental (1) and simulated (2) ESR-ST spectra obtained upon irradiation of: A) Iod under argon, B) Iod under air and C) TiOx1/Iod under air. Xe-Hg lamp exposure. Solvent = tert-butylbenzene. [PBN] = 0.05 M.

Therefore, a plausible photolysis mechanism occurring both in dry toluene and in the monomer matrix is depicted in reactions (r1-r4): the photolysis of Iod[40] under air leads to a fast decomposition on the picosecond time scale[41] (r1, r2) and the fast formation of C_6H_5OO• with rate constants (see in [9]) close to the diffusion limit (r3). Ti-centered radicals Ti• are also generated from the photolysis of TiOx through a known homolytic Ti-O bond cleavage[42] (r4). Then the peroxyls add to Ti• to generate surface titanium (IV) phenyl peroxide complexes PhOO-Ti$(OC_3H_7)_3$ (r5). DFT calculations (using CH_3OO• as a model of peroxyls) confirm the occurrence of reaction (r5) as supported by the obtained favourable reaction enthalpies (-84 kcal/mol). Finally, multiple photochemical fragmentations of the titanium peroxide complexes (r6a) and multiple additions of peroxyls to Ti• (r6b) likely occur to form the carbon-doped Ti NPs. This is fully consistent with the presence of carbon and oxygen atoms in the NPs as shown in Figure 1. By the way, the generated radicals (alkoxyl and Ti•) also ensures the initiation of the free radical polymerization of TMPTA (Figure S4 in SI).

Iod → ^{1}Iod (hν) and ^{1}Iod → ^{3}Iod **(r1)**

^{1,3}Iod → Ph$^{\bullet}$ + H^+ + by side product **(r2)**

Ph$^{\bullet}$ + O_2 → $C_6H_5OO^{\bullet}$ **(r3)**

Ti$(OC_3H_7)_4$ (TiOx1) → $^{\bullet}$Ti$(OC_3H_7)_3$ + $^{\bullet}OC_3H_7$ (hν) **(r4)**

PhOO$^{\bullet}$ + $^{\bullet}$Ti$(OC_3H_7)_3$ → PhOO-Ti$(OC_3H_7)_3$ **(r5)**

PhOO-Ti$(OC_3H_7)_3$→ PhOO-Ti$^{\bullet}(OC_3H_7)_2$ + $^{\bullet}OC_3H_7$ (hν) **(r6a)**

PhOO$^{\bullet}$ + PhOO-Ti$^{\bullet}(OC_3H_7)_2$ →→→ Ti-based NPs **(r6b)**

In propan-2-ol, an additional photoinduced sol-gel process mechanism, is operative, thereby explaining the presence of the hybrid Ti networks in addition to the Ti-based NPs. Indeed, a polar solvent usually favors the sol-gel chemistry (as known in [40, 43]) thus allowing the diffusion of the H^+ generated in (r2) and leading to the hydrolysis/condensation of the titanium (IV) phenyl peroxide complexes (as observed in other titanium (IV) complexes [44, 45]).

Conclusion

In conclusion, a facile photochemical route for the synthesis of visible-light absorbing Ti-based NPs in solution and in photopolymerizable films using titanium (iso)propoxide/iodonium salt couples has been developed. This route is new as outlined by reactions (r1-r6a) compared to (ra-rg) or (rh-ri). The nature of the solvent used here affects the morphology of the formed particles (well-defined Ti NPs and/or hybrid Ti networks). Oxygen plays a key role. In film experiments, the final polymer material and the NPs are concomitantly formed during the polymerization process. Such a photochemical route opens the way for rapidly developing novel Ti-based supported materials for numerous applications like e.g. the degradation of toxic organic pollutants or the generation of H_2 from the splitting of water under visible light illumination.

Notes and references

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Electronic Supplementary Information (ESI) available: Materials, ESR Spin trapping (ESR-ST) experiments, Cationic and Free Radical Polymerization Processes, Transmission Electron Microscopy (TEM) conditions and Density Functional Theory Calculations. TEM images of the irradiated TiOx alone and TiOx2/Iod systems in toluene, and TiOx2/Iod systems in aerated propan-2-ol. Photopolymerization profiles of TMPTA, photolysis experiments of TiOx2/Iod/PBN in toluene and TiOx/Iod in aerated propan-2-ol solutions and UV-absorption spectra of TiOx and Iod. See DOI: 10.1039/c000000x/

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