

Kinetics and mechanisms of EDTA photocatalytic degradation with TiO₂ under different experimental conditions

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ABSTRACT. The photocatalytic degradation of EDTA over TiO₂ has been analyzed to establish the influence of oxidants on the reaction rate, the nature of the intermediates and the kinetic regime. Degussa P-25 suspensions containing EDTA at initial pH 3 in different concentrations were irradiated under near UV light. A Langmuirian behavior was observed. O₂ at saturation concentrations was found to be crucial for EDTA degradation. The rapid depletion of EDTA was not accompanied by a corresponding TOC decrease, indicating formation of refractory intermediates. An enhancement in TOC reduction could be achieved by keeping pH constant or by hydrogen peroxide addition. Addition of Fe(III) caused a remarkable increase on the initial rate of EDTA consumption and also on TOC decrease. Changes in both parameters clearly increased under the simultaneous addition of Fe(III) and H₂O₂, until limiting values.

Some of the possible intermediates of EDTA degradation were evaluated in the filtered solution. So far, glycine, ethylenediamine, ammonium, formaldehyde, and formic, iminodiacetic, oxalic, oxamic, glycolic and glyoxylic acids have been identified in different proportions, depending on the experimental conditions. Different degradation pathways are proposed. In the presence of Fe(III), photo-Fenton reactions would contribute also to the degradation process.

1. INTRODUCTION

Ethylenediaminetetraacetic acid (EDTA) is nowadays extensively used in several industrial and domestic applications (e.g., detergents, fertilizers, herbicides, cleaning of boilers, decontamination of components of nuclear reactors), and the amount of this compound in residual waters is (and will be) increasing constantly. The effect as a water pollutant is indirect: although it does not present a high toxicity, its ability for metal complexation induces the mobilization of toxic metal ions; it can even produce detrimental effects on biological treatment of effluents by removing metals essential for bacteria. Destruction of EDTA is not possible by biological treatments [1], chlorine is scarcely efficient [2], and the compound is hardly retained by activated carbon filters [3]. Advanced oxidation technologies (AOTs) for its elimination have been tested with variable results: ozonation [4, 5], UV/H₂O₂ [6–11], UV with other oxidants [12], radiolysis [13] and combined techniques [14–16]. In recent papers, we have initiated a comparative study on the efficiency of different AOTs for EDTA treatment, still underway [17–19], with the final aim of establishing the best procedure in terms of highest mineralization degree and lowest economical costs.

Mechanisms associated to EDTA photocatalytic degradation are very complicated due to the amount of intermediates that can be formed during the progress

of the reaction. Related papers mention some of the possible routes [20–23] but the true steps of the mechanism have not been yet completely elucidated. Moreover, several recalcitrant intermediates are formed, which make very difficult total mineralization. Some of our previous papers report aspects of the photocatalytic degradation of EDTA using TiO₂ and other semiconductors [24–28]. In a recent work, we have initiated a complete study, establishing the influence of several parameters on the reaction rate, the nature of the intermediates and the kinetic regime [29]. Analysis of the filtered solution by ion chromatography and capillary electrophoresis monitored the disappearance of EDTA and the formation of degradation products after different irradiation times [29, 30]. In this preliminary work, glycine (Gly), ethylenediamine (EDA), ammonium, iminodiacetic acid (IMDA), formic, oxalic and glyoxylic acids have been identified. Later on, additional studies on the system have been performed, especially in the presence of Fe(III) and under the simultaneous addition of Fe(III) and H₂O₂. The present paper collects and correlates the results, allowing to propose different routes for the degradation, dependent of pH and of the presence of Fe(III). In the last case, the contribution of photo-Fenton reactions to the degradation process is analyzed.

2. MATERIALS AND METHODS

2.1. Chemicals. TiO₂ (Degussa P-25) was a com-

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mercial sample, kindly supplied by the manufacturer (Degussa A.G., Germany). Na₂EDTA (Carlo Erba) was of quality grade and used as provided. Fe(III) was added as a NH₄Fe(SO₄)₂·12H₂O (Mallinckrodt) aqueous solution. 30% w/w (Merck) hydrogen peroxide was used. All other reagents were at least of reagent grade and used without further purification. Water was double-distilled in a quartz apparatus and purified by a Nanopure system in the case of chromatographic and electrophoretic analyses. Diluted HClO₄ was used for pH adjustments. Complete conditions for chromatographic and electrophoretic analyses are described elsewhere [30].

2.2. Photocatalytic studies. Irradiations were performed using high-pressure xenon arc lamps (Osram XBO, 150 or 450 W) with a bandpass filter (Schott BG 1 or BG 25, thickness 3 mm; 300 nm < λ < 500 nm; maximum transmission at 360 nm). The IR fraction of the incident light was removed by a suitable filter (Schott KG 5). Actinometric measurements were performed by the ferrioxalate method [31]. Photon flows per unit volume of 1.1 × 10⁻⁵ and 1.8 × 10⁻⁵ Einstein L⁻¹ s⁻¹ were calculated for the 150 and the 450 W lamp, respectively.

Photocatalytic runs were done at 25 °C in a thermostatted cylindrical Pyrex cell. In all cases, a fresh solution (10 mL) of EDTA at a known concentration was adjusted to pH 3, the catalyst (1.0 g L⁻¹) suspended in the solution, and the suspension ultrasonicated for 2 min. A water-saturated nitrogen, oxygen or air stream was bubbled in the suspension at a constant rate throughout the experiment. Prior to irradiation, suspensions were stirred in the dark for 30 min and the extent of dark adsorption was calculated by measuring EDTA concentrations before and after the stirring. The adsorbed amount was discounted to correct the initial EDTA concentration in photocatalytic runs. Irradiations were performed under magnetic stirring. Samples were periodically withdrawn and filtered through 0.22 μm Millipore filters. At least, duplicated runs were carried out for each condition, averaging the results. EDTA concentration was evaluated by spectrophotometric analysis with bis(2,4,6-tripyridyl-S-triazine)iron (II) in the visible range [32]; in the presence of Fe(III), EDTA was evaluated by the EDTA-Fe(III) complex method in the UV range [33]. UV-visible absorption measurements were performed with a Shimadzu 210A spectrophotometer. Total organic carbon (TOC) was measured with a Shimadzu 5000A TOC analyzer.

2.3. Chromatographic and capillary electrophoretic determination of degradation products. After different irradiation times, some of the possible intermediates and products of EDTA degradation in the filtered solution were evaluated by methodologies whose optimization is discussed elsewhere [30].

The cation chromatographic system was a Konik KNK-500A liquid chromatograph equipped with a

Rheodyne Model 7125 injector. Detection was achieved via an Alltech 320 conductivity detector and processed with a Konikrom Chromatography Data System V. 5.2 integration software. Nitric acid, pH 2.5, was used as eluent at a flow rate of 1 mL min⁻¹. Gly and ammonium were analyzed on a 10 cm silica-base cationic column (Wescan 269-004), and EDA on a 12 cm silica-based cationic column (Methrom Sep 904315). All chromatographic analyses were performed at room temperature.

Anion capillary electrophoresis was performed in a Thermo Separation Products SpectraPHORESIS ULTRA capillary electrophoresis system controlled by PC1000 software, with a UV-Vis detector SpectraPHORESIS UV3000. Separations were run at 25 °C in a fused silica capillary tube (40.1 cm × 75 μm I.D., effective length 36.5 cm). Samples were injected hydrodynamically (8 psi) for 5 s. The running buffer was 5 mM potassium acid phthalate and 0.3 mM hexadecyltrimethylammonium bromide (CTAB) as electroosmotic flow modifier. As internal standard, 10.0 μg mL⁻¹ nitrate was used. EDTA, formic, glyoxylic and acetic acids were analyzed with addition of 1 mM Cu²⁺ to the buffer electrolyte at pH 3.3. Oxalic acid and IMDA were analyzed at pH 4. Glycolic acid was evaluated semiquantitatively at pH 5.5.

Formaldehyde was qualitatively detected with chromotropic acid [34].

3. RESULTS AND DISCUSSION

Aqueous suspensions of TiO₂ (Degussa P-25, 1 g L⁻¹) containing EDTA in concentrations ranging 0.3–5.0 mM at initial pH 3 were irradiated under near UV light for different illumination times, and samples were taken periodically for analysis. The profiles for the time course of EDTA depletion at different concentrations up to 120 min were linear in the range 3.0–5.0 mM, and at lower concentrations they presented a deceleration after some irradiation time (graphics not shown), typical of a Hinshelwood-Langmuir behavior. Initial rates were calculated from these profiles, and a linear plot of 1/R₀ vs. 1/C₀ was obtained in accordance with the kinetic regime (Figure 1). Kinetic constants $k = 6.3 \times 10^{-7} \text{ M s}^{-1}$ and $K = 4690 \text{ M}^{-1}$ have been calculated. This last constant is very similar to the (thermal) adsorption constant of EDTA over TiO₂ that can be calculated from data reported elsewhere [35].

Experiments with 5.0 mM EDTA (zero order regime) were performed for 3 h irradiation under different conditions (Figure 2). No reaction was observed in the absence of TiO₂. Under N₂ bubbling, depletion of EDTA was very low (*ca.* 16%). Under O₂ (different fluxes at saturation in water) or air bubbling, a decrease of EDTA concentration up to *ca.* 90% was obtained in the different cases (Figure 3). The initial photonic efficiency in the presence of oxygen was $\xi_0 \% = 4.2$, calculated from

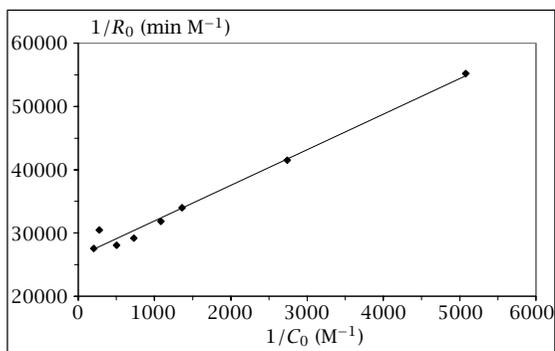


Figure 1. Langmuirian plot for the photocatalytic degradation of EDTA. Conditions: pH 3, $[P-25] = 1 \text{ g L}^{-1}$, near UV, $I_0 = 1.1 \times 10^{-5} \text{ Einstein L}^{-1} \text{ s}^{-1}$, oxygen bubbling at 0.2 mL min^{-1} .

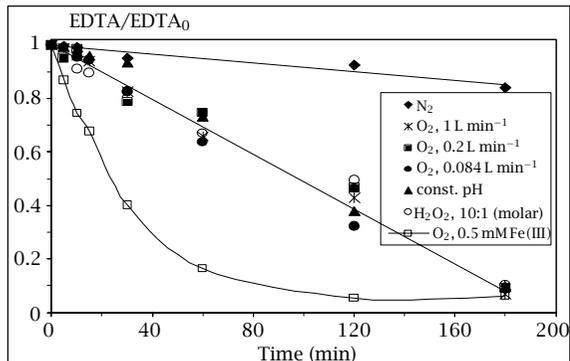


Figure 2. Photocatalytic experiments with $[\text{EDTA}] = 5.0 \text{ mM}$ under different conditions. Other conditions as in Figure 1.

the slope of the straight line in Figure 2 and the incident photon flow. Although an increase of more than 1 unit in pH was observed after 3 h irradiation, only negligible changes on the degradation rate occurred by keeping pH constant by periodical HClO₄ addition. Similar results were obtained after the initial addition of hydrogen peroxide (10:1 molar ratio H₂O₂ to EDTA) or adding a drop each 10 min of irradiation (not shown). Addition of 0.5 mM Fe(III) (1 order of magnitude lower than the molar EDTA concentration) caused a dramatic increase on the initial rate of EDTA depletion, and $\xi_0\% = 25.0$ was calculated in these conditions from the initial slope of the curve. In contrast, TOC decrease ranged only between 4.5 and 9% in the absence of oxidants other than oxygen, and was considerably improved (21% or more) by keeping pH constant, by hydrogen peroxide addition or in the presence of Fe(III) (Figure 3).

Another set of experiments was performed with 5.0 mM EDTA under similar conditions but using dif-

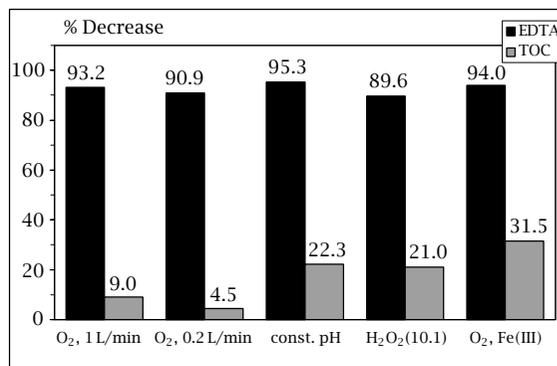


Figure 3. Degree of EDTA degradation and TOC decrease after 180 min irradiation time. Conditions as in Figure 2.

ferent Fe(III)/EDTA molar ratios. Figure 4 shows the results: all experiments indicate an improvement in degradation in comparison with the system without Fe(III) (especially in the extent of TOC reduction), but a decrease is observed with high Fe(III) contents. In the case of EDTA depletion, the highest Fe(III) concentration (1:1 to EDTA) is frankly detrimental. Therefore, a large amount of Fe(III) should be avoided.

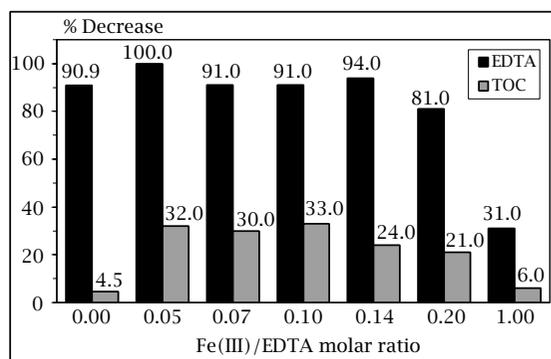


Figure 4. Decrease of EDTA and TOC after 180 min irradiation in experiments with different Fe(III)/EDTA molar ratio. All other conditions as in Figure 2.

Experiments under more prolonged irradiation were performed to assess TOC degradation (oxygen 0.2 L min^{-1} , no other oxidants). Only isolated points after 12 and 24 h were evaluated, which yielded 39 and 63% TOC decrease respectively, indicating the recalcitrance of the system to mineralization.

The following runs were performed with simultaneous addition of Fe(III) and H₂O₂ in different ratios, irradiating only up to 30 minutes to control the initial changes in the system (Figure 5). Changes in EDTA depletion and TOC decrease depended on the relative concentration of oxidants and substrate. Changes in pH

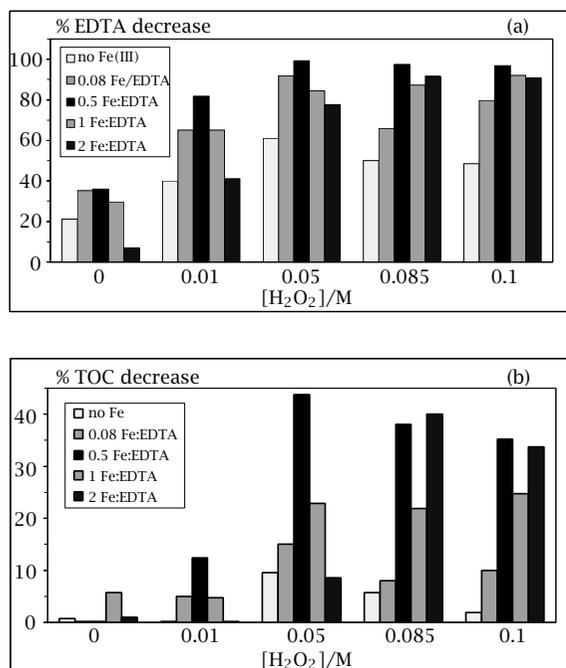


Figure 5. Decrease of (a) EDTA and (b) TOC in the photocatalytic degradation of EDTA after 30 min of irradiation in the presence of different Fe(III) and H_2O_2 concentrations. Conditions: $[\text{EDTA}] = 5.0 \text{ mM}$, $\text{pH } 3$, $[\text{P-25}] = 1 \text{ g L}^{-1}$, near UV, $I_0 = 1.8 \times 10^{-5} \text{ Einstein L}^{-1} \text{ s}^{-1}$, oxygen bubbling at 0.2 mL min^{-1} .

were generally larger than in the absence of Fe(III) or H_2O_2 , and reached 7 or more in the cases of the highest conversions. Fe(III) concentrations higher than 2.5 mM, i.e., at a molar ratio Fe(III) to EDTA higher than 0.5:1, were detrimental until a 50 mM H_2O_2 concentration. This result is in accordance with the previous ones in the absence of H_2O_2 . Similarly, in most conditions, TOC decrease was enhanced until the same H_2O_2 concentration. However, with higher amounts of H_2O_2 the trend is not clear, depending on the amount of Fe(III) added to the system. The best condition for conversion found in this work (44% TOC decrease and 99% EDTA disappearance) was in the presence of 2.5 mM Fe(III) and 50 mM H_2O_2 , i.e., at a 1:2:20 molar ratio Fe(III)/EDTA/ H_2O_2 . Note that these values of decomposition are extremely good for an irradiation time of only 30 min, in comparison with the previous results. This experiment was then repeated up to 180 min, achieving 52% TOC reduction. The initial photonic efficiency, calculated from the initial slope of the profile of EDTA degradation (not shown), was $\xi_0 \% = 33$.

The following intermediates and products were detected after photocatalytic runs of different duration: formic, oxalic, oxamic, glyoxylic and glycolic acids, IMDA, Gly, ammonium and EDA. Formaldehyde was also qualitatively detected, but not quantified. Nitrate

and nitrite were never detected, even after 24 h irradiation. Other unknown compounds were observed, whose identification is underway.

As stated in our previous work [29], in the absence of oxidants other than oxygen, formic acid, IMDA, oxalic acid and Gly were the most abundant products after 180 min irradiation, formed at concentrations in the mM range. Glyoxylic acid, glycolic acid and ammonium were detected in lower amounts (two orders of magnitude), whereas EDA was the less abundant product, found in concentrations about $3.5 \mu\text{M}$. Further experiments comparing those up to 180 min irradiation yielded more information about the fate of the decomposition products. Up to 60 min, glyoxylic acid concentration remained higher than Gly. Isolated experiments up to 12 and 24 h showed a decrease in the concentration of Gly, IMDA, EDA, glyoxylic and formic acids, indicating that they are degradable intermediates. Glycolic acid disappeared completely after 12 h. On the contrary, oxamic acid, not observed at 180 min, could be detected after 12 h and even at a higher concentration after 24 h irradiation, although always lower than 0.1 mM. Similarly, oxalic acid concentration also increased constantly, these results suggesting the refractory nature of both compounds. Ammonium concentration increased continuously up to 24 h, being undoubtedly a final product, taking into account that neither nitrate nor nitrite could be detected. In the presence of Fe(III) and no H_2O_2 (experiments up to 30 min), a slightly increase in EDA concentration could be observed. When H_2O_2 was added, this increase occurred only when important changes in pH took place.

According to the accepted mechanism for heterogeneous photocatalytic processes, electrons and holes are generated after light absorption by the semiconductor. The organic compound can be oxidized directly by holes or by hydroxyl radicals, whereas conduction band electrons reduces oxygen to superoxide, forming additional HO^\bullet , through successive steps. Taking into account the identity and amount of products detected in our experiments, and similarly to previously proposed mechanisms with other oxidants [4, 7, 10, 36], it can be suggested that EDTA photocatalytic degradation proceeds through three possible pathways (a), (b) and (c), depending on the point of attack to the molecule, through which ED3A, IMDA and glyoxylic acid can be respectively formed in the initial steps (Scheme 1). Successive h^+ or HO^\bullet attacks, combined with other dark processes, induce EDTA cleavage forming the intermediates indicated in Scheme 1, together with CO_2 , CH_2O and NH_4^+ . Formaldehyde is further oxidized to formic acid. IMDA is decomposed to Gly, which is known to transform slowly to oxamic acid [10], and this explains why this compound cannot be seen during the first times of the reaction. Glyoxylic acid is further oxidized to oxalic and/or formic acids. Pathway (a), which im-

ton reaction, but it is known that an excess can be detrimental because this reagent acts as a HO• scavenger [38]. In addition, a large concentration of Fe(III) can be deleterious as found in previous cases [37]. As said, the best conversion was found at a 1:2:20 molar ratio Fe(III)/EDTA/H₂O₂, with an unclear behavior at higher H₂O₂ concentrations, depending on the amount of added Fe(III). Probably, there is an optimum relationship between Fe and hydrogen peroxide, which leads to the best degradation. More detailed experiments are underway to explain these results.

It must be pointed out that the increase in quantum efficiency in the presence of Fe(III) (with or without added H₂O₂) does not mean an increase in the efficiency of the photocatalytic reaction (an always desired purpose in photocatalysis), because this system should be considered a combined AOT, heterogeneous photocatalysis + photoFenton-type reactions. Therefore, the active species generated in these complex systems are probably involved in more rapid reactions in solution phase compared with those in the interface.

4. CONCLUSIONS

A Langmuirian regime describes accurately the kinetic behavior of EDTA photocatalytic degradation. Oxygen is crucial for the reaction, and almost complete EDTA depletion takes place after 180 min irradiation. In contrast, a very low decrease of TOC is observed, which suggests that reluctant intermediates are formed during the degradation. Decrease of TOC can be helped by: a) keeping a constant pH; b) H₂O₂ addition; c) addition of Fe(III). In this last case, photoFenton-type reactions would contribute also to the degradation process. A higher acceleration is observed under the simultaneous presence of Fe(III) and H₂O₂. However, high amounts of Fe(III) are detrimental, and the compartment of the system is unclear with high H₂O₂ concentrations. Different intermediates of the reaction have been identified in agreement with proposed mechanistic pathways, depending on the experimental conditions.

More systematic experiments are underway to find the optimum Fe(III) and H₂O₂ concentrations and to determine more precisely the fate and nature of the intermediates.

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Call for Papers

Polymers reinforced with nanoparticles, such as carbon nanotubes, are of great interest due to their remarkable mechanical, thermal, chemical properties as well as optical, electronic, and magnetic applications. In the general research area of polymer nanocomposites, a number of critical issues need to be addressed before the full potential of polymer nanocomposites can actually be realized. While a number of advances have recently been made in the area of polymer nanocomposites, the studies on understanding of the effects of processing parameters on the structure, morphology, and functional properties of polymer nanocomposites are deficient. There is a need for characterization techniques to quantify the concentration and distributions of nanoparticles as well as to assess the strength at the interface between the polymer and nanoparticles. Also, there is a need for the development of better models able to predict the mechanical properties of the polymer nanocomposites as functions of myriad factors including nanoparticle orientation, the type of functional groups, and the molecular weight of polymer chain. The relationships between the structural distributions and the ultimate properties of the polymer nanocomposites also need to be elucidated.

This special issue of the Journal of Nanomaterials will be devoted to emerging polymer nanocomposite processing techniques and call for new contributions in the field of characterization and applications of multifunctional nanocomposites. It intends to cover the entire range of basic and applied materials research focusing on rheological characterization, nanoparticle dispersion, and functional properties of polymer nanocomposites for sensors, actuators, and other applications. Fundamental understanding of the effects of processing and nanoparticles on the polymer structure and morphology, their optical, electrical, and mechanical properties as well as novel functions and applications of nanocomposite materials will be the highlights of this special issue.

Papers are solicited in, but not limited to, the following areas:

- Solution and melt processing of polymer nanocomposites
- Rheological and thermal characterization of nanocomposites

- Generation of nanofibers using extrusion and electrospinning of nanocomposites
- Processing-induced orientation of nanoparticles
- Quantification of nanoparticle dispersion
- Effect of nanoparticle incorporation on polymerization
- In situ nanoparticle formation in polymer matrix
- Noncovalent functionalization techniques and characterization of properties at polymer-nanoparticle interface
- Novel applications of polymer nanocomposites

Before submission authors should carefully read over the journal's Author Guidelines, which are located at <http://www.hindawi.com/journals/jnm/guidelines.html>. Prospective authors should submit an electronic copy of their complete manuscript through the journal Manuscript Tracking System at <http://mts.hindawi.com/> according to the following timetable:

Manuscript Due	November 1, 2009
First Round of Reviews	February 1, 2010
Publication Date	May 1, 2010

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Special Issue on 1D Nanomaterials

Call for Papers

Nanotechnology has had a significant global impact in redefining existing and developing novel research avenues over the last two decades. Where bottom-up assembly meets conventional top-down refinements, nanomaterials proffer the necessary bridge between atomistic processes and useable macroscale devices. Focus has largely been toward preparative methods with specific interest in controlling the fundamental properties and architecture, where the inextricable link between size and geometry and properties of one-dimensional (1D) nanomaterials, for example, nanotubes, nanowires, nanorods, reveals a wide variety of promising applications. However, only a small number of nanomaterial-based devices are currently available in the market place.

The main focus of this issue will be on the development, use, and exploitation of 1D nanomaterial systems as well as their incorporation into larger devices. The special issue will become an international medium for researchers to summarize their most recent developments and ideas in the field. The topics to be covered include, but are not limited to:

- 1D nanomaterial production of inorganic and organic systems
- 1D nanomaterials and biological hybrids
- Theoretical modeling of 1D nanomaterial properties
- Functionality on the nanoscale or from the nanoscale to the macroscale
- Fabrication and/or assembly of 1D nanomaterials into macroscale devices
- New techniques for imaging and manipulation of 1D nanomaterials
- Engineering applications of 1D nanomaterials

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