A Continuous-Flow Photocatalytic Reactor for Precisely-Controlled Deposition of Metallic Nanoparticles
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Corresponding Author:	Selmiye Gürsel, PhD Sabanci Universitesi Istanbul, TURKEY
Corresponding Author's Institution:	Sabanci Universitesi
Corresponding Author E-Mail:	selmiye@sabanciuniv.edu
Order of Authors:	Sina Abdolhosseinzadeh
	Mirsajjad Mousavi
	Navid Haghmoradi
	Selmiye Gürsel
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2   **A Continuous-flow Photocatalytic Reactor for the Precisely Controlled Deposition of Metallic**
3   **Nanoparticles**
4
5   **AUTHORS AND AFFILIATIONS:**
6   Sina Abdolhosseinzadeh[1,2], Mirsajjad Mousavi[3], Navid Haghmoradi[3], Selmiye Alkan Gürsel[3,4]
7   [1]Institut des matériaux, École Polytechnique Fédérale de Lausanne (EPFL), Lausanne, Switzerland
8   [2]Laboratory for Functional Polymers, Swiss Federal Laboratories for Materials Science and
9   Technology (Empa), Dübendorf, Switzerland
10 [3]Faculty of Engineering and Natural Sciences, Sabanci University, Istanbul, Turkey
11 [4]SUNUM Nanotechnology Research Centre, Sabanci University, Istanbul, Turkey
12
13 **Corresponding Author:**
14 Selmiye Alkan Gürsel   (selmiye@sabanciuniv.edu)
15 T: +90-216-483-9573
16
17 **Email Addresses of Co-Authors:**
18 Sina Abdolhosseinzadeh   (sina.abdolhosseinzadeh@epfl.ch)
19 Mirsajjad Mousavi   (mousavi@sabanciuniv.edu)
20 Navid Haghmoradi   (nhaghmoradi@sabanciuniv.edu)
21
22 **KEYWORDS:**
23 platinum nanoparticles, gold nanoparticles, TiO_2 nanocomposite, metallic nanoparticles, partially
24 reduced graphene oxide, photocatalytic deposition, continuous flow reactor, photoreduction
25
26 **SUMMARY:**
27 For a continuous and scalable synthesis of noble-metal-based nanocomposites, a novel
28 photocatalytic reactor is developed and its structure, operation principles, and product quality
29 optimization strategies are described.
30
31 **ABSTRACT:**
32 In this work, a novel photocatalytic reactor for the pulsed and controlled excitation of the
33 photocatalyst and the precise deposition of metallic nanoparticles is developed. Guidelines for
34 the replication of the reactor and its operation are provided in detail. Three different composite
35 systems (Pt/graphene, Pt/TiO_2, and Au/TiO_2) with monodisperse and uniformly distributed
36 particles are produced by this reactor, and the photodeposition mechanism, as well as the
37 synthesis optimization strategy, are discussed. The synthesis methods and their technical aspects
38 are described comprehensively. The role of the ultraviolet (UV) dose (in each excitation pulse) on
39 the photodeposition process is investigated and the optimum values for each composite system
40 are provided.
41
42 **INTRODUCTION:**
43 Metallic nanoparticles, especially noble metals (e.g., Pt, Au, Pd) have vast applications in
44 catalysis[1]. In general, decreasing the size of the nanoparticles (NPs) increases their catalytic

45 activity while maintaining the cost (weight) constant, but it also makes their application more
46 difficult. NPs (usually smaller than 10 nm) have great tendencies to aggregation, which degrades
47 their catalytic activity; however, immobilization on suitable substrates can mostly resolve this
48 problem. Furthermore, depending on the application type (e.g., electrocatalysis), it is sometimes
49 necessary to immobilize the NPs on conductive substrates[2,3]. NPs can also be hybridized with
50 semiconductors to form a Schottky barrier and avoid (delay) the electron-hole recombination
51 (acting as electron traps)[4,5]. Hence, in most of the applications, the noble metal NPs (NNPs) are
52 deposited either on a conductive (e.g., graphene) or a semiconductive (e.g., TiO_2) substrate. In
53 both cases, metal cations are usually reduced in the presence of the substrate, and the reduction
54 technique differs from one method to another.
55
56 For the deposition of NNPs via a reduction of their cations, electrons (with proper electrical
57 potential) should be provided. That can be done in two ways: by oxidation of other chemical
58 species (a reducing agent)[6,7] or from an external power source[8]. In any case, for the
59 homogeneous deposition of monodispersed NPs, it is necessary to impose a strict control on the
60 generation and transfer of the (reducing) electrons. This is very difficult when a reducing agent is
61 used since there is virtually no control over the reduction process once the reactants (cations and
62 reducing agent) are mixed. Furthermore, NPs can form anywhere and not necessarily on the
63 target substrate. When using an external power source, the control over the number of the
64 provided electrons is much better, but NPs can only be deposited on an electrode surface.
65
66 Photocatalytic deposition (PD) is an alternative approach, which offers more control over the
67 number of the (photo)generated electrons since it is directly related to the dose of the
68 illuminated photons (with a proper wavelength). In this method, the substrate material has a
69 dual role; it provides the reducing electrons[9] and stabilizes the formed NPs[10]. Moreover, NPs
70 form only on the substrate since the electrons are generated by the substrate. A proper electrical
71 connection between composite components (made by the photocatalytic reduction method) is
72 also guaranteed[11]. Nevertheless, in conventional photocatalytic deposition methods in which the
73 whole batch of reactants (photocatalyst and metal cation) is illuminated simultaneously, there is
74 no control over the nucleation of the NNPs. Indeed, once a few particles (nuclei) are formed, they
75 act as preferred transfer sites for the photogenerated electrons[5] and act as a preferred growth
76 site. This superior electron transfer promotes the growth of the existing particles and disfavors
77 the formation of new nuclei, which results in the formation of large NNPs. This problem can be
78 addressed by the pulsed illumination of UV light in a special continuous-flow reactor (**Figure 1**)
79 that has recently been developed by our group[12]. The unique feature of this reactor is that it
80 allows researchers to control both NP-size-determining factors, namely, nucleation and growth.
81 In this reactor, a very small portion of reactants is illuminated for a very short period of time,
82 promoting the formation of nuclei (more nuclei are formed) and restricting the growth (smaller
83 particles are attained). In this method, by controlling the illumination dose (i.e., by adjusting the
84 exposure duration [changing the length of uncovered parts of the reaction tube; **Figure 1C**] or
85 intensity of the incident light [number of the lamps]), a very precise control over the number of
86 photogenerated electrons and, consequently, on the reduction process (NNP deposition) can be
87 exerted.
88

89   [Place **Figure 1** here]

90

91   Despite the great potential of the PD method for the controlled deposition of NNPs, its
92   application is limited to semiconducting materials. Fortunately, it is possible to open a wide band
93   gap in graphene (one of the best-conducting substrates[13]) by its simple chemical
94   functionalization. Afterward, these functional groups (FGs) can be mostly removed and the
95   resulting graphene will still be conductive enough for most of the applications. Among numerous
96   functionalized derivatives of graphene, graphene oxide (GO), which exhibits considerable
97   semiconducting properties[14], is the most promising candidate for this purpose. This is mainly due
98   to the fact that GO's production has the highest production yield among the others. Nevertheless,
99   since GO consists of different types of FGs, its chemical composition varies continuously under
100   UV illumination. We have recently shown that by a selective removal of weakly bonded FGs
101   (partial reduction; PRGO), the chemical structure and electronic properties of GO can be
102   stabilized, which is an essential requirement for homogeneous depositions of the NNPs[12]. In this
103   report, we describe the structure of the reactor and provide detailed information for its
104   replication and operation. The deposition mechanism (working mechanism of the reactor) and
105   possible optimization strategies are also discussed in great detail. To validate the applicability of
106   the developed PD reactor for both types of common substrates (conductor and semiconductor)
107   and different NNPs, the deposition of platinum on PRGO and TiO_2, as well as of gold on TiO_2, is
108   demonstrated. It is noteworthy that by a proper selection of the metal, photocatalyst and
109   precursor materials (e.g., salt, hole scavenger), and the dispersion media, several other metallic
110   particles (such as Ag and Pd[15]) can also be deposited. In principle—since, in the photodeposition
111   of NNPs, the cations of the metal are reduced by the photoexcited electrons—the energy level
112   of the semiconductor's conduction band minimum (CBM) should match with (be more negative
113   than) the reduction potential of the aimed cations. Due to the extensive technical production
114   aspects, the synthesis of PRGO is also described in detail. For further information regarding the
115   chemical structure and electronic properties of PRGO, please refer to previous work[12].

116

117   The detailed structure of the reactor is schematically depicted in **Figure 2**. The reactor has two
118   main components: a UV illumination and a reservoir compartment. The illumination section
119   consists of a quartz tube, which is exactly fixed along the central axis of a cylindrical tube with a
120   polished aluminum liner. The reservoir consists of a 1 L sealed-cap glass bottle with gas and liquid
121   (reactants) inlets and outlets. Use a silicon septum with an open-top screw cap for inserting the
122   tubes. To take samples during the reaction without letting oxygen enter the reactor, an outlet
123   with a valve is also installed. It should be mentioned here that the samplings on specific time
124   intervals are not a part of the nanocomposite production process, and sampling only needs to be
125   done once to obtain the concentration-time curves for each set of synthesis parameters (the
126   application of these curves will be discussed in the Discussion section). The reservoir is placed
127   inside an ice-water bath while being vigorously mixed on a magnetic stirrer. A magnetic pump
128   circulates the reactant from the reservoir to the reaction chamber (illumination section) and back
129   to the reservoir. A magnetic one is used since high flow rates are necessary (the flow rate in this
130   work = 16 L·min^{-1}) and peristaltic pumps (or other similar pumps) can hardly provide those flows.
131   When using a magnetic pump, care should be taken to completely fill the impeller casing (pump
132   housing) with the reactant liquid and evacuate any trapped air (oxygen source). The trapped air

133 can also decrease the pump's real flow rate.

135 For a pulsed excitation of the photocatalyst material, specific lengths of the quartz tube are
136 covered by a thick aluminum foil, leaving equal lengths between them uncovered (**Figure 2**). The
137 duration of the pulsed excitation can be adjusted by changing the length of the uncovered parts
138 (exposure length). The optimum exposure length is determined by various parameters, such as
139 the quantum yield of the photocatalyst and the intended NP loading (concentration of the
140 precursors; see Discussion).

142 **PROTOCOL:**

144 **1. Fabrication and operation of the photocatalytic deposition reactor**

146 CAUTION: When UV lamps are turned on, use UV-C protective glasses.

148 **1.1. Fabrication of the photocatalytic deposition reactor**

150 1.1.1. Cover the inner surface of a polyvinyl chloride (PVC) pipe (diameter x length = 15 cm x 55
151 cm; other materials can also be used) with a thick, polished, and adhesive-backed aluminum foil.
152 Install five 55 W UV-C lamps (see **Table of Materials**) on the inner surface of the tube at equal
153 distance.

155 1.1.2. Fix a quartz tube (diameter x length = 0.5 cm x 55 cm) along the central axis of the PVC
156 tube (concentric configuration). For the pulsed excitation of the photocatalyst, cover the desired
157 equal lengths of the quartz tube with the same adhesive-backed aluminum foil (in this work, for
158 the Pt/graphene composites: 5 cm x 0.4 cm, 5 cm x 2 cm, and 1 cm x 50 cm, and for the Pt/TiO$_2$
159 and Au/TiO$_2$ composites: 5 cm x 1 cm). Note that 2.5 cm of the quartz tube on each side is used
160 for connecting the plastic tubes.

162 1.1.3. Install a heavy-duty fan at one end of the PVC tube (to cool down the whole illumination
163 chamber).

165 [Place **Figure 2** here]

167 **1.2. Feeding the reactants to the reactor**

169 1.2.1. Use a setup like the one shown in **Figure 2**. Place a separation funnel in a higher vertical
170 position than the pump and the reservoir (the pump should also be in a higher vertical position
171 than the bottom of the reservoir) and fill the reactants into the separation funnel.

173 1.2.2. Open the valve V$_0$ to feed the reactant to the reactor and close the valve (V$_0$) immediately
174 when the funnel is depleted (otherwise, air will also enter the pump).

176 NOTE: The flow rate of the magnetic pumps is affected by the gravitational forces exerted on the

liquid, meaning that any alteration in the position of the reactor parts (vertical displacements) will change the flow rate (thus, do not displace the reactor parts once they are set up).

2. Synthesis of partially reduced GO

CAUTION: All the following experiments should be carried out inside a fume hood.

2.1. Synthesis of GO

2.1.1. Add 100 mL of 98% sulfuric acid and 2 g of graphite to a 500 mL Erlenmeyer flask. Cool down the flask to ~0 °C in an ice-water bath while mixing its contents on a magnetic stirrer.

NOTE: Use a big magnetic stir bar, since the suspension will become very viscous at the end of the reaction.

2.1.2. Gradually add 6 g of potassium permanganate (over a period of 30 min) as it is a very exothermic reaction. Remove the ice-water bath and continue stirring for 6 h.

2.1.3. Put the flask inside an ice-water bath and continue stirring for 15 min. Add 250 mL of distilled water dropwise, using a separation funnel. Remove the ice-water bath, gradually add 30 mL of hydrogen peroxide, and keep stirring for 30 min.

2.1.4. Centrifuge the suspension at 3,500 x g for 15 min and discard the supernatant. Wash the precipitates with distilled water. Repeat this process (wash-centrifuge) till pH reaches 5.

NOTE: Higher rotational speeds (if available) would be better but lower speeds should be compensated with longer centrifugation times. Also note that when the pH value rises to above 3–4, even long-time centrifugation (and also higher rotational speeds) cannot precipitate all the particles[16] and a considerable part of the suspension will be lost (roughly 1 g will remain at the end). The reaction can be paused here (store the reactants in an amber bottle, or wrap a normal bottle with aluminum foil).

2.1.5. Add the product of the previous step to 0.5 L of 1 M hydrochloric acid and stir it for 1 h. Wash the product as described in step 2.1.3 until the pH reaches 5. Add the product to 1 L of distilled water and sonicate it in a bath-sonicator for 3 h (add ice to the bath during the sonication to avoid a temperature rise).

2.1.6. Centrifuge the product for 3x 20 min at 3,500 x g and, each time, discard the precipitates. Store the obtained GO suspension in a capped glass bottle (use an amber bottle, or wrap a normal bottle with aluminum foil).

NOTE: If necessary, the centrifuge times can be broken down to shorter intervals (with cooling periods in between) to avoid temperature rises (higher than room temperature [RT]) of the suspension since, otherwise, the unwanted precipitates will not settle down.

221

222 2.1.7. Weigh three dry crystallizing dishes (of a volume of 100–200 mL) with an analytical grade
223 balance (0.01 mg readability), each of them 3x. Shake the GO suspension well and, after 1 min,
224 add exactly (with the highest possible accuracy) 100 mL of it to each of the crystallizing dishes.
225 Leave the dishes in a 70–80 °C oven to dry completely.

226

227 2.1.8. By means of the final dry weight (weigh each dish 3x on the same analytical balance) and
228 empty dish weight, determine the solid content of the GO suspension by averaging the values
229 obtained from the three dishes. Adjust the concentration to 0.2 g/L by adding the required
230 amount of distilled water.

231

232 NOTE: To check if the drying is complete or not, check the weight changes during two consecutive
233 days. The weighing should be done immediately after taking the dishes out of the oven (before
234 the temperature falls below 50 °C) since, otherwise, considerable weight increase will be
235 observed. Although this process is time-consuming, since the solid content is not high, it is more
236 accurate than other solid-content-determination methods.

237

238 **2.2. Partial reduction of GO (synthesis of PRGO)**

239

240 2.2.1. Gradually add the diluted GO suspension (the product of step 2.1.5) to an equal volume of
241 a 4 M sodium hydroxide solution in a round-bottom flask. Attach a condenser to the flask and
242 reflux-stir the suspension at 90 °C for 8 h (with a heater mantle).

243

244 2.2.2. After cooling down, "wash-centrifuge" the precipitates with distilled water (as described
245 in step 2.1.4) to near neutral pH (~7–8).

246

247 NOTE: Since PRGO has much less hydrophilicity than GO, all the precipitates should settle down
248 during the centrifugation and the supernatant should be a completely clear solution. If this is not
249 the case for any reason (e.g., not sufficient rotational speed), the solid content measurement
250 (see step 2.1.8) should be conducted at this stage too.

251

252 **3. Photocatalytic deposition of NNPs**

253

254 **3.1. Synthesis of Pt/graphene composite**

255

256 3.1.1. Adjust the concentration of the product from section 2.2 to 50 mg·L^{-1} and sonicate the
257 suspension with a probe sonicator for 1 h in an ice-water bath. Take 540 mL of the product and
258 add 60 mL of ethanol (hole scavenger) and continue the sonication (in ice) for an extra 1 h. For a
259 20 wt% Pt/graphene composite, add 11.5 mg of 8 wt% hexachloroplatinic acid aqueous solution
260 (commercially available) to the product and stir it at room temperature for 15 min (for other Pt
261 loadings, calculate the amount accordingly).

262

263 NOTE: It is advised to use aqueous solutions of the noble metal salts (if commercially available)
264 or initially prepare a highly concentrated stock solution from the powder-form salts. These salts

265 are hygroscopic materials and, due to their extensive water absorption, precise weighing and
266 obtaining reproducible results will be difficult or even impossible.
267
268 3.1.2. Fill the ice-water bath with ice and feed the product of the previous step to the reactor, as
269 described in section 1.2. Start the magnetic pump and open the N_2 gas inlet valve with a high
270 flow. Put and fix the gas outlet tube (T_1 in **Figure 2**) in a 1 L Erlenmeyer flask and fill it with ~0.7 L
271 of water so that the gas bubbles out.
272
273 3.1.3. To flush out the dissolved O_2 gas from the system and cool down the suspension, vigorously
274 mix the suspension with the magnetic stirrer for 30 min. Reduce the N_2 gas flow and turn on the
275 five UV lamps.
276
277 NOTE: The N_2 gas flow has no effect on the synthesis process itself and, hence, has no specific
278 value. However, it is continuously applied to maintain a positive pressure inside the system and
279 avoid O_2 penetration. Bubble formation at the endpoint of the T_1 tube inside the water-filled
280 Erlenmeyer flask is the only requirement for the flow adjustment.
281
282 **3.2. Sampling Pt/graphene deposition (and reduction of PRGO to RGO)**
283
284 CAUTION: Although wearing goggles in a chemistry lab is always mandatory, it is worth it to be
285 reminded again, since in this experiment, there is a high risk of splashing.
286
287 3.2.1. Increase the N_2 gas flow 5 min after turning on the UV lights. Attach a syringe to point P_S
288 (**Figure 2**). While holding the syringe piston to prevent it from coming out, open the valve V_1, fill
289 the syringe with 20 mL of the suspension, and close the valve (V_1). Detach the syringe and open
290 the valve V_2 to evacuate the remaining suspension inside the tube T_2, and close it (V_2) afterward.
291 Reduce the N_2 gas flow to the previous level.
292
293 3.2.2. Centrifuge the product of the previous step at 10,000 x g for 10 min. Store the supernatant
294 for inductively coupled plasma–optical emission spectrometry (ICP-OES) analysis. Wash the
295 precipitates with distilled water and centrifuge it at 10,000 x g for 10 min (discard the supernatant
296 this time). Repeat the washing process 1x more.
297
298 3.2.3. Disperse the product of the previous step in 50 mL of distilled water by gentle sonication
299 in a bath sonicator for 1 h. Dissolve 1 mg of ascorbic acid and heat-stir it at 90 °C for 1 h.
300 Centrifuge the product at 10,000 x g for 10 min, take the precipitates, and discard the
301 supernatant.
302
303 3.2.4. Repeat the washing process 2x more and store the precipitates for characterization
304 purposes.
305
306 3.2.5. Repeat steps 3.2.1 and 3.2.2 for sampling times of 10, 15, 20, 30, 45, 60, 75, 90, 105, and
307 120 min (after turning on the UV lights).
308

3.3. Synthesis of Pt/TiO₂ composite

3.3.1. Add 200 mg of TiO₂ nanoparticles (commercially available, ~100–150 nm in particle size) to 570 mL of distilled water and 30 mL of ethanol and sonicate it with a probe sonicator in an ice-water bath for 1 h.

3.3.2. For a 5 wt.% Pt/TiO₂ composite, add 21 mg of 8 wt.% hexachloroplatinic acid aqueous solution to the prepared suspension and stir it at room temperature for 15 min (for other Pt loadings, calculate the amount accordingly). Repeat step 3.1.2 for the prepared mixture, with four and two UV lamps.

3.4. Sampling Pt/TiO₂ deposition

3.4.1. Repeat section 3.2 for the products of section 3.3 at time intervals of 2.5, 5, 7.5, 10, 20, and 40 min.

3.5. Synthesis of Au/TiO₂ composite

3.5.1. For a 5 wt.% Au/TiO₂ composite, add 345 µL of a 50 $g \cdot L^{-1}$ hydrogen tetrachloroaurate(III) aqueous solution to the product of step 3.3.1 and stir it at room temperature for 15 min (for other Au loadings or other Au sources, calculate the amount accordingly). Repeat step 3.1.2 for the prepared mixture, with four and two UV lamps.

NOTE: Since the gold salt used here was in powder form, we initially prepared a 50 $g \cdot L^{-1}$ hydrogen tetrachloroaurate(III) solution in distilled water.

3.6. Sampling Au/TiO₂ deposition

3.6.1. Repeat section 3.2 for the products of section 3.5 at time intervals of 2.5, 5, 7.5, 10, 20, and 40 min.

4. Sample preparation for characterizations

4.1. For ICP-OES analysis of supernatants, simply filter the liquids with polytetrafluoroethylene (PTFE) syringe filters with a 0.2 µm pore size. For more information on ICP-OES of the solid samples, refer to Ma and Wei[17].

NOTE: When the samples are in solution form, ICP-OES is a very simple and fast technique, but for solid samples, especially for noble metals, it requires multiple microwave digestion processes with aqua regia, hydrogen peroxide, and hydrochloric acid, which makes it very time-consuming (at least 12 h for each sample preparation). Hence, for monitoring the photodeposition rate and process optimization, concentration changes of the metallic cations in the supernatant can be monitored.

353 4.2. For transmission electron microscopy (TEM) imaging, disperse collected precipitates in
354 distilled water (a very dilute suspension) and drop-cast them on TEM grids (or dip-coat the grid
355 into the suspension). For X-ray photoelectron spectroscopy (XPS) analysis, simply drop-cast
356 concentrated dispersions of the precipitates on oxygen-plasma-treated glass substrates and dry
357 them on a hot plate.
358
359 **REPRESENTATIVE RESULTS:**
360 XPS is one of the most powerful techniques for confirming the formation of metallic NPs and
361 study their chemical states. For this purpose, both survey spectra and high-resolution spectra (of
362 Pt_{4f} and Au_{4f}) were recorded, which confirms the complete reduction of the metallic cations and
363 successful deposition of the NNPs (**Figure 3**). For the deconvolution of both Pt_{4f} and Au_{4f}, initially,
364 a Shirley background subtraction was performed. Afterward, the core-level spectra were
365 decomposed into their components with mixed Gaussian/Lorentzian (70% Gaussian and 30%
366 Lorentzian) lines by a nonlinear least-squares curve-fitting procedure, using the XPSPEAK 4.1
367 software. The reduced chi-square value for all the fittings was kept below 0.01. The binding
368 energy separation of the $Pt_{4f7/2}$ and $Pt_{4f5/2}$ peaks was set to 3.33 eV and the intensity ratio
369 between the $Pt_{4f7/2}$ and $Pt_{4f5/2}$ peaks was set to 0.75. Those values for $Au_{4f7/2}$ and $Au_{4f5/2}$ were
370 3.71 eV and 0.78, respectively.
371
372 [Place **Figure 3** here]
373
374 The distribution of the nanoparticles and their morphologies, which have significant effect on the
375 performance of nanocomposite catalysts, have been studied by TEM. These two characteristics
376 are affected by numerous synthesis parameters, but in this work, through the optimization of the
377 illumination dose per exposure (IDE), we have been able to obtain a fairly monodisperse and
378 uniformly distributed NNPs on both of the substrates (RGO and TiO_2) (**Figure 4**).
379
380 [Place **Figure 4** here]
381
382 In the photocatalytic deposition of NNPs, since photoexcited electrons are responsible for the
383 reduction of metallic cations, the reaction progress (NNP loading) can be studied by monitoring
384 the concentration changes of the metallic cations. ICP-OES is one of the most accurate techniques
385 for determining the cations concentration. The direct relation of the PD with IDE is clearly shown
386 in these experiments, which provide significant insights and information for understanding the
387 working mechanism of the developed reactor (**Figure 5**).
388
389 [Place **Figure 5** here]
390
391 Interestingly, by comparing the photodeposition rate (obtained from the ICP-OES results) for
392 different synthesis conditions (**Table 1**), a direct relation between the number of photoexcited
393 electrons and the amount of the deposited NNPs can be demonstrated (see Discussion). The
394 working (deposition) mechanism of the developed reactor is also explained based on this data
395 set.
396

397   [Place **Table 1** here]

398

399   **FIGURE AND TABLE LEGENDS:**

400

401   **Figure 1: The fabricated photocatalytic deposition reactor.** (**A**) The reactor. (**B**) Inside the
402   illumination chamber. (**C**) A quartz tube with 5 cm x 1 cm illumination exposure length.

403

404   **Figure 2: Schematic illustration of the photocatalytic deposition reactor.** T_1 is the N_2 gas outlet
405   that goes into the bubbler. T_2 is the sampling tube and Ps is the point for attachment of the
406   syringe (for sampling). V_0 is the initial feeding valve and V_1 and V_2 are the sampling and tube
407   evacuation valves (after sampling), respectively.

408

409   **Figure 3: XPS survey spectra.** Spectra for the (**A**) Pt/graphene composite, (**B**) Pt/TiO_2 composite,
410   and (**c**) Au/TiO_2 composite. Deconvoluted spectra for (**D**) Pt_{4f} in the Pt/graphene composite, (**E**)
411   Pt_{4f} in the Pt/TiO_2 composite, and (**F**) Au_{4f} in the Au/TiO_2 composite.

412

413   **Figure 4: TEM images.** (**A**) Pt/graphene composite produced by a 1 cm x 50 cm exposure tube
414   (this figure has been modified from Abdolhosseinzadeh et al.[12]. (**B**) Au/TiO_2. (**C**) Pt/TiO_2. (**D**) Effect
415   of a high IDE in the formation of large particles and the depletion of its surroundings in
416   Pt/graphene composite. The mean particle sizes for panels **A**, **B**, and **C** are 1.75, 3.8, and 3.77,
417   respectively.

418

419   **Figure 5: Concentration changes of the metallic cations during the PD in the developed reactor**
420   **with various IDEs.** Changes in (**A**) Pt/graphene, (**B**) Au/TiO_2, and (**C**) Pt/TiO_2.

421

422   **Table 1: Slope values of linear fits to cation concentration changes obtained from ICP-OES**
423   **analysis.**

424

425   **DISCUSSION:**
426   Nanoparticles are the most widely used form of noble-metal-based catalysts. In almost all cases,
427   NNPs are deposited either on a conductive or a semiconductive support material. This
428   hybridization is mostly done by the reduction of the cations of the noble metal in the presence
429   of the intended substrate (material). Hence, a successful synthesis method for the production of
430   NNP-based nanocomposite should meet at least two main requirements: 1) the reduction of the
431   cations should be efficient and complete; 2) the deposition rate, location, and amount should be
432   controllable. In this work, we have demonstrated that the developed reactor (and synthesis
433   method) can successfully address both of the aforementioned requirements.

434

435   The XPS survey spectra (**Figure 3**) clearly demonstrated the successful deposition of Pt and Au on
436   RGO and TiO_2 (a conductive and a semiconductive material). Deconvolution of the high-
437   resolution Pt_{4f} and Au_{4f} peaks revealed no nonmetallic components, which verifies that the
438   photocatalytic reduction method with both PRGO and TiO_2 can completely reduce the Pt^{4+} and
439   Au^{3+} to Pt^0 and Au^0, respectively. Considering the deposition yield and required time for it (**Figure**
440   **5**), the output of this method is comparable with (or even better than) most of the conventional

441   NNP deposition methods (i.e., polyol method[18]).

442

443   As mentioned earlier, since photoexcited electrons (produced by the substrate itself) reduce the
444   metal cations in a PD reaction, NNPs only form on the substrate, which allows researchers to
445   control the deposition location (not everywhere in the suspension). Furthermore, thanks to the
446   unique pulsed excitation of the substrate (photocatalyst), both nucleation and growth can be
447   controlled. This is mainly due to the fact that, by limiting the exposure time (and/or UV light
448   intensity), a very small and controlled amount of photoexcited electrons are produced in a
449   specific location on the substrate. These electrons have a short lifetime and, due to the poor
450   conductivity of the photocatalyst (semiconductor), cannot move too far from the location that
451   was generated there. Hence, in order to form a stable nucleus which should possess a minimum
452   radius, a specific number of electrons should be generated in one excitation pulse (exposure).
453   This implies that a minimum IDE (exposure length and/or UV light intensity) was required to
454   initiate the PD in the reactor, which can explain the unsuccessful Pt deposition on PRGO with the
455   5 cm x 0.4 cm exposure tube (**Figure 5A**, negligible concentration changes). Similar behavior was
456   observed when using very low IDEs for TiO_2-based composites (corresponding data are not
457   provided here). This is mainly due to the fact that the critical IDE value for the formation of stable
458   nuclei is directly related to the quantum yield (since it is usually hard to measure the absolute
459   quantum yield, apparent quantum yield can also be used[19]) of the photocatalyst material (0.36%–
460   0.41% for PRGO and 0.97%–1.1% for TiO_2).

461

462   When the number of photoexcited electrons (per exposure) are larger than the value needed for
463   a stable nucleus formation, as shown in **Figure 5** and **Table 1**, the photodeposition rate
464   (monitored by ICP-OES) has a linear relation with the exposure time and UV light intensity. Even
465   when comparing the Au/TiO_2 and Pt/TiO_2 systems, since Pt^{4+} needs one more electron than Au^{3+},
466   the photodeposition rate is higher (1.46) for Au/TiO_2 (the expected ratio is 4/3 = 1.33). It should
467   be mentioned here that in some cases, the obtained PD rate ratios have slight differences with
468   the expected values (especially for Pt), which is probably due to the fact that the proposed simple
469   model for the nucleation and growth in the PD systems presented here is not completely valid in
470   multi-electron reductions, and other parameters should also be taken into account. At the final
471   stages of the PD in all the systems (**Figure 5**), an abrupt change in the deposition rate has
472   happened, which implies that a significant change in the deposition process has occurred. This is
473   due to the fact that in the proposed model, it was assumed (but not specifically stated) that for
474   each photogenerated electron, a metallic cation will be available immediately to consume it,
475   which is apparently not the case when concentrations of the metal cations fall below a specific
476   value (the diffusion of the cations should also be taken into account).

477

478   Since this deviation from the linear behavior occurs in low concentrations, where the major part
479   of the cations is deposited, and the deposition of the remaining cations will require much more
480   time, it is reasonable to conduct the PD in the linear region and recover the remaining cations
481   from the solution by the well-developed hydrometallurgical extraction methods[20]. In this case,
482   the developed reactor can operate in a continuous manner and the desired product can be
483   collected (taken out of the reactor) after a known period of circulation. It is also possible that, by
484   increasing the reactor length, by using either multiple parallel tubes or spring-like tubes, the

precursors can enter the reactor from one side and the products can exit from the other side.

Considering the aforementioned discussions, it is clear that by minimizing the IDE (but keeping it higher than the critical value needed for the formation of the nuclei), researchers can get small monodisperse particles with a uniform distribution, but the production time will also increase significantly. For instance, as also shown in **Figure 6**, the time required for obtaining the same amount of Pt loading in the Pt/graphene system when using the 5 cm x 2 cm and 1 cm x 50 cm tubes is approximately five times longer (in the linear region). On the other hand, by increasing the IDE (either the exposure length or the UV light intensity), growth will dominate the nucleation (similar to the conventional PD methods) and large particles will form. In very high IDEs, as described earlier, a formed particle may suck the electrons from its vicinity (since it has a better conductivity) and disfavor the formation of other nuclei around it. In this case, the particle grows enormously, and the particle size distribution of the final product will be very wide (**Figure 4D**). This phenomenon is more problematic in high quantum-yield photocatalysts (comparing TiO_2 with PRGO), and proper IDE adjustment is more challenging. As a result, shorter exposure lengths and a lower illumination dose (number of the UV lamps) are used for TiO_2-based composites and still, as can be seen in TEM images, the graphene-based composite has a better monodispersity than the two other TiO_2-based composites. Hence, the IDE should be carefully optimized to get the highest quality product with the highest yield. The results and discussions presented here clearly demonstrate the potential and abilities of the developed reactor for a precisely controlled synthesis of NNP-based catalysts (on both types of substrates) on a large scale and in a continuous manner.

DISCLOSURES:
The authors have nothing to disclose.

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Figure 1

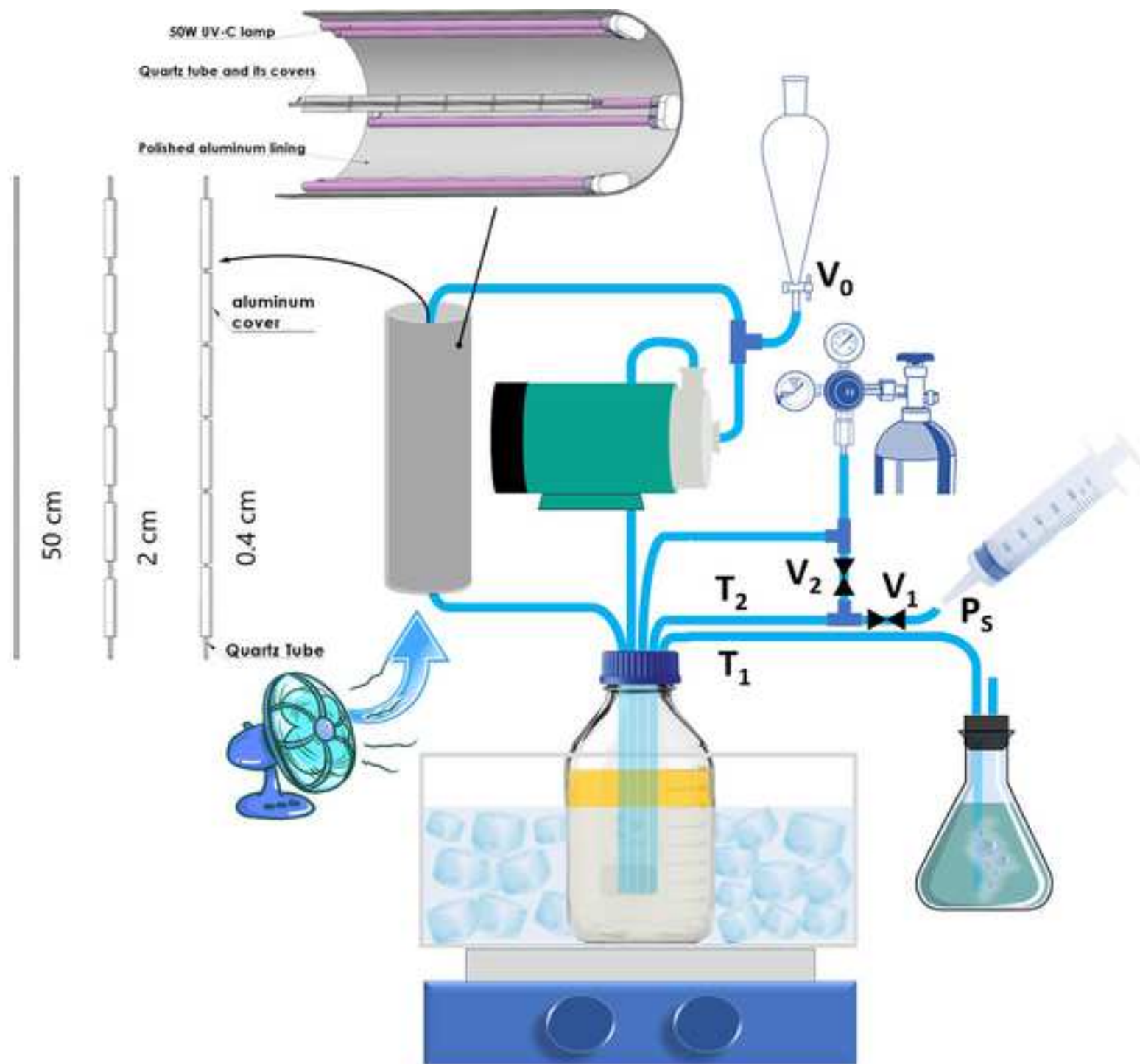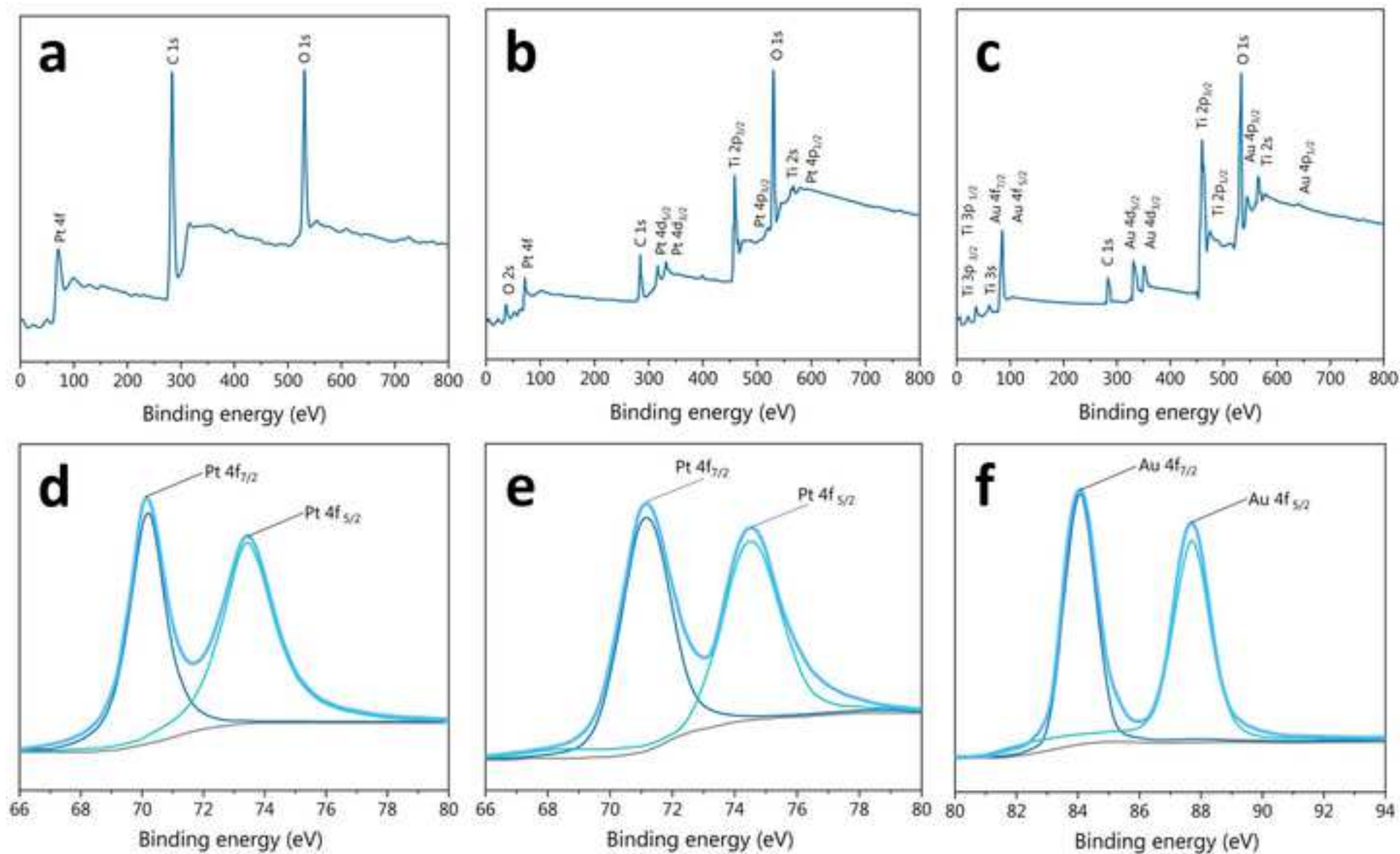Figure 2 Click here to access/download;Figure;Figure 2.psd
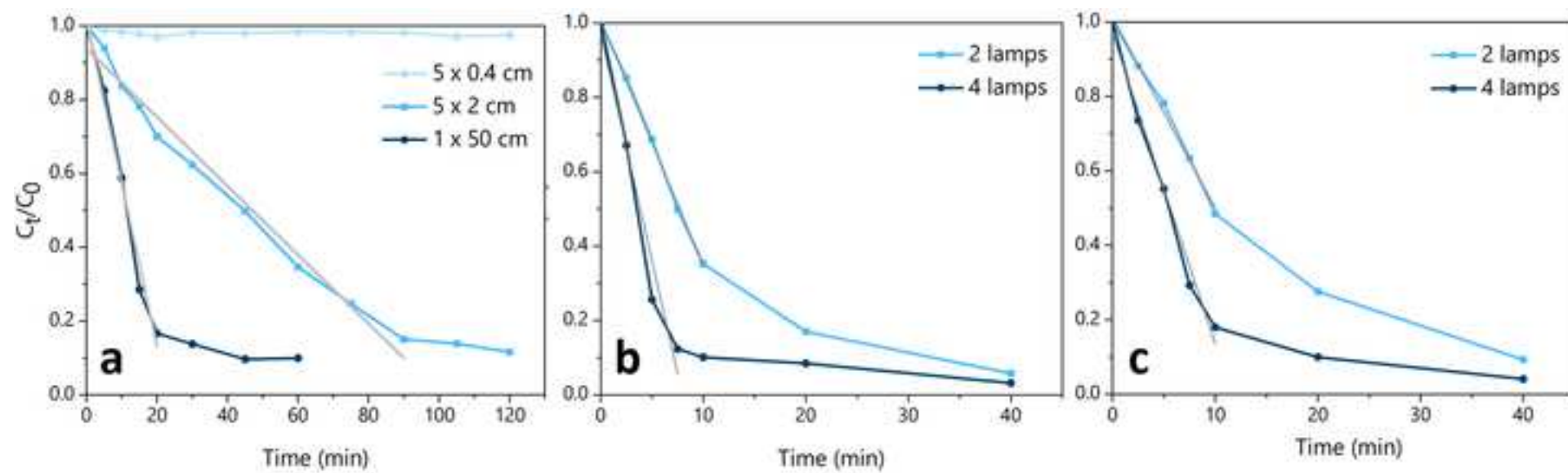

Figure 2

Figure 3

Figure 4

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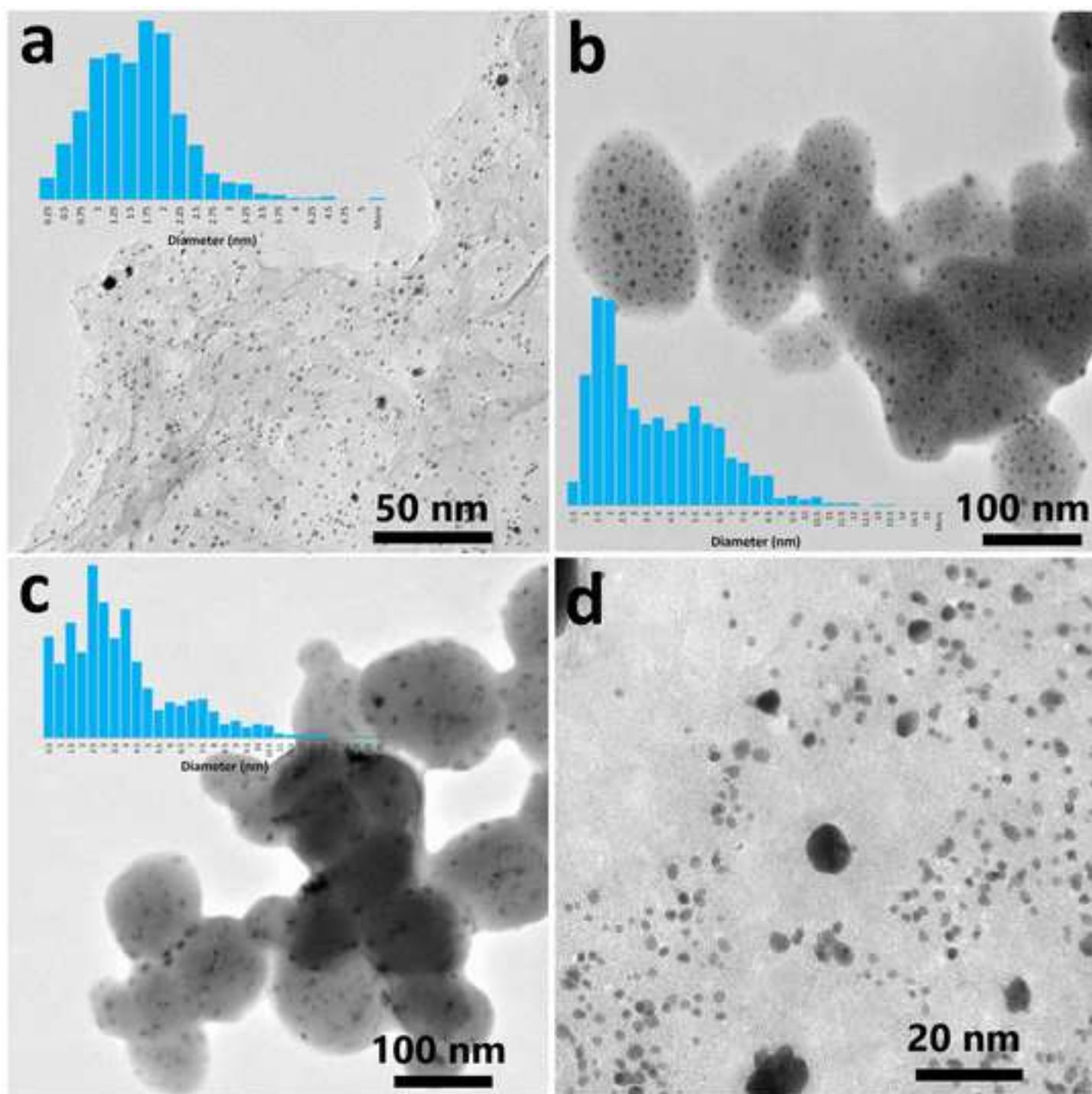
Figure 5

Table 1

System	Pt/graphene	Pt/graphene	Pt/graphene	Au/TiO2	Au/TiO2
Condition	5 x 0.4 cm	5 x 2 cm	1 x 50 cm	2 lamps	4 lamps
Slope in the linear region	~0	-0.00932	-0.04412	-0.066	-0.12179

Pt/TiO2	Pt/TiO2
2 lamps	4 lamps
-0.05112	-0.08332

Table

Name of Material/ Equipment	Company
Chloroplatinic acid solution	Sigma Aldrich
Hydrogen tetrachloroaurate(III) hydrate	Alfa Aesar
TiO2 Nanopowder (TiO2, anatase, 99.9%, 100nm)	US research nanomaterials
Graphite flakes	Sigma Aldrich
Sulfuric acid	Sigma Aldrich
Hydrogen peroxide	Sigma Aldrich
L-Ascorbic acid	Sigma Aldrich
Hydrochloric acid	Sigma Aldrich
Sodium hydroxide	Sigma Aldrich
Potassium permanganate	Merck
Corning® Silicone Septa for GL45 Screw Cap	Sigma Aldrich (Corning)
Polyvinyl chloride pipe	Koctas
Fuded silica (Quartz) tube	Technical Glass Products
UV−C lamps	Philips

Catalog Number	Comments/Description
262587-50ML	
12325.03	
US3411	
332461-2.5KG	
1120802500	
H1009-100ML	
A92902-500G	
320331-2.5L	
S5881-1KG	
1050821000	
CLS139545SS	
	UV-Reactor casing
TUV PL-L 55W/4P HF 1CT/25	

Name of Material/ Equipment	Company
Chloroplatinic acid solution	Sigma Aldrich
Corning Silicone Septa for GL45 Screw Cap	Sigma Aldrich (Corning)
Fuded silica (Quartz) tube	Technical Glass Products
Graphite flakes	Sigma Aldrich
Hydrochloric acid	Sigma Aldrich
Hydrogen peroxide	Sigma Aldrich
Hydrogen tetrachloroaurate(III) hydrate	Alfa Aesar
L-Ascorbic acid	Sigma Aldrich
Polyvinyl chloride pipe	Koctas
Potassium permanganate	Merck
Sodium hydroxide	Sigma Aldrich
Sulfuric acid	Sigma Aldrich
TiO2 Nanopowder (TiO2, anatase, 99.9%, 100nm)	US research nanomaterials
UV−C lamps	Philips

Catalog Number	Comments/Description
262587-50ML	
CLS139545SS	
332461-2.5KG	
320331-2.5L	
H1009-100ML	
12325.03	
A92902-500G	
	UV-Reactor casing
1050821000	
S5881-1KG	
1120802500	
US3411	
TUV PL-L 55W/4P HF 1CT/25	

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Dear Dr. Steindel,

We truly appreciate your kind efforts for reviewing and evaluating our manuscript. Your constructive and valuable comments have been implemented in the submitted revised manuscript. We have done our best to address all your concerns, but any additional improvement or correction will be appreciated as well.

Thank you for your kind attention,
Best regards,
Selmiye Alkan Gursel

Professor of Materials Science and Engineering,
Faculty of Engineering and Natural Sciences
Sabanci University,
Istanbul, 34956, Turkey
Tel: +902164839573
Fax: +902164839550
Email: selmiye@sabanciuniv.edu

---

1. 1: Some more details on the reactor setup should be added; e.g., how exactly are T1 and T2 attached to the bottle? How exactly is the quartz tube fixed inside the illumination tube? Please also include materials used here in the Table of Materials.

Previous sentences were revised, and more accurate descriptions were added from line 127 to 128 and 154 to 155. Table of Materials was updated.

---

2. 3.1.2/3.2.1: What exactly are the gas flows in these steps?

The following sentience was added from line 270 to 275.

"The N_2 gas flow has no effect on the synthesis process itself and hence, has no specific value. However, it is continuously applied to maintain a positive pressure inside the system and avoid O_2 penetartion. Bubble formation at endpoint of the T_1 tube inside the water filled Erlenmeyer is the only requirement for the flow adjustment."

---

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4. Figure 2: Please explain V0, T1, etc. in the Figure legend.

Corresponding explanations were added to the figure legend.

---

5. Figure 4: Please explain the distributions in the Figure legend. Also, do you have a distribution for 4d?

Corresponding explanations were added to the figure legend. Figure 4d is provided as an undesirable synthesis condition and hence including particle distribution curves does not seem to be very appropriate.

---

6. Figure 5: Please explain how the lines were fit and how well they fit (e.g., R-squared; possibly in Table 1 instead).

Corresponding fitting data were added to the manuscript from line 350 to 357.