Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supplementary information for

UV-induced syntheses of surfactant-free precious metal nanoparticles in alkaline methanol and ethanol

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1. Experimental Section

Pt nanoparticle synthesis

For the synthesis of the Pt nanoparticles the mono-alcohol synthesis was used. Unless otherwise specified the nanoparticles were obtained using 2 mM $H_2PtCl_6 \cdot 6H_2O$ (99,9 % Alfa Aesar) in alkaline NaOH (98.9%, Fisher Chemical) methanol (≥ 99.8 %, Sigma-Aldrich) or ethanol (99.9 %, Kemetyl) at a concentration indicated in the text and for a volume of typically 3 mL.
The reaction mixtures were placed in quartz cuvettes and placed in home-built container equipped with controllable cooling system (T max = 40 °C) and 10 standard UV mercury lamps (PL-L- 24 W/10/4P Hg, Philips) for 2 hours (unless otherwise specified).

Ir nanoparticle synthesis

It is important to note that regardless of the approach chosen, the size of the nanoparticle evaluated by TEM was always in the range 1.0-1.7 nm without clear size control.

For the Ir nanoparticle synthesis a homebuilt UV set-up was used. In a typical experiment four UV-C lamps (TUV PL-S 9W/2P, Philips) were placed around a double jacket Quartz glass reactor. 4.4 mM Ir ($IrCl_3$, 99.8 %, Alfa Aesar; H_2IrCl_6, 99.9%, Stream Chemicals; Na_2IrCl_6, ≥ 99.9 %, Acros Organics), NaOH (0, 22, or 44 mM; from pellets, Hänseler), and Millipore water (0, 10, or 25 %) in ethanol (100 %, VWR) or methanol (≥ 99.8 %, Fisher Chemicals) were used. The reactor was closed with a septum to enable the introduction of gas (for 90s; 5% H_2 in Ar) into the reaction mixture to obtain a hydrogen/argon saturated atmosphere before the reduction. The reaction mixture was stirred with a magnetic stirring bar. The temperatures of 10, 20 or 40°C of the reactor were controlled by a continuous water flow through the double jacket. The inside of the set-up was cooled down by ventilation. Pictures were taken of the reaction mixture in the reactor before the reduction and then by interrupting the irradiation for less than 1 min and disconnecting the water cooling tubes after 10 minutes up to 24 h.

For the interest of the reader we detail here our attempts to perform seed mediated growth. Experiments were performed in ethanol and methanol to attempt increase the nanoparticle size by the deposition of fresh monomer on pre-formed seeds as summarized in **Table S1** and detailed below.

Table S1: Overview of the performed seed-mediated growth experiments concerning the seed and monomer solution, as well as the treatment of the mixture for the different solvents.

Solvent	Seed	Monomer	Treatment
Methanol	S1: MW, NaOH S2: UV, NaOH, H_2	M1: UV, NaOH	M1: no UV, no H_2 M2: no UV, H_2 M3: UV, no H_2 M4: UV, H_2
Ethanol		M2:no NaOH M3: NaOH	

$IrCl_3$ precursor (monomer) was added to 1 mL of pre-formed nanoparticles (seeds). The seeds were synthesized (S1) with 4.4 mM $IrCl_3$ and 44 mM NaOH heated for 3 min at 160 °C using a microwave (MW) reactor (CEM Discover SP, 100 W) or (S2) by 1h UV-C irradiation at 20°C (90 s H_2 in Ar). The monomer in methanol (green solution detailed below) was formed by (M1) reducing 4.4 mM $IrCl_3$ and 44 mM NaOH at 20°C for 1 h under UV-C light. As monomer sources in ethanol, (M2) 1 mL of 8.8 mM $IrCl_3$ or (M3) 2 mL of 4.4 mM $IrCl_3$ and 44 mM NaOH were used. The mixtures were afterwards treated in different ways. In the thermal treatments the mixtures were kept for 6h at 40°C (T1) without or (T2) with H_2 (5% in Ar, 90s) pre-treatment. In the UV light treatments, the mixtures were irradiated for 1h at 20°C with UV-C light (T3) without or (T4) with or H_2 (5% in Ar, 90s) introduced before synthesis.

FTIR characterization

The as-synthesised colloidal solutions were characterized by FTIR absorption spectroscopy. The colloidal suspensions in alkaline mono-alcohol were placed in a cell allowing to record IR absorption spectra of liquid in an attenuated total reflectance mode. Infrared spectra were captured using a Nicolet 6700 FT-IR (Thermo Electra Corporation) with a zinc selenide prism. All spectra were recorded with a resolution of 4 cm^{-1} and averaging over 100 scans. Background spectra of methanol or ethanol were measured and subtracted from the spectra recorded for the colloidal suspension. The difference spectra are reported.

Gas-chromatography coupled to mass spectroscopy (GC-MS) characterization

Head-space GC-MS was used to charaterise possible low boiling point species formed during the nanoparticle formation. A headspace sampler (Agilent G1888 Network Headspace Sampler) connected to a GC (Agilent 6890N Network GC System) equipped with an Agilent 19091S-433 non-polar column (HP-5ms (5%-phenyl) methyl poly siloxane, 30.0 m, 250 µm, 0.25µm) was connected to a mass spectrometer (Agilent 5973 inert Mass Selective Detector). Chromatographs were acquired with a ramp from 30 to 140 °C at 20 °C min^{-1}.

TEM characterization

For TEM the Pt nanoparticles were washed and re-dispersed in pure methanol or ethanol, the Ir nanoparticles (or reaction mixtures) were used as prepared without washing. Small drops of colloids then were placed on carbon coated copper grids (300 mesh grids, Quantifoil) and dried in room conditions. TEM images were taken using a Jeol 2100 microscope operated at 200 kV. Samples were characterized by taking images at different magnification (at least 3) in different areas (at least 3) of the TEM grids and the size analysis was performed by measuring the size of at least 100 nanoparticles.

Fluorescence measurements

In all cases the samples were first diluted to a suitable concentration before spectroscopic measurements (typically 0.1 mM of metal precursor). An excitation wavelength of 360 nm was used with a Cary Eclipse fluorescence spectrophotometer (Agilent Technologies). Reported spectra are not corrected for detector response to different wavelengths.

2. Results

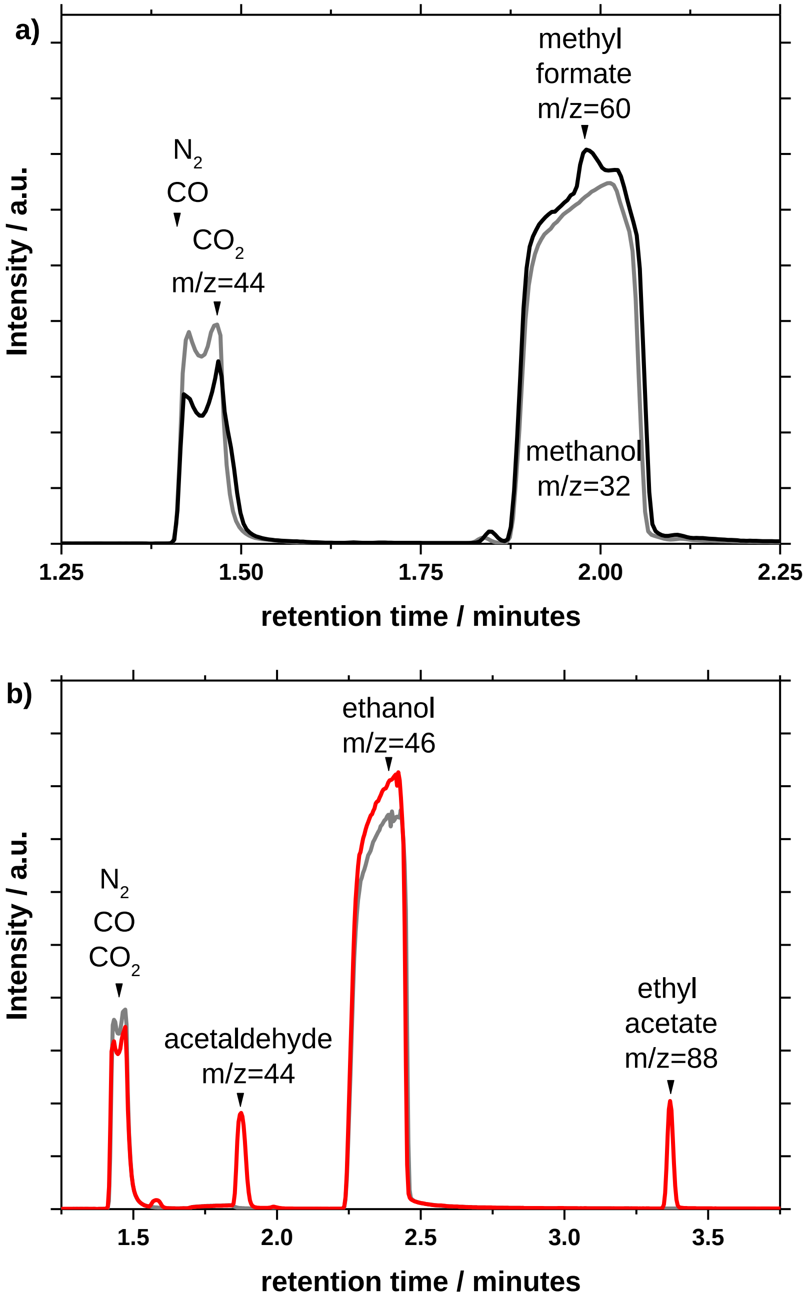

Fig. S1. Head space GC-MS chromatographs of (a) methanol (grey) and H_2PtCl_6 in alkaline methanol after UV irradiation (black) and (b) ethanol (grey) and H_2PtCl_6 in alkaline ethanol after UV irradiation (red).

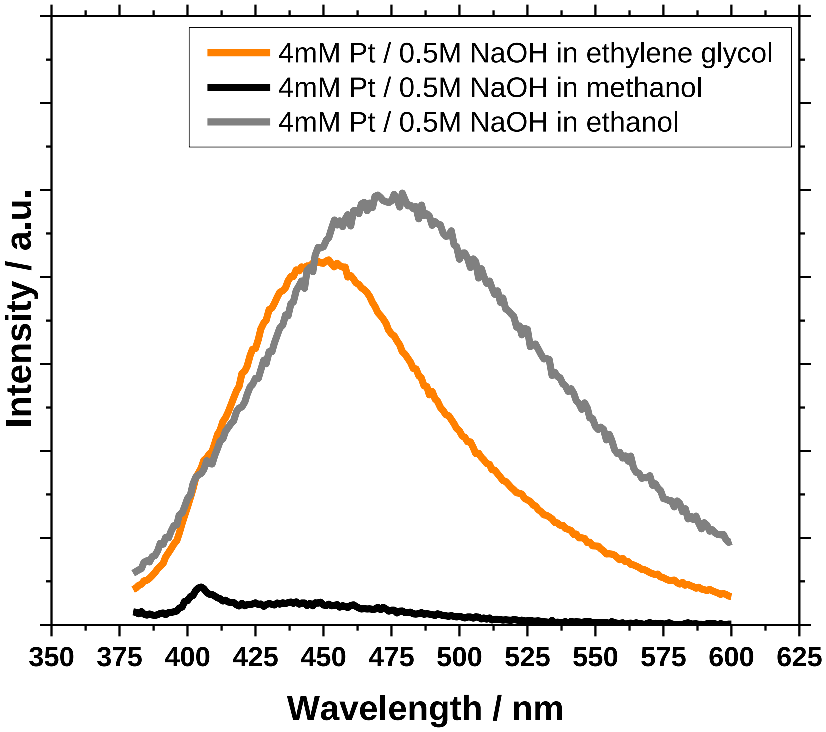

Fig. S2. Fluorescence spectra of alkaline solution of H_2PtCl_6 in different solvents after irradiation for a same period of time by UV light. The precursor used was H_2PtCl_6 and the concentration indicated are the final concentrations in the reaction mixture. Excitation wavelength of 360 nm. Emission peak around 410 nm correspond to Raman scattering from the solvent.

The formation of fluorescent species can be attributed to side reaction of the solvent with NaOH and formation for instance of carbon dots[1] or polymers for instance by aldol condensation in alkaline ethanol. The formation of fluorescent by-products is not observed in methanol.

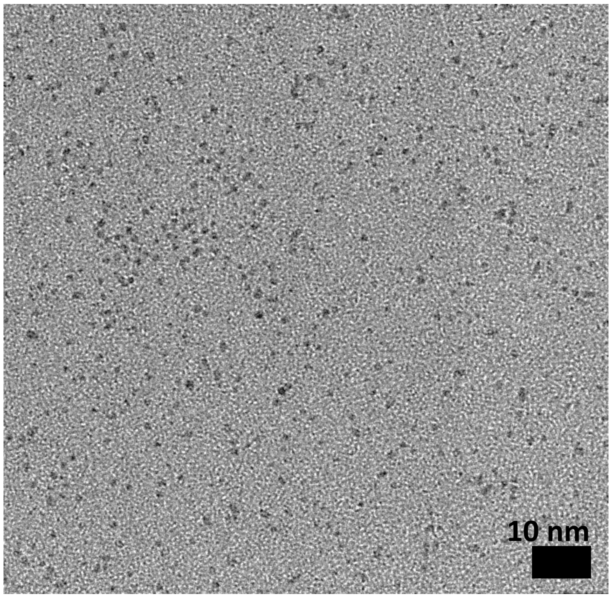

Fig. S3. TEM micrograph representative of Ir NPs obtained using UV-light.

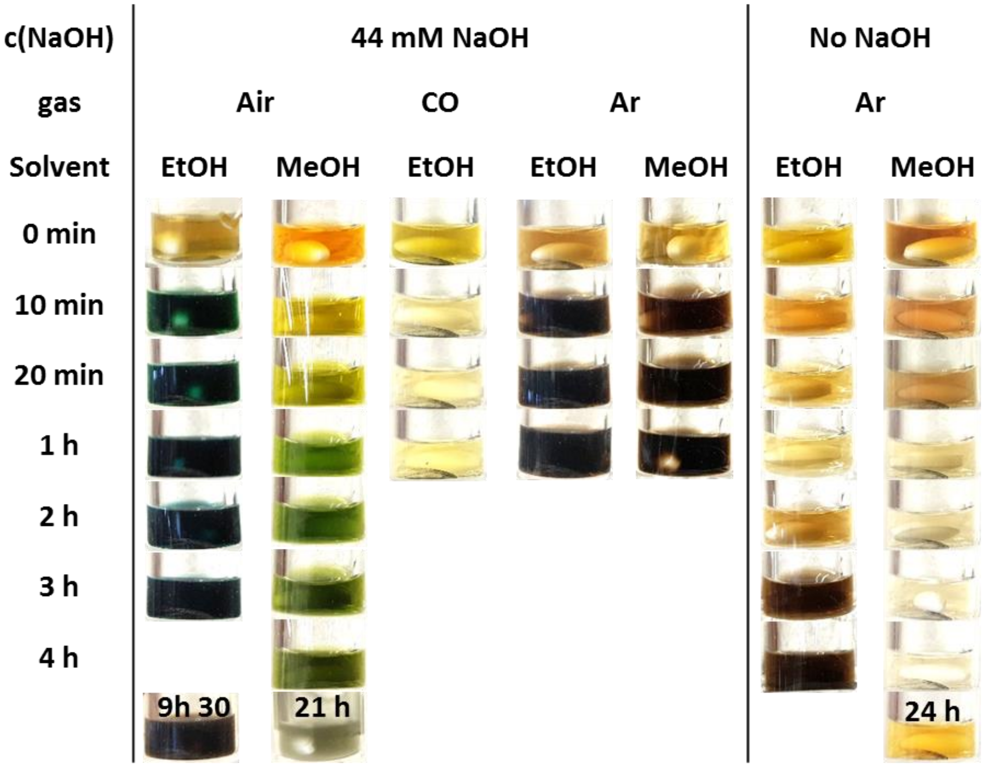

Fig. S4. Photos of the synthesis mixtures and nanoparticle dispersions under different conditions using 4.4 mM H_2IrCl_6 as precursor is ethanol and methanol before the reduction (0 min) and after 10 min to 24 h irradiation with UV-C light.

References

1. Gao, X. H.; Lu, Y. Z.; Zhang, R. Z.; He, S. J.; Ju, J.; Liu, M. M.; Li, L.; Chen, W., One-pot synthesis of carbon nanodots for fluorescence turn-on detection of Ag+ based on the Ag+-induced enhancement of fluorescence. *Journal of Materials Chemistry C* **2015,** *3* (10), 2302-2309.