

Quantum photoinitiators –Novel photoinitiators for water-based and solvent-free photocuring

Nir Waiskopf, Shlomo Magdassi & Uri Banin

Institute of Chemistry and the Center for Nanoscience and Nanotechnology,
The Hebrew University of Jerusalem, Jerusalem, Israel

E-mail: waiskopf@gmail.com; uri.banin@mail.huji.ac.il

Introduction

The discovery of nanomaterials and their entrance into research and industry a few decades ago has opened a new world of materials with exciting properties and capabilities. Among the materials that were developed, is the intriguing family of semiconductor nanocrystals, with dimensions of few to tens of nanometers. Such nanocrystals manifest quantum confinement effects bridging the bulk to the molecular characteristics of their composing elements. This allows unprecedented tuning of their traits by changing their size and dimensionality.

Absorption of light by semiconductor materials, results in the excitation of an electron from the valence band, to the higher energy conduction band, leaving behind an absence of an electron, a hole. These two charge carriers, the electron and hole, can later recombine, emitting a photon with the characteristic bandgap energy, or alternatively, be transferred and take part in diverse redox reactions. In comparison to the bulk, the presence of the charge carriers in the small finite size of the nanocrystal results in quantum confinement effects, similar to what is known as the particle in a box model. As the nanoparticles become larger, their bandgap becomes smaller, resulting in red-shift of their absorption and emission spectra accompanied by lower redox potential.

The exceptional qualities of semiconductor nanocrystals have already led to their implementation as light-emitting components in displays and as fluorescent agents for tagging of biomolecules.^{1,2} Along with the development of these applications, the advantages in using quantum materials versus organic molecules have been repeatedly demonstrated, including enhanced photochemical stability, high light sensitivity for single and two-photon absorption, high efficiency, etc.³ Furthermore, the nanocrystals met industrial demands, such as cost-effective and a scale-up capacity, opening the path for the commercialization of these colloidal quantum materials also in new markets.

Recently, suitably designed colloidal quantum materials have been demonstrated as efficient photocatalysts for reactive species formation while in tandem, they were capable to consume molecular oxygen, laying the foundations for their use as a new family of efficient photoinitiators for the

photocuring industry. Herein, we discuss these quantum photoinitiators (PIs) and the unique advantages they offer for coatings, UV inks, and 2&3D printing.

Quantum PIs

Semiconductor nanoparticles can be synthesized by diverse routes to yield the desired composition and dimensionality. Figure 1a,b presents an electron microscopy image of Quantum PI prepared in high-temperature batch reactor (up to 280⁰C) and the ability to tune the absorption spectra of these photoinitiators by changing their size through modification of the reaction time and conditions. The TEM image, in Figure 1a, displays rod-shaped quantum PIs with all their dimensions in the nano-regime (diameter of 4.5±0.5 nm, length of 20±3 nm). This nanosize range minimizes the migration of quantum PI and increase their absorption cross-section, which is manifested in a 3-4 orders of magnitude higher light-sensitive in comparison to conventional organic PIs. The latter is emphasized in Figure 1b, comparing the absorption spectra and y-axis scales for quantum PIs and traditional organic photoinitiator (dark green, right y-axis). The quantum PIs also show broad absorption spectra, starting with an onset, determined by their diameter, and up to the deep-UV range making them highly compatible with the emerging near-UV LED light sources as well as with traditional excitation light-sources such as mercury lamps. Moreover, in formulations comprising additives which absorb in some specific wavelengths, the use of such quantum PI allows to still polymerize in a small excitation window without changing the photoinitiator.

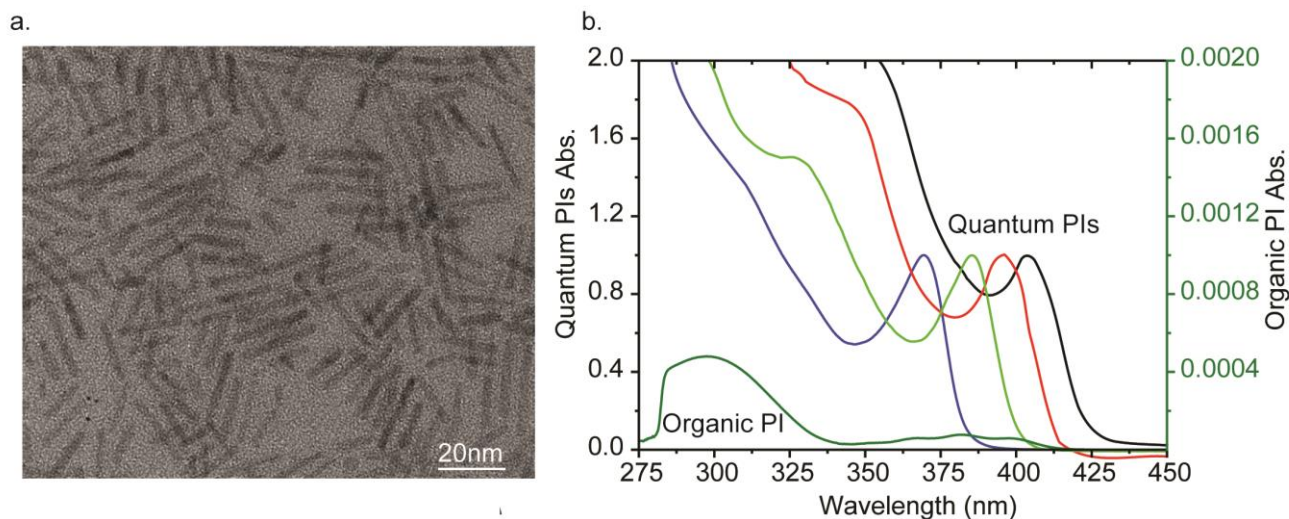


Figure 1. a. Transmission electron microscopy image of quantum PIs with a nanorod morphology. b. Absorption spectra of quantum PIs with different sizes and a widely used organic photoinitiator (dark green). The quantum PIs have a broad and tunable absorption spectra ranging from the blue VIS range to the deep UV. Upon increasing the nanoparticle size, the absorption spectrum is shifted to longer wavelengths. Additionally, quantum PIs have 3-4 orders of magnitude higher light sensitivity compared to organic molecules, as can be seen comparing the absorbance for the quantum PIs (left scale) to that of the organic PI (right scale).

The quantum PIs were found to exhibit significant dual photocatalytic activity of reactive species formation and oxygen consumption.⁴⁻⁷ Figure 2. presents a kinetic measurement of oxygen consumption in water upon illumination on two types of quantum PIs, semiconductor nanorods (NRs) and hybrid semiconductor-metal nanoparticles (HNPs), as measured by polarography.⁷ Alongside with the fast consumption of oxygen, the same quantum PIs were found to produce a significant amount of hydroxyl radicals by oxidation of water and hydroxide. Figure 2b presents kinetic measurements of hydroxyl radical formation by the two types of quantum PIs, performed using a fluorometric assay that monitors the oxidation of terephthalic acid (TPA) to a fluorescent 2-hydroxyterephthalate. Control experiment with ethanol as hole acceptor and hydroxyl radical scavenger prevented this reaction (orange).⁷ While both systems show catalytic activity, a significant difference in their performances can be seen. The same trend was reported also for photocatalytic hydrogen generation by water reduction and was attributed to the better charge separation in semiconductor-metal hybrid systems.⁸⁻¹⁰ However, it is important to note, specific catalytic reactions may require different properties⁴ raising the need for knowhow to optimize the quantum PI (e.g. their size, shape, composition) for specific applications.

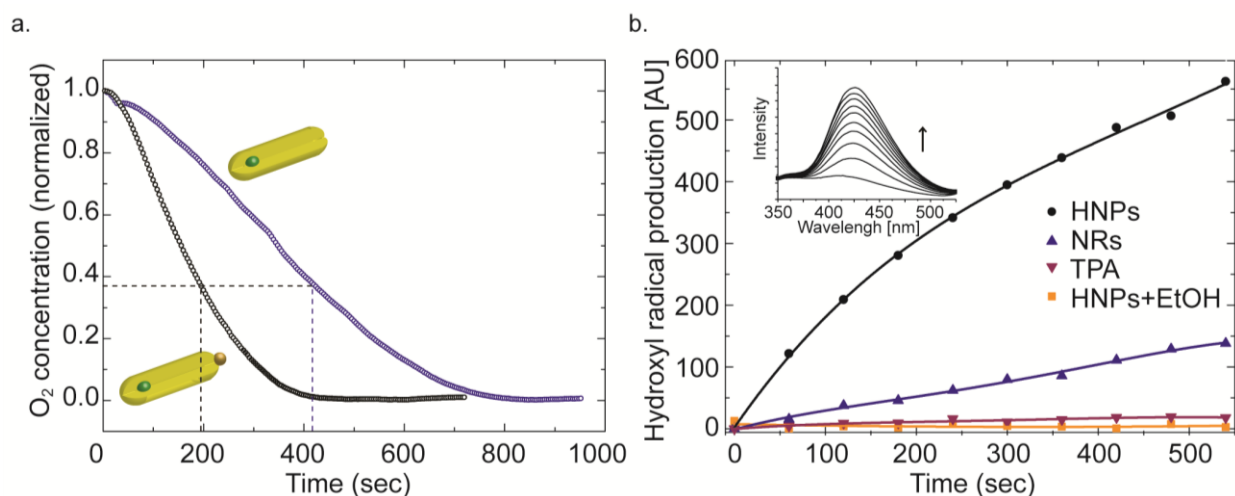


Figure 2. a,b Kinetic measurement of oxygen consumption and hydroxyl radical formation in water by two types of quantum PIs. Reprinted with permission from Waiskopf N. et al., *Nano Lett.* 2016, 16, 7, 4266-4273.⁷ Copyright (2016) American Chemical Society.

Besides the nanocrystals themselves, their surface coating, which can vary between, bare, organic and/or inorganic capping, also play an important role. This coating determines the solubility, stability, and activity of the nanocrystals in different formulations.^{5,11,12} Likewise, the ability to engineer the surface of the nanocrystals by polymer encapsulation, by ligand exchange or by ligand stripping procedures along with the capacity to functionalize the surface to introduce extra features, provides additional knobs for controlling quantum PIs, beyond those available for traditional organic photoinitiators.

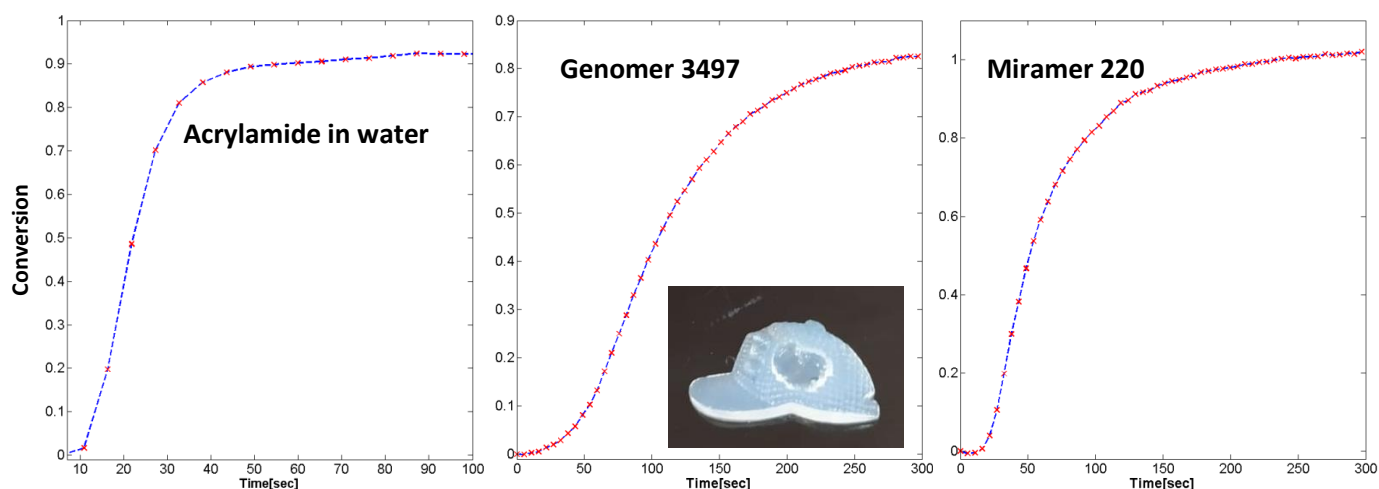


Figure 3. Conversion curves for the polymerization of acrylamide in aqueous formulation and of Miramer 220 and Genomer 3497 in solvent-free formulations using quantum PIs, left and right, respectively. The conversions were calculated based on the opening of the double bond in 988 cm^{-1} or 810 cm^{-1} normalized to internal standards, such as the carbonyl stretch peak at 1654 cm^{-1} or the ether signal at 1096 cm^{-1} .

Organic photoinitiators absorb the light and utilize its energy to break an internal chemical bond to produce the reactive species, whereas quantum PIs employ the energy to convert molecules from their surrounding into radicals. Figure 4 illustrates schematically the unique mechanism of action for quantum PIs in water, which provides a dual effect that includes both reactive species formation through oxidation of water, and simultaneously reducing oxygen to additional reactive species, thus limiting the undesired oxygen retardation effect.¹³

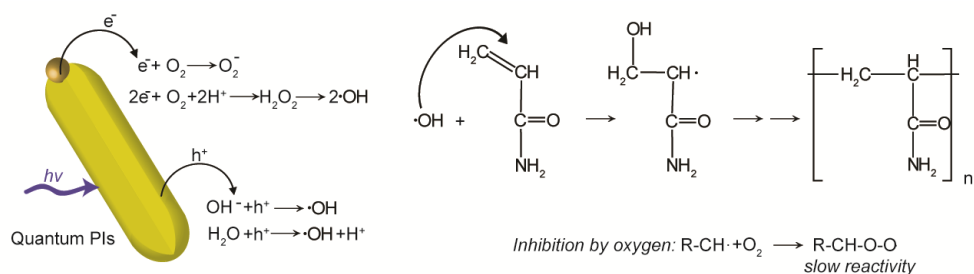


Figure 4. Quantum PIs mechanism of action, includes catalytic production of reactive species as well as consumption of molecular oxygen, a known polymerization retarder. Reprinted with permission from Pawar A.A. et al., *Nano Lett.* 2017, 17, 7, 4497-4501.¹³ Copyright (2017) American Chemical Society.

The distinct inherent mechanism of action, between quantum PIs and organic photoinitiators, plays a crucial role and is responsible for the differences between their characteristics. First, the quantum PIs catalytic activity along with their high light sensitivity enables using much lower concentrations compared to organic photoinitiators. This is demonstrated in Figure 5a which shows significant solvent-free polymerization of hydroxyethyl acrylate with two types of quantum PIs compared to limited polymerization using the same concentration of a widely used organic photoinitiator.⁶ Second, quantum

PIs are much more thermally stable compared to organic photoinitiators. Figure 5b presents thermogravimetric measurement with bare quantum PIs, which in comparison to organic PIs, shows almost no change in the weight percent up to elevated temperatures (black). This results from the inorganic crystal nature of quantum PIs. Yet, when using coated quantum PIs, similar measurements may show weight loss, as can be seen in the red curve. In these cases, the onset temperatures for the weight loss are usually slightly higher than those seen for control samples of free ligands. The thermal stability of the quantum PIs is also manifested in shelf-stability measurements. Figure 5c shows similar FTIR spectra for a formulation of quantum PIs, acrylamide and SR9035 in water, before and after 72hr at 70°C. In comparison to organic molecules wherein the energy for breaking the bond can be provided by means other than photons, such as temperature, nanocrystal are more robust and hence outperform in shelf-stability tests.

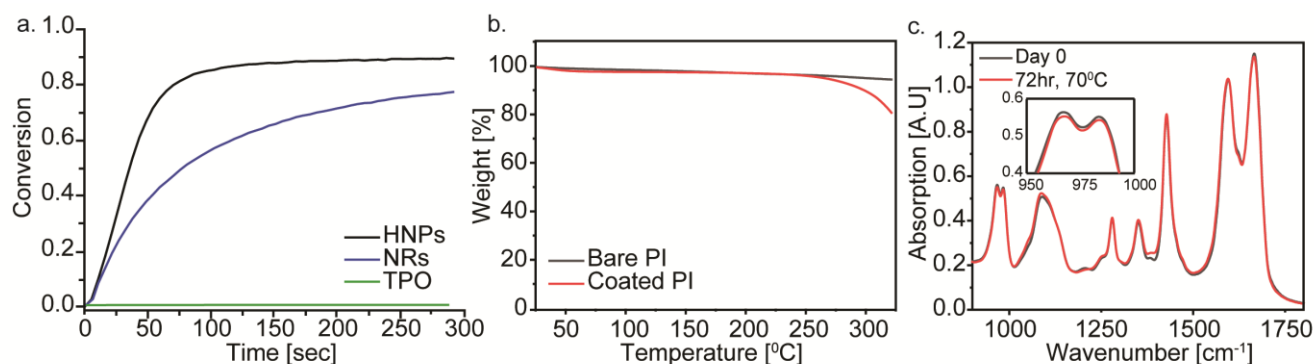


Figure 5. Comparison of quantum PIs (black and blue) and TPO (green) activity in solvent-free polymerization of HEA, using 5 μ M of PIs under illumination with 405nm LED 25mW/cm². Excitation of the quantum PIs resulted in significant conversion of the acrylic double bond whereas formulation containing the same concentration of organic photoinitiators didn't show polymerization. Control experiment, illumination on formulation comprising the regular mM concentrations of TPO, showed the expected fast polymerization of the monomers. Adapted from Verbitsky L. et al., *Nanoscale*, 2019, **11**, 11209 with permission from The Royal Society of Chemistry.⁶ b. Thermogravimetric analysis with bare and coated quantum PIs (black and red, respectively), showing high thermal stability resulting from the inorganic crystal nature of the quantum PIs. b. Shelf-stability test for quantum PIs in water showing no-change in the FTIR spectra of the monomers, indicating that high-temperature doesn't initiate radical-polymerization by quantum PIs.

Last but not least, the high stability of the nanocrystals allows their use for post-printing functionality. Engineering of the quantum PIs may be used to engineer them with a “clock” for their photocatalytic activity under light stimulation, allowing their use for example as integrated “non-active” additives for UV blocking. In other cases, the quantum PIs can have emission, producing fluorescent polymerization products and or in other scenarios they can have long-term photocatalytic activity, which can be of benefit in applications such as self-cleaning or antibacterial surfaces. Figure 6 demonstrates such multi-functional capacity in printing of a microscale gear structure that was polymerized utilizing a

high resolution 2 photon printer, in solvent-free formulation using quantum PIs as photoinitiators and fluorescent agents. The latter allowed easy detection of the printed structure under the confocal microscope. The high-resolution printing process relied on the giant 2 photon absorption cross-section of the quantum PIs, few orders of magnitude higher than traditional organic PIs.

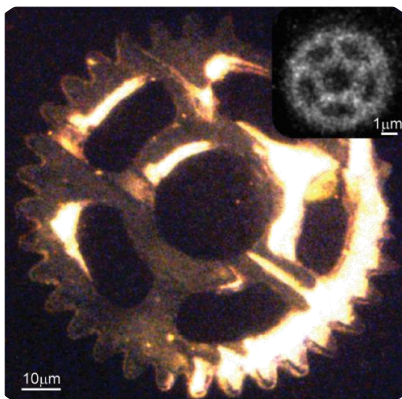


Figure 6. Confocal microscope image of a fluorescent high-resolution gear structure printed with quantum PIs using a two-photon Nanoscribe's printer. Reproduced from Verbitsky L. et al., *Nanoscale*, 2019, **11**, 11209 with permission from The Royal Society of Chemistry.⁶

Summary

Quantum PIs offer significant advantages over current traditional organic PI technology, including (1) Efficient photocatalytic reactive species formation and oxygen consumption in comparison to traditional stoichiometric initiation mechanism and polymerization retardation by oxygen; (2) Wide and tunable absorption spectra suitable for excitation of the quantum PIs with emerging near-UV-VIS energy-efficient and safe LED-based illumination as well as with traditional light sources; (3) Giant single and 2-photon light sensitivity in comparison to currently known organic molecules based photoinitiators, making them superior for polymerization in the presence of chromophores and for highest resolution 2- photon printing; (4) High compatibility in various media enabling efficient polymerization in aqueous and solvent-free formulations; (5) Low migration within the matrices; (6) Excellent stability for prolonged use and multi-functionality, such as photoinitiation and antibacterial activity. These advantageous properties position Quantum PIs as innovative technology that addresses unmet needs in the photo-curing industry and in addition, enabling new emerging applications.

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